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ORIGINAL PAPER

Synthesis and characterization of pyrrole and thiophene functional polystyrenes via "click chemistry"

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Abstract Novel side-chain pyrrole or thiophene functional polystyrenes (PS-Py and PS-Th) were synthesized by using ''click chemistry'' strategy. First, approximately 40% of chloro groups of poly(styrene-*co*-chloromethylstyrene) P(S-*co*-CMS), prepared by nitroxide mediated radical polymerization (NMRP), were converted to azido groups by using NaN_3 in *N*,*N*-dimethylformamide. Propargyl pyrrole was prepared by etherification of 4-(1*H*-pyrrol-1-yl)phenol prepared by Clauson-Kaas reaction using propargylbromide. Propargyl thiophene was synthesized by heterogeneous esterification reaction between 3-thiophenecarboxylic acid and propargylbromide. Finally, azido-functionalized polystyrene was coupled to these propargyl functional heterocyclics with high efficiency by click chemistry. The intermediates at various stages and final polymers were characterized by spectral analysis and cyclic voltammetry.

Keywords Pyrrole · Thiophene · Polystyrene · Click chemistry ·
1,3-Dipolar cycloadditions

Introduction

In recent years, many various controlled/living polymerization methods have been developed to control the polymer structure and properties for desired applications. Such synthetic methodologies also provide possibility to further modify existing properties or introduce additional properties through post-functionalization [1–3]. However, the most of the post-functionalization methods suffer from the low yields and side reactions with other groups within the polymer. Therefore, the selection and application of an efficient specific reaction play an important role for a

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successful functionalization of a particular polymer. In this context, 1,3-dipolar cycloadditions, through the reactions between azides and alkynes, known as "click chemistry" have been used as a useful synthetic method [4–7]. Click chemistry is particularly important in preparative methods, in which high conversion of functional groups and high atom economy is desirable. Many examples of click reactions involving macromolecules were reported [8–17]. In this laboratory, we have focused on the use of such click reactions for the synthesis of various macromolecular architectures [9, 16–19].

Being inspired by the one-pot 1,3-dipolar cycloaddition of alkynes to azides, polymers containing oxidatively polymerizable groups can be prepared with near quantitative yields. Such polymers have attracted great interest due to their electrical, electrochemical, and optical properties [20–24]. Copolymers of polypyrrole-polytetrahydrofuran [25], alternating copolymers of thiophene-containing *N*-phenyl maleimide [26], H-type polysiloxane-polypyrrole copolymers [27], block and graft copolymers of pyrrole with polyether segments [28], block copolymers of polypyrrole with polytetrahydrofuran and polytetrahydrofuran-*b*-polystyrene [29–31], copolymers of polypyrrole-graft-poly(ε-caprolactone) [32, 33], were previously synthesized by using various polymerization and synthetic methods.

It seemed that click chemistry could be an important tool for extending possible combinations of conventional polymers with polyconjugated systems. Typical example of the application of click chemistry on the modification of conjugated polymers involves the use of conducting polymer coated electrodes as a versatile platform [34]. Selective functionalization of conducting polymers via "electroclick" chemistry was also reported [35].

In the present work, we report, for the first time, the use of click chemistry as potential route to incorporate electro-active groups into conventional polymers. As it will be shown below, poly(styrene-*co*-chloromethylstyrene) P(S-*co*-CMS), prepared via nitroxide-mediated radical polymerization (NMP), and pyrrole and thiophene were selected as the polymeric platform and electro-active moieties, respectively, while the azide and alkyne groups served as reactive sites for the covalent binding of functional units.

Experimental

Materials

Acetic acid (Merck, 99.5%), 2,5-dimethoxytetrahydrofuran (Sigma, 99%), 4-aminophenol (Acros Organics, 99%), 3-thiophenecarboxylic acid (Fluka, 99%), propargylbromide (Fluka, 99%), sodium hydroxide (Carlo Erba, 97%), anhydrous magnesium sulfate (Alfa Aesar, 99.5%), chloroform (Riedel-de Haën, 99.4%), tetrahydrofuran (THF) (Acros Organics, 99.9%), methanol (MeOH) (Acros Organics, 99 + %), copper(I)bromide (Acros Organics, 98%), 2,2′-dipyridyl (Acros Organics, 99+%), tetrabutylammoniumbromide (Acros Organics, %99), silicagel 60 (Merck) were used as received.

Characterization

The molecular weights of polymers were measured by GPC at 30 °C with an Agilent instrument (Model 1100) consisting of a pump, refractive index and UV detectors, and four Waters Styragel columns (HR 5E, HR 4E, HR 3, and HR 2). THF was the eluent and have a flow rate of 0.3 mL/min, device was calibrated with polystyrene standards. Toluene was used as an internal standard. ^{1}H-NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. FT-IR spectra were measured on Perkin-Elmer FT-IR Spectrum One spectrometer with an ATR Accessory (ZnSe, Pike Miracle Accessory) and cadmium telluride (MCT) detector. Resolution was 4 cm^{-1} and 24 scans with 0.2 cm/s scan speed. Cyclic voltammetry measurements were carried out using a Princeton Applied Research Model 2263. Cyclic voltammetry was performed using a 3-electrode cell (BAS model solid cell stand) with a polished 0.32 cm^2 platinum foil electrode as working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode, in acetonitrile–tetrahydrofuran solvent system with a solution of polymer (5 g/L) and tetrabutylammonium perchlorate (TBAP, 0.1 M) as supporting electrolyte. All solutions were purged with nitrogen for at least 10 min before starting the measurements.

Synthesis of 4-(1*H*-pyrrol-1-yl)phenol

A cooled solution of (6.45 g, 60 mmol) of 4-aminophenol in 50 mL glacial acetic acid is placed in a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. 2,5-Dimethoxytetrahydrofuran (7.5 mL, 58 mmol) is added to the cooled solution during 10–15 min. The solution refluxed for 1.5 h, during which time the solution turns deep red to black in color. The heating discontinued and the acetic acid is removed by distillation. The dark residue was dissolved in 20 mL of methanol and subsequently poured into water. The precipitate was filtered and washed with water, then dissolved in chloroform and filtered again to remove insoluble products. Chloroform was evaporated, and the remaining residue dissolved in 20 mL methanol to precipitate in water. Precipitates were filtered and washed with water then dried. Beige colored solid was obtained (Yield: 62%).

Synthesis of 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol

In a flask, 4-(1*H*-pyrrol-1-yl)phenol (5.5 g, 35 mmol) was dissolved in 100 mL NaOH (0.8 N) solution. The mixture was heated at 60 °C until a clear solution was formed. Tetrabutylammoniumbromide (1.12 g, 35 mmol) was added to this solution as a phase transfer catalyst. A solution of propargyl bromide (4.28 g, 35 mmol) in 50 mL toluene was added portion-wise to the solution. The mixture was kept stirring at 60 °C for 24 h. The precipitates were filtered and washed with copious amount of water. Then, the solid was recrystallized from MeOH/water (1/1 by volume) to obtain a white solid (Yield: 80%).

Synthesis of prop-2-ynyl thiophene-3-carboxylate

In a 250-mL flask, 3-thiophenecarboxylic acid (2 g, 15 mmol) was dissolved in 100 mL of 0.1 N NaOH. The mixture was heated at 50 °C until a clear solution was formed. To this solution, tetrabutylammonium bromide (0.5 g, 1.55 mmol) was added as a phase transfer catalyst. A solution of propargylbromide (2.04 g, 17 mmol) in 30 mL of toluene was added to the solution. The mixture was kept stirring at 60 °C for 24 h. Then the toluene layer was separated and washed two times with cold 1% NaOH solution and finally with distilled water. Evaporation of toluene and propargyl bromide residues under vacuum afforded semi-solid. This solid was washed with cold hexane, and dried under vacuum (Yield: ca. 60%).

Synthesis of poly(styrene-*co*-chloromethyl styrene) (PS-*co*-PCMS) copolymer

PS-*co*-PCMS copolymers containing CMS moieties (40%) were prepared via NMRP of styrene and CMS at 120 °C according to the previously described procedure [11].

Synthesis of azidocopolymer (PS-N_3)

PS-*co*-PCMS copolymer was dissolved in *N,N*-dimethylformamid (DMF), and NaN3 (two times excess to the mole of chloromethyl group of each copolymers) was added to this solution. The resulting solution was allowed to stir at ambient temperature overnight then the polymer was precipitated into methanol/water mixture (1/1 by volume), filtered and dried under vacuum [11].

General synthesis of pyrrole or thiophene functional polystyrene

In a flask, PS-N_3 (0.3 g), 4-(1*H*-pyrrol-1-yl)phenol or prop-2-ynyl thiophene-3-carboxylate (1.5 mmol), copper(I)bromide (0.3 g, 2 mmol), and 2,2′-dipyridyl (1.4 g, 9 mmol) were added. The flask was capped with a septum and purged with nitrogen for 2 min. Degassed THF (12 mL) was then added by using a syringe, and the mixture became a homogeneous brown/dark-red solution. The mixture was stirred overnight at room temperature. The solution was filtered from silica gel and the polymer precipitated in 200 mL of methanol, dried under vacuum.

Results and discussions

The click components, namely 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol and prop-2-ynyl thiophene-3-carboxylate, were synthesized via pyrrole synthesis, etherification, and esterification processes. It is known that Clauson-Kaas reaction is a facile method to transform 2,5-dialkoxy substituted tetrahydrofurans into *N*-substituted pyrroles using primary amines or ammonia [36–41]. Hence, 2,5-dimethoxytetrahydrofuran and 4-aminophenol was used to synthesize the corresponding pyrrole derivative, 4-(1*H*-pyrrol-1-yl)phenol (Scheme 1). The pure product was obtained with 62% yield and used in heterogeneous etherification reaction to obtain propargyl containing pyrrole, subsequently (Scheme 1).

The chemical structure of propargyl pyrrole was confirmed by both FT-IR and ^{1}H-NMR spectroscopy. As can be seen from Fig. 1, the ^{1}H-NMR spectrum reveal the structural characteristics of both acetylene and pyrrole. Terminal acetylene proton of propargyl moiety appears as triplet at 2.55 ppm with 2.4 Hz J. Moreover, protons of pyrrole heterocycle and phenyl ring emerge between 6.32 and 7.35 ppms.

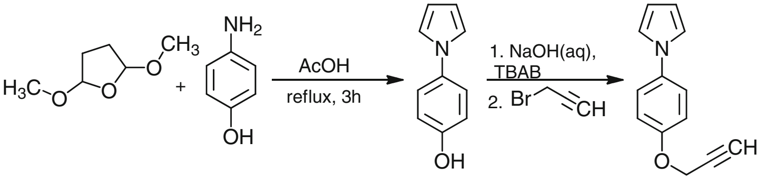
In addition, the FT-IR spectrum of the propargyl pyrrole further verifies the expected structure. As can be seen form Fig. 2a, the bands corresponding to the acetylenic C–H, C–C, triple bond stretching vibration and aromatic C–H stretching vibration emerge at 3290 cm^{-1}, 2121 cm^{-1}, and 1001 cm^{-1} respectively. Furthermore, a strong CH δ oop band of pyrrole ring arises at 725 cm^{-1} [42].

The other clickable monomer, propargyl thiophene, was prepared by heterogeneous esterification reaction between 3-thiophenecarboxylic acid and propargyl bromide in basic medium (Scheme 2).

FT-IR and ^{1}H-NMR spectral measurements were used to confirm the structure of propargyl thiophene. ^{1}H-NMR spectrum presented in Fig. 3 exhibit structural characteristics of both acetylene and thiophene units. The signal of terminal acetylene proton emerges as triplet at 2.50 ppm with 2.4 Hz J. Additionally, protons of thiophene heterocycle appear between 8.16 and 7.53 ppms.

Moreover, the FT-IR spectrum of the propargyl pyrrole further validates the structure. In Fig. 4a, in addition to the band corresponding to the acetylenic C–H at 3294 cm^{-1}, C–C triple bond stretching vibration emerges at 2128 cm^{-1} and aromatic C–H stretching vibration at 3112 cm^{-1}. Furthermore, strong C=O stretching vibration peak for ester at 1716 cm^{-1} CH δ oop band of thiophene ring appear at 744 cm^{-1} [42].

For the preparation of azide functionalized polymer (PS-N$_3$), first, poly(styrene-*co*-chloromethylstyrene) P(S-*co*-CMS) was synthesized by NMRP of styrene (St) and chloromethylstyrene (CMS) at 120 °C. The composition of copolymer was determined using ^{1}H-NMR spectroscopy. The mole fractions of CMS and St were calculated from the ratio of the peak area around 4.5 ppm, which is corresponding to two chloromethylene protons of in the side chain of CMS, to the total area of aromatics between 6.3 and 7.4 ppm. P(S-*co*-CMS) having 11.300 $M_{n(GPC)}$ and $\approx$40 mol% chloromethyl groups was then quantitatively converted into polystyrene-azide (PS-N$_3$) in the presence of NaN$_3$/DMF at room temperature. The overall process for the synthesis of PS-N$_3$ was presented in Scheme 3.



Scheme 1 Synthesis of 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol

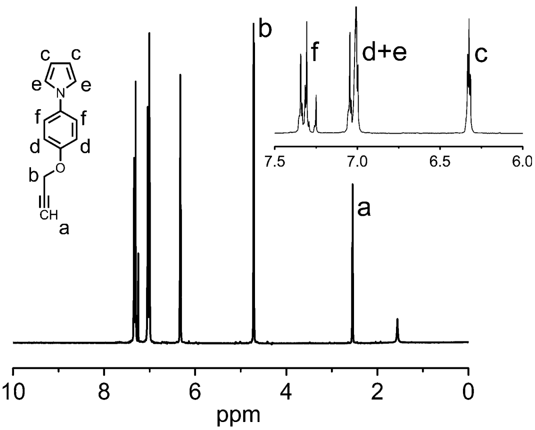


Fig. 1 ^{1}H-NMR spectrum of 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol

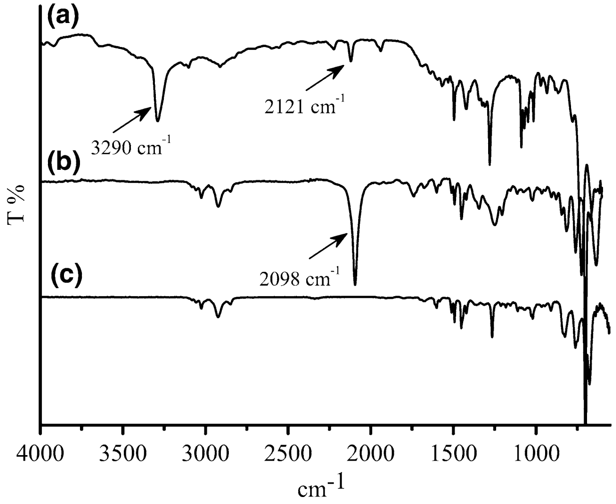
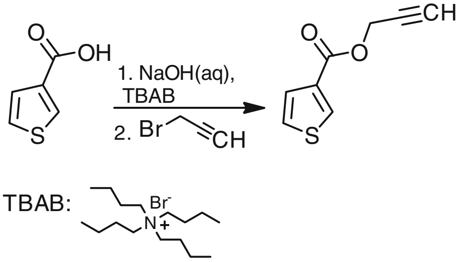


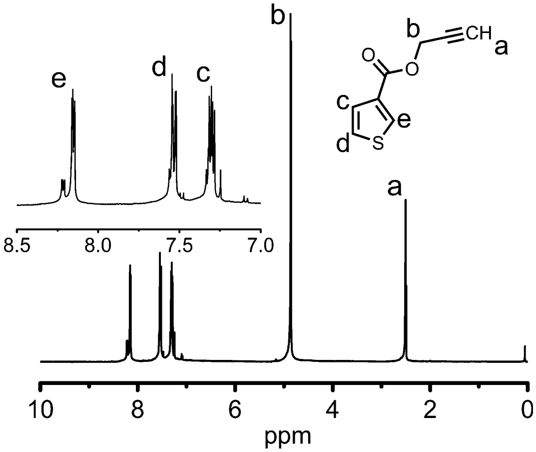
Fig. 2 FT-IR spectra of 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol (*a*), PS-N_3 (*b*), and PS-Py (*c*)

Scheme 2 Synthesis of prop-2-ynyl thiophene-3-carboxylate



From the ^{1}H-NMR spectrum of PS-N_3 shown in Fig. 5a, it was observed that a new signal appeared at 4.25 ppm due to azide linked CH_2 groups and the signal corresponding to $C\boldsymbol{H}_2$–Cl protons of the precursor P(S-*co*-CMS) at 4.5 ppm

Fig. 3 ^{1}H-NMR spectrum of prop-2-ynyl thiophene-3-carboxylate



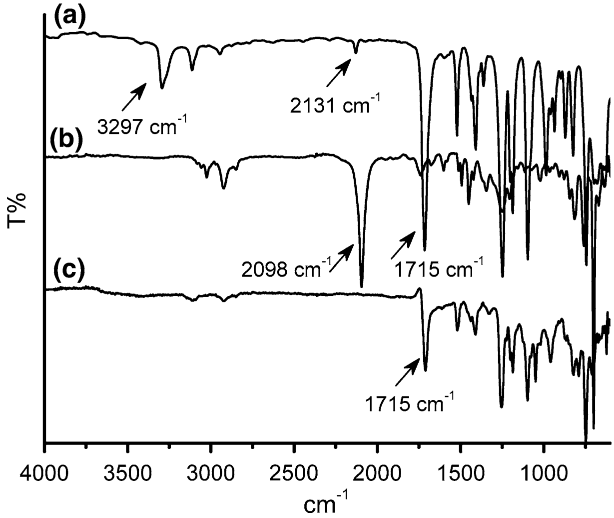
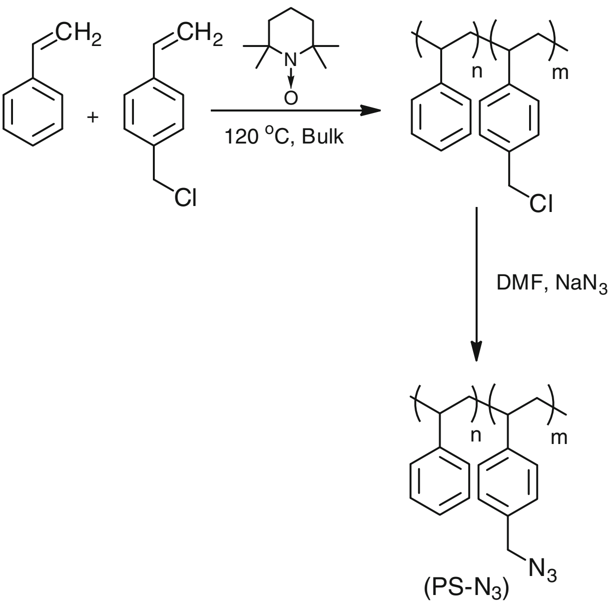


Fig. 4 FT-IR spectra of prop-2-ynyl thiophene-3-carboxylate (*a*), PS-N_3 (*b*), and PS-Th (*c*)

completely disappeared. The structure of PS-N_3 was further supported by FT-IR spectrum, in which azide stretching band appeared at 2094 cm^{-1} (see Figs. 2b, 4b).

For the ultimate click reaction, PS-N_3 was dissolved in THF and reacted with propargyl containing pyrrole or thiophene in the presence of CuBr/2,2′-dipyridyl ligand (dPy) at room temperature (Scheme 4).

After removing the catalyst by filtering from silica, the polymer was precipitated in MeOH, then filtered, washed, and dried under vacuum. The extent of conversion of the side azido moieties and the effect of click reaction on the stability of pyrrole or thiophene derivatives were important. The first issue was monitored by ^{1}H-NMR spectroscopy by observing the disappearance of the methylene protons adjacent to the azido group (N_3-CH_2Ph) at 4.2 ppm and the appearance of the new methylene



Scheme 3 The synthesis of azido containing polystyrene (PS-N_3)

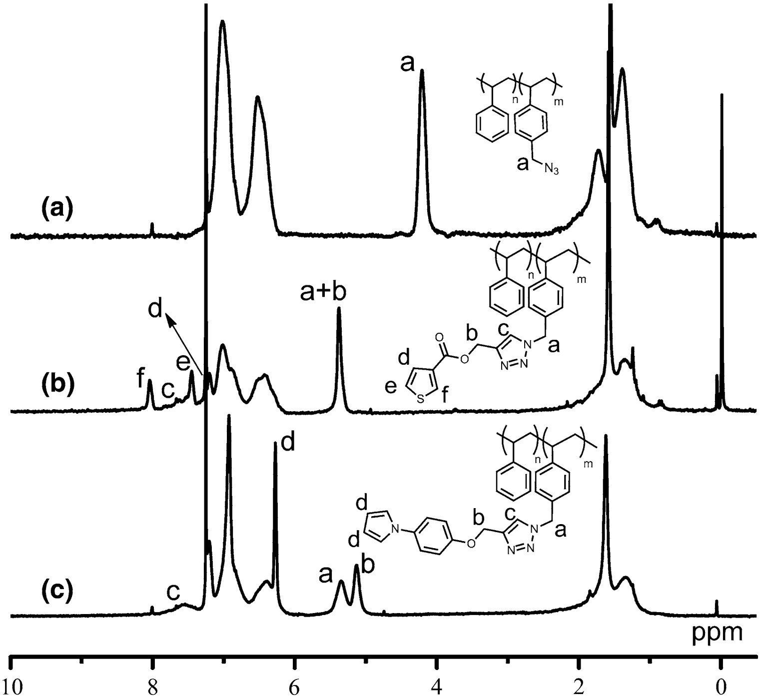
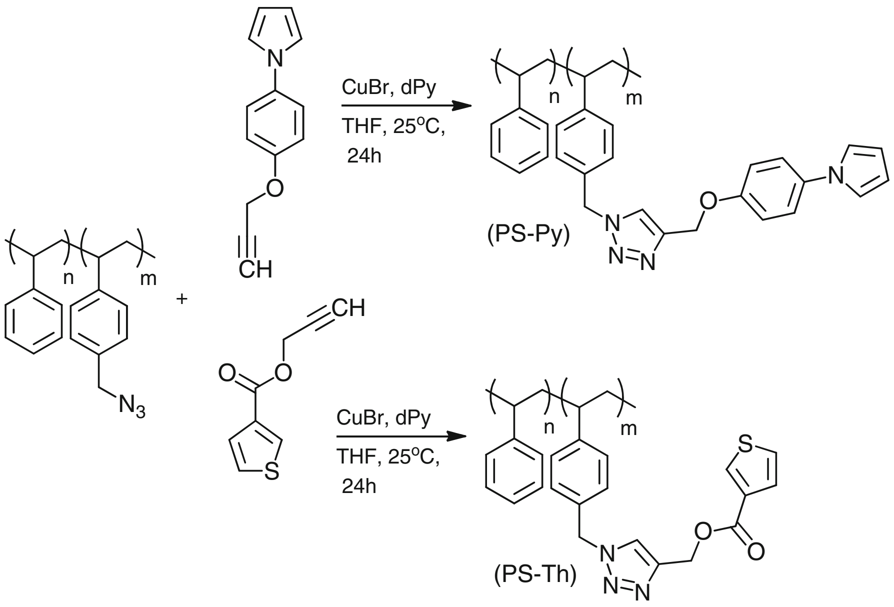


Fig. 5 ^{1}H-NMR spectra of PS-N_3 (*a*), PS-Th (*b*), and PS-Py (*c*)

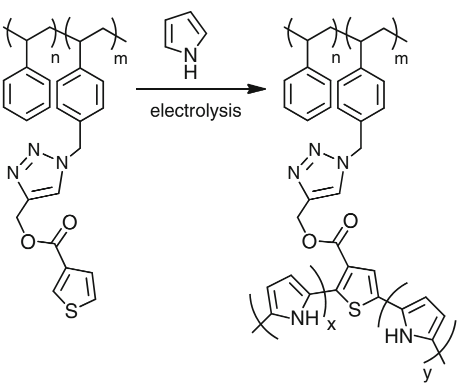


Scheme 4 Synthesis of PS-Py and PS-Th by click reaction

protons adjacent to the triazole ring at 5.3 ppm (triazole-CH_2Ph) (see Fig. 5b, c). Moreover, the band corresponding to the –N_3 group at 2094 cm^{-1} completely disappeared (see Figs. 2c, 4c). Thus, the side group click reaction was efficient and quantitative for the conversion of azides to triazoles. Also, the peaks of pyrrole or thiophene were observed from ^{1}H-NMR indicating that these heterocycles are stable under click reaction conditions. Moreover, general agreement between the molecular weights of the clicked polymers as determined by GPC (M_n: 12900 for pyrrole (PS-Py) and 12670 for thiophene (PS-Th) derivatives) and that of the precursor azido-polymer (M_n: 7480) also confirms efficient coupling by the increases in the molecular weight due to the incorporated pyrrole or thiophene moieties.

Electrochemical properties of the polymers were investigated by cyclic voltammetry (CV). No detectable redox behavior was observed for both 1-(4-(prop-2-ynyloxy)phenyl)-1*H*-pyrrol and the corresponding polymer, PS-Py. This is likely due to steric interactions and inductive effects of the aryl group which inhibit electrochemical polymerization processes. Although pyrroles with larger substituents undergo polymerization, those with *N*-alkyl groups having two or three carbons were found to be non-polymerizable [43]. It was also reported that it is much more difficult to oxidize *N*-arylpyrroles by electrochemical techniques [44]. It is interesting to note the electroactivity of two structurally related *N*-substituted pyrroles with azide and terminal alkyne groups, namely *N*-(10-azidodecyl)pyrrole and *N*-[10-(propargyl ether)decyl]pyrrole. These pyrrole derivatives were readily electropolymerized as the electroactive group was separated from the triazole ring by a long spacer group [34]. It is also worth to mention that no detectable redox behavior

Scheme 5 Electrolysis of PS-Th with pyrrole



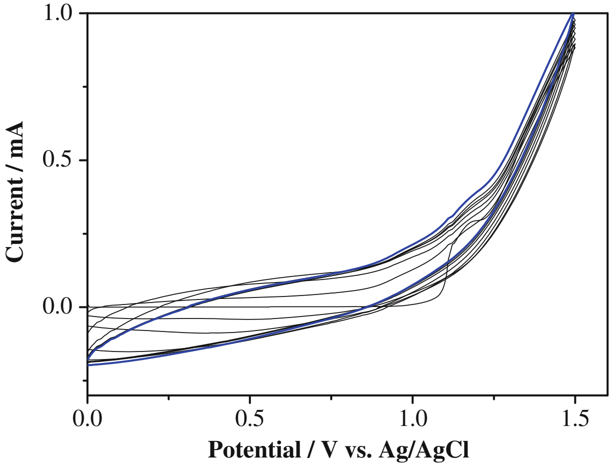


Fig. 6 Cyclic voltammograms of the electrochemical polymerization of PS-Th in the presence of Py in acetonitrile-tetrahydrofuran solvent system (supporting electrolyte: tetrabutylammonium perchloride; scan rate: 0.10 Vs^{-1}; working electrode: 0.32 cm^2 platinum foil electrode)

was observed with the polymers possessing non-conjugated backbone and thiophene side groups [26, 45]. They become electroactive only in the presence of bare monomers such as thiophene (Th) and pyrrole (Py). Moreover, anodic polymerization of 3-cyclohexylthiophene was found to be ineffective. This monomer could only be polymerized by using $FeCl_3$ as the oxidizing reagent [46]. In the present work, we attempted to polymerize PS-Th in the presence of pyrrole electrochemically in acetonitrile–tetrahydrofuran solvent system (Scheme 5).

The CV of the system exhibited similar behavior to that of bare pyrrole (Py). Figure 6 shows cyclic voltammograms corresponding to the electrochemical polymerization of PS-Th in the presence of pyrrole using tetrabutylammonium perchloride as supporting electrolyte in acetonitrile–tetrahydrofuran solvent system. The electrochemical polymerization of materials was achieved by consecutive

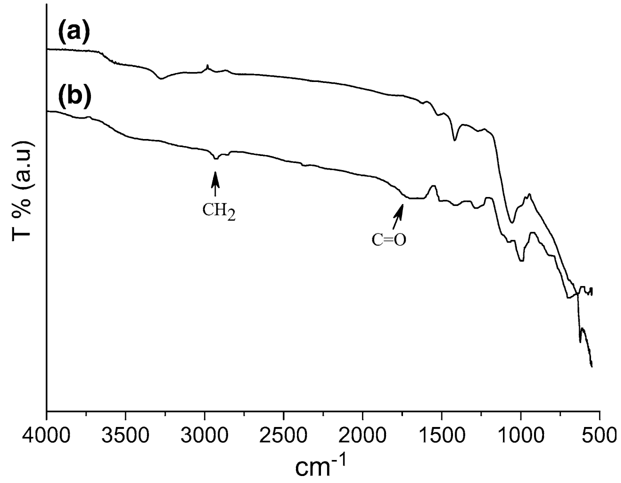


Fig. 7 FT-IR spectra of polyPy (*a*) and poly(Py-*co*-PS-Th) (*b*)

cycles between 0.0 and 1.5 V potentials at scan rate of 0.10 V s^{-1} and monitored by increasing of anodic peak current and shift the oxidation potential toward more positive potentials.

The coated polymer films formed from the polymerization of neat Py alone and PS-Py/Py system, washed with acetonitrile and tetrahydrofuran, were easily peeled off from the surface of platinum foil electrode. The FT-IR spectra of the materials were rather different. The spectrum of the copolymer (Fig. 7b) exhibited C=O bond stretching vibration at around 1715 cm^{-1} and C-H$_2$ symmetric and asymmetric stretching vibrations at 2932 and 2866 cm^{-1} (see Fig. 7) indicating presence of polystyrene segment.

In conclusion, we have reported a facile method for the preparation of polymers with Py and Th side chains by click chemistry strategy. Independently prepared propargyl functional Py and Th were coupled with azido polystyrene in the presence of CuBr/2,2'-dipyridyl ligand at room temperature with high efficiency. The obtained polymers were structurally and electrochemically characterized.

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