Synthesis of Conductive Polyethylene glycol Copolymers

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Abstract**—**This work presents synthesis of α,ω-dithienyl terminated poly(ethylene glycol) (PEGTh) capable for further chain extension by either chemical or electrochemical polymeriztion. PEGTh was characterized by FTIR and ^{1}H-NMR. Further copolymerization of PEGTh and pyrrole (Py) was performed by chemical oxidative polymerization using ceric (IV) salt as an oxidant (PPy-PEGTh). PEG without end group modification was used directly to prepare copolymers with Py by Ce (IV) salt (PPy-PEG). Block copolymers with mole ratio of pyrrole to PEGTh (PEG) 50:1 and 10:1 were synthesized. The electrical conductivities of copolymers PPy-PEGTh and PPy-PEG were determined by four point probe technique. Influence of the synthetic route and content of the insulating segment on conductivity and yield of the copolymers were investigated.

Keywords**—**Chemical oxidative polymerization, conducting copolymer, poly(ethylene glycol), polypyrrole.

I. INTRODUCTION

THE unique properties of conducting polymers have brought these materials to forefront in miscellaneous applications such as electrochromic devices [1], energy storage systems [2], [3], sensors [4]-[6], catalysts [7], [8], actuators [9], electromagnetic interference shielding [10], textiles [11] and anticorrosive coatings [12]-[14]. Emerging developments in such spesific fields have promoted scientists searching for advanced materials capable to achieve expected performance. Since preparation method gives opportunity to tailor conducting polymers they have been widely used to design novel materials with improved features. Several approaches to synthesis and modification of conducting polymers have been proposed. Side-chain introduced monomers [15], bulky dopants [16], [17], polymeric stabilizers [18], templates [19]-[21] and nanofillers [6], [22] have been used to prepare homopolymers, copolymers or composites of conducting polymers. It has been concured that character of final product depends on a synthetic route and reaction conditions. Besides process may result in product with diverse physical forms (powders, films, nanoparticles, nanofibers, colloids and so forth).

Among the conducting polymers polypyrrole (PPy) is one of the most intensively studied. (PPy)s synthesized by chemical oxidative, electrochemical, enzyme-catalized [23], [24], photo-induced [25], [26] and vapor phase [27], [28] polymerization methods have been reported. Copolymers, composites or blends of PPy and insulating polymers have been produced in order to obtain significant changes in electrical, mechanical, thermal and morphological properties of pristin conducting polymer.

Composites of pyrrole with insulating polymes are acrylic polymers [29]-[34], cellulose [35]-[37], polysterene [38]-[42], polyurethane [43], polydimethylsiloxsanes [44], [45], poly(ethylene glycol) [18], [46]-[54]. PEG is an inexpensive surfactant-like polymer with good solubility in most common solvents and can be easily reached commercially with wide range of molecular weights. Sterically stabilized colloids of polypyrrole were prepared using PEG as a stabilizer [18]. These conducting polymer colloids are two component systems, consisting of an inner core of conducting polymer surrounded by an outer layer of adsorbed, solvated, electrically insulating polymeric stabilizer. Upon solvent removal this stabilizer collapses down and coats the conducting polymer core forming an outer layer of negligible thickness. The results showed that such systems can significantly improve the processability of the electroactive component whilst retaining usefully high electrical conductivity, $2x10^{-3}$ $S.cm^{-1}$. Lim and coworkers have reported soluble polypyrrole composites advanced in electrical conductivity. The composites were synthesized chemically with ammonium persulfate as an oxidant, dodecyl benzene sulfonate (DBS) sodium salt as a dopant, and PEG as an additive [53]. The PPy-DBS-PEG samples were found to be soluble in organic solvents such as N-methylpyrrolidinone and m-cresol. The solubility of the PPy-DBS-PEG samples increased when the molar percentage ratio of DBS was higher. The maximum electrical conductivity at room temperature for PPy-DBS-PEG was 1.02 $S.cm^{-1}$, in the case of mole % ratio of PPy:DBS:PEG was 100:10:40. Eisazadeh prepared polypyrrole and PEG composites chemically using $FeCl_3$ as an oxidant in aqueous and non-aqueous media. Results showed that conductiviy is dependent on additive and type of solvent [49]. Solvents with more polar character (e.g. water) lead to polymers with higher conductivities since becomes more compatible with pyrrole. The conductivity decreases in nonaqueous media due to increase stabilizer adsorption, but as a result of an increase in the polymerization rate in the polar organic media, polydispersed particles are formed. PEG is stabilizing agents and could affect the size, morphology and the homogeneity of particles, because the surfactants are adsorbed physically to the polymer by the growing polymer. The PPy-PEG composite nanofibers were fabricated by electrospinning a solution of PEG and $FeCl_3$ in a water/ethanol solvent, followed by exposure to pyrrole vapors at ambient conditions [50]. PPy-PEG composite films were synthesized by electrochemical method, using *p*-toluene sulfonate as a dopant [48]. Both the electrical conductivity and thermal diffusivity exhibited the highest values with the process condition of 0.2 M pyrrole, 0.1 M *p*-toluene sulfonate and $1x10^{-3}$ M PEG at 1.2 V (versus SCE). α-Methoxy ω-Na carboxylate poly(ethylene glycol) has been synthesized and used as a bulky dopant for the electrochemical synthesis of polypyrrole films. The ion exchange properties of the formed composite have been analyzed in aqueous solution containing various salts [51]. The surface properties of electrodeposited PPy doped with sodium dodecylbenzenesulphonate are modified by two methods: addition of PEG during the electrodeposition and through redox cycling post electrodeposition [52]. Posudievsky et al. prepared a nanocomposite based on vanadium oxide and polypyrrole (PPy) and polyethylene glycol (PEG) by solventless mechanochemical synthesis. The composite containing two polymers with different types of conductivity (ionic and electronic) was choosen to obtain cathode material for lithium batteries [54].

Copolymer synthesis is another strategy used for modification of conducting polymers. Mainly chemical and electrochemical polymerization methods have been performed. Brittle, insoluble and infusable structure of conducting polymers, can be partially solved by preparing block copolymers prepared with a conducting polymer segment and a low-Tg polymer segment. This approach is most successful with systems like poly(3-hexylthiophene), where the conducting polymer can be functionalized to provide end groups suitable for block extension. Segmented copolymers containing PPy are most often prepared by endcapping the low-Tg block with a pyrrole or thiophene unit that can be chain extended via chemical or electrochemical polymerization, resulting in block and graft copolymers with moderate conductivities (10^{-2} S.cm^{-1}) [55]. The studies related to synthesis of PPy based copolymers prepared with either PEG or end-capped PEG have been reported [55]-[57]. Luebben et. al have reported chemically synthesized copolymers of pyrrole and thiophene/pyrrole terminated insulating polymers, poly(ethylenedioxythiophene), poly(propylene glycol), poly(ethylene glycol), etc. [55]. Yildiz et al. have obtained electrochemically copolymer films of PEGTh and thiophene or pyrrole [56]. Gabriel et al. produced α-pyrrolyl-ω-acrylate-poly(ethylene glycol) as a dual macromonomer and prepared electrochemically copolymers in the mixture of pyrrole and α-pyrrolyl-ω-hydroxypoly(ethylene glycol) [57].

The present work deals with the synthesis of block copolymers of pyrrole and α,ω-dithienyl terminated poly(ethylene glycol). The copolymers were synthesized by chemical oxidative polymerization in aqueous medium using cerium(IV) ammonium nitrate (CAN) as an oxidant and ptoluene sulfonic acid (PTSA) as a dopant. Two different mole ratios of pyrrole to PEGTh was applied, 50:1 and 10:1. Since cerium(IV) salt is capable to oxidize both Py and hydroxymethyl groups of PEG, alternative copolymerization route was performed as a comperative study. The electrical conductivities were measured via 4-point probe technique. Influence of synthetic route and ratio of conducting to insulating segment on conductivities and yield of the copolymers were demonstrated.

II. Materials And Methods

Pyrrole, poly(ethylene glycol) (Mn=1000), ammonium cerium(IV) nitrate, and 2-thiophenecarbonyl chloride (SigmaAldrich), p-toluenesulfonic acid monohydrate and pyridine (Acros Organics) were purchased with analytical grade and were used without any purification.

Infrared spectra were recorded on an FTS-6000 Excalibur FTIR, using Varian Resolutions Pro as software. ^{1}H-NMR measurements were performed on Varian Mercury 400 spectrometer at room temperature, using $CDCl_3$ as deuterated solvent. Electrical conductivities (σ) of polymers were determined by four point probe technique using Keithley 2400 model multimeter, Lucas Labs 302 model probe holder and SP4-180-TFS type probe. Thin pellets with typical sample diameter of 13 mm were prepared by compaction of the polymer powders under 10 tons of pressure. Conductivities were calculated from the following equation:

$$\sigma = V^{-1} . I (\ln 2/ \pi dn) \qquad (1)$$

where V is the potential in volts, I is the current in ampere and dn is the thickness of the samples in cm.

Morphologies of products were examined by scanning electron microscope, ESEM XL30 ESEM-FEG Philips.

III. Experimental

A. Synthesis of Polypyrrole with Ceric(IV) Salt in Aqueous Medium

0.3 ml (4.3 mmol) pyrrole and 2.53 g (13 mmol) PTSA were added into 45 ml of water and stirred. Calculated amount of cerium(IV) ammonium nitrate (CAN) was dissolved in 10 ml of water. Then prepared solution of ceric(IV) salt was added dropwise. Reaction was maintained for 1 hour at room temperature. Precipitated PPy was filtered off and washed with water, methanol and acetone. Polymer was dried at 45 °C for 24 hours. (PPy)s were prepared using n(CAN):n(Py) mole ratio of 0.25, 0.33, 0.5 and 1.0. The set of experiments were carried out without PTSA.

B. Synthesis of α,ω-Dithienyl Terminated Poly(Ethylene Glycol)

10 g (10 mmol) poly(ethylene glycol) (Mn:1000) was dissolved in 40 ml dry chloroform inside the three-necked flask equipped with dropping funnel and cooler. Then 1.77 ml (22 mmol) pyridine was added and the mixture was stirred under argon atmosphere. The system was placed in an icebath. Solution of 2.35 ml (22 mmol) 2-thiophenecarbonyl chloride in 10 ml dry chloroform was added dropwise for 30 min. The temperature of the ice bath was left to be increased spontaneously up to room temperature. The mixture was stirred over period of 20 h. Dichloromethane was added to the mixture and washed with diluted HCl to remove pyridinium chloride. Then mixture was washed with $NaHCO_3$ solution. Polymer was re-crystalized in hot ethanol and was dried at 60°C for 2 h under vacuum. The product in a wax form was obtained after cooling to room temperature.

C. Synthesis of Pyrrole and α,ω-Dithienyl Terminated Poly(Ethylene Glycol) Copolymers

2.53 g (13 mmol) PTSA and 0.3 ml (4.3 mmol) Py were dissolved in 25 ml water. Solution of 0.095 g (0.086 mmol) PEGTh in 20 ml of water was prepared and was added to the mixture containing Py and the dopant. 1.18 g (2.15 mmol) CAN dissolved in 10 ml water was added dropwise. The reaction was maintained for 24 h at room temperature. The copolymer (PPy-PEGTh1) was filtered off then was washed with water, methanol, acetone and finally with dichloromethane to remove unreacted PEGTh. The copolymer PPy-PEGTh2 was synthesized at the same conditions using 0.475 g (0.43 mmol) PEGTh.

D. Synthesis of Pyrrole and Poly(Ethylene Glycol) Copolymers

The procedure described for PPy-PEGTh synthesis was followed to synthesize copolymers of pyrrole and poly(ethylene glycol) (PPy-PEG). PEG was used directly instead of PEGTh, without end group modification. 0.086 g (0.086 mmol) and 0.43 g (0.43 mmol) PEG were taken for copolymers with n(Py):n(PEG) mole ratio of 50:1 (PPy-PEG1) and 10:1 (PPy-PEG2), respectively.

IV. RESULTS AND DISCUSSION

The optimum oxidant to monomer mole ratio for polypyrrole synthesis was investigated in the presence of pyrrole at constant molarity (0.078 M) and variable concentrations of CAN salt (0.020-0.026-0.039-0.078 and 0.098 M). Reactions were carried out without a dopant in aqueous medium for 1 hour.

Results summarized in Fig. 1 showed that the yield (%) of PPy is almost directly proportional to the concentration of CAN in the range of 0.020-0.098 M. Polypyrroles with conductivities between 0.6 and 1.3 S.cm^{-1} were obtained. The highest conductivity values were determined to be 1.3 and 1.1 S.cm^{-1} for 0.026 and 0.039 M CAN, respectively. The further increase in the oxidant concentration resulted in decrease of conductivity.

0.24 M of PTSA was added for making contribution to the conductivity of PPy. 0.039 M CAN was accepted as an optimum concentration in order to produce PPy with both high conductivity and yield. This optimum concentration corresponding to 0.5 mole ratio of CAN to Py was used also for synthesis of copolymers.

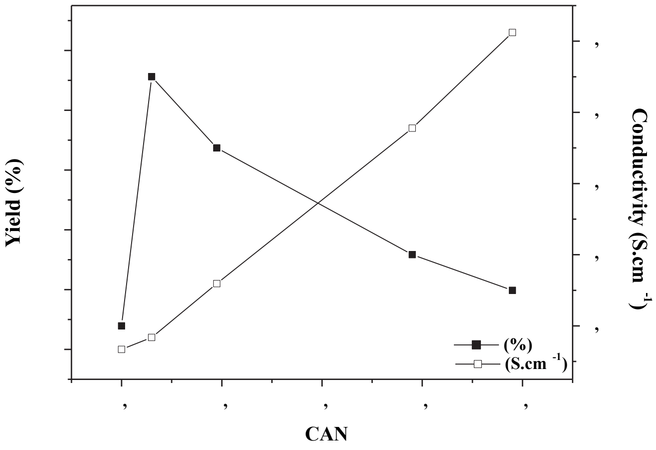

Fig. 1 Effect of CAN concentration on the conductivity and the yield of PPy

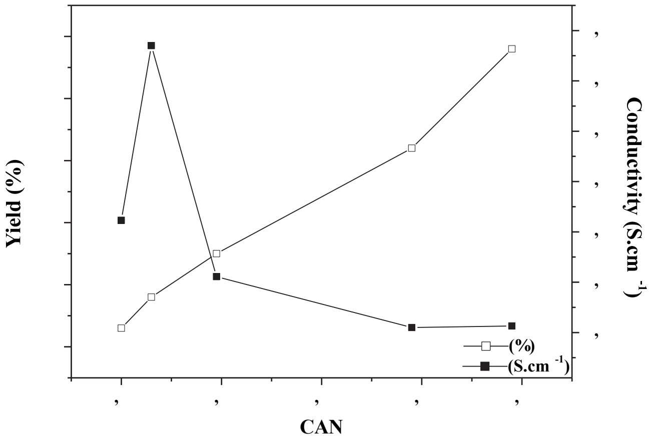

Fig. 2 Effect of CAN concentration on the conductivity and the yield of PPy in the presence of PTSA

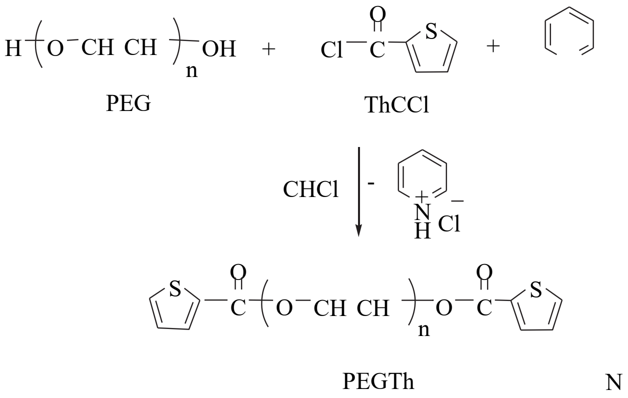

Fig. 3 Synthesis of PEGTh

PPy-PEGTh copolymers were produced in two steps. First step was performed to modify the hydroxyl end groups of PEG with thiophene units. Then copolymerization process of the product (PEGTh) and pyrrole was carried out.

Esterification reaction between poly(ethylene glycol) and 2thiophenecarbonyl chloride leading to α,ω-dithienyl terminated poly(ethylene glycol) (PEGTh) was represented in Fig. 3. The product was characterizied with spectroscopic methods, FTIR and ^{1}H-NMR (Figs. 4 and 5). Infrared spectra of PEG and PEGTh were compared in Fig
4.

The spectra mainly differ from each other by additional absorption bands appeared in the spectrum of PEGTh. The bands coming from the thiophene moiety were observed at 3089 cm^{-1} and 1707 cm^{-1} corresponding to aromatic C–H and C=O stretching vibrations, respectively.

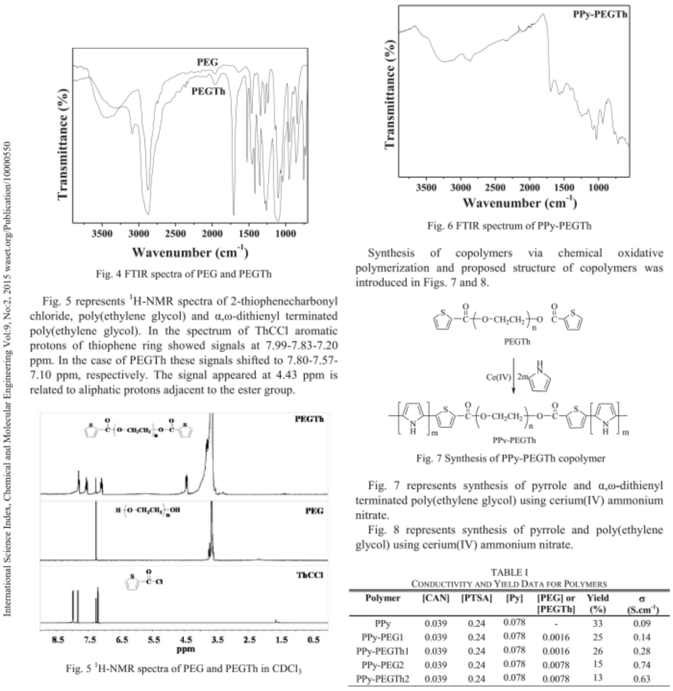

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Fig. 4 FTIR spectra of PEG and PEGTh

Fig. 5 represents ^{1}H-NMR spectra of 2-thiophenecharbonyl chloride, poly(ethylene glycol) and α,ω-dithienyl terminated poly(ethylene glycol). In the spectrum of ThCCl aromatic protons of thiophene ring showed signals at 7.99-7.83-7.20 ppm. In the case of PEGTh these signals shifted to 7.80-7.57-7.10 ppm, respectively. The signal appeared at 4.43 ppm is related to aliphatic protons adjacent to the ester group.

Fig. 5 ^{1}H-NMR spectra of PEG and PEGTh in $CDCl_3$

Fig. 6 FTIR spectrum of PPy-PEGTh

Synthesis of copolymers via chemical oxidative polymerization and proposed structure of copolymers was introduced in Figs. 7 and 8.

Fig. 7 Synthesis of PPy-PEGTh copolymer

Fig. 7 represents synthesis of pyrrole and α,ω-dithienyl terminated poly(ethylene glycol) using cerium(IV) ammonium nitrate.

Fig. 8 represents synthesis of pyrrole and poly(ethylene glycol) using cerium(IV) ammonium nitrate.

TABLE I
CONDUCTIVITY AND YIELD DATA FOR POLYMERS

Polymer	[CAN]	[PTSA]	[Py]	[PEG] or [PEGTh]	Yield (%)	σ ($S.cm^{-1}$)
PPy	0.039	0.24	0.078	-	33	0.09
PPy-PEG1	0.039	0.24	0.078	0.0016	25	0.14
PPy-PEGTh1	0.039	0.24	0.078	0.0016	26	0.28
PPy-PEG2	0.039	0.24	0.078	0.0078	15	0.74
PPy-PEGTh2	0.039	0.24	0.078	0.0078	13	0.63

The chemical structure of copolymers were determined by means of FTIR. Products were found to have similar absorbtion bands. The spectrum of PPy-PEGTh copolymer is shown in Fig. 6. Aromatic and aliphatic protons showed bands at 3107 cm^{-1} and 2900-2800 cm^{-1}, respectively. The absorbtion band related to C=O stretching vibrations shifted and appeared at 1694 cm^{-1}. Signals observed at 1580-1520 cm^{-1} belong to aromatic C=C stretching, and signals obtained at 1300-1000 cm^{-1} belong to C–N and C–O stretching vibrations.

In Table I results were compared in the terms of conductivity and percentage of yield. The copolymers have conductivities in the range of 0.14 $S.cm^{-1}$-0.74 $S.cm^{-1}$. Increase in concentration of PEGTh (PEG) caused decrease in yield and increase in conductivity of copolymers.

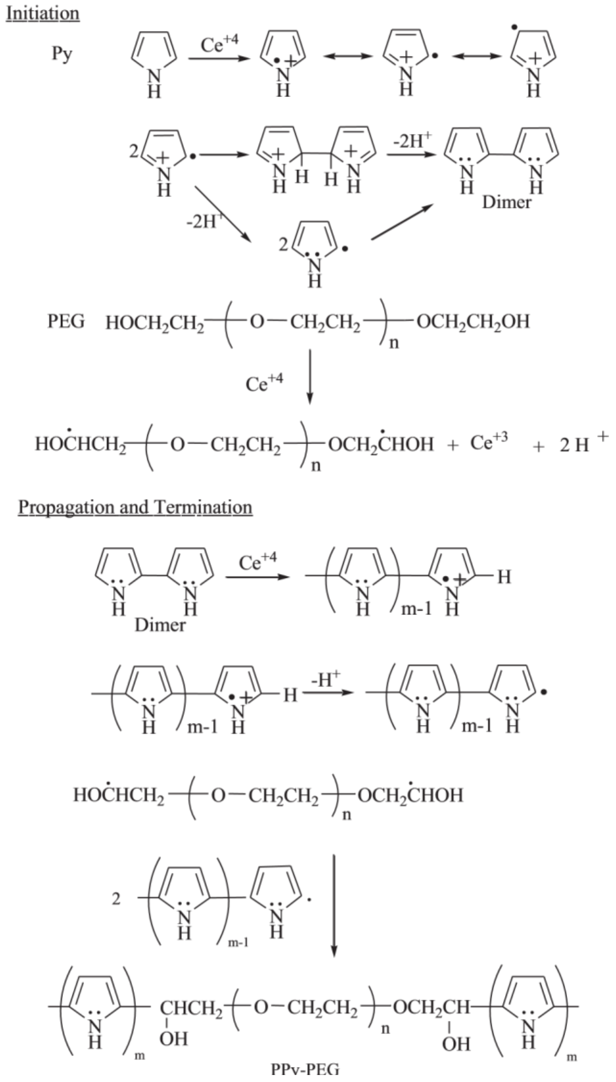

Fig. 8 Synthesis of PPy-PEG copolymer

Morphologies of PPy-PEGTh2 and PPy samples were compared in Figs. 9 and 10. Surface of polypyrrole was found to be more compact and denser then copolymer.

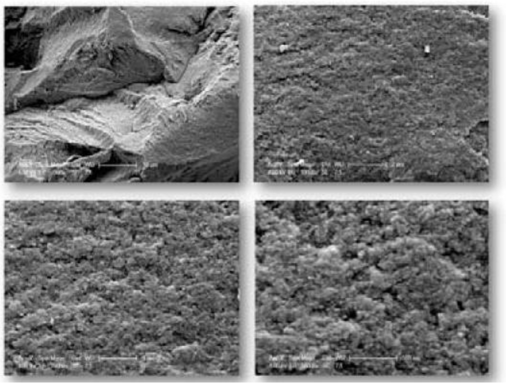

Fig. 9 SEM micrographs of PPy

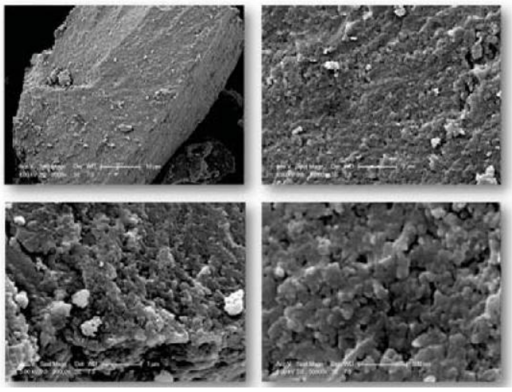

Fig. 10 SEM micrographs of PPy-PEGTh2

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