

Heterophase Polymerization of Pyrrole and Thienyl End Capped Ethoxylated Nonyl Phenol by Iron (III) Chloride

Görkem Ülkü, Esin A. Güvel, Nesrin Köken, Nilgün Kızılcın

Abstract—This study presents synthesis of novel block copolymers of thienyl end capped ethoxylated nonyl phenol and pyrrole via chemical oxidative polymerization. Ethoxylated nonyl phenol (ENP) was reacted with 2-thiophenecarbonyl chloride in order to synthesize a macromonomer containing thienyl end-group (ENP-ThC). Then copolymers of ENP-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. ENP-ThC served both as a macromonomer and an emulsifier for pyrrole with poor solubility in water.

The synthesized block copolymers (ENP-ThC-b-PPy) were characterized by spectroscopic analysis and the electrical conductivities were investigated with 4-point probe technique.

Keywords—End capped polymer, ethoxylated nonyl phenol, heterophase polymerization, polypyrrole.

I. INTRODUCTION

THE conducting polymers possess the electronic, electrical and optical properties of a metal while retaining the processability and mechanical properties usually associated with a conventional polymer [1], [2]. Several of the important advances in the area of conducting polymers have centered on the design and synthesis of new conjugated polymers whose structures have been suitably modified to introduce processability without compromising the electrical conductivity of the system [3]–[8].

Polypyrrole (PPy) exhibits good electrical conductivity and high air stability and is a useful conductive polymer. Polypyrrole has become a material of importance because of its wide range of technological applications in several areas such as secondary batteries [9], electrochromic display devices [10], light-emitting diodes [11], capacitors [12], sensors [13], membranes [14] and enzyme electrodes [15]. Electrical transport in polymeric materials [16] has become an area of increasing research interest because these materials have potential for solid-state devices [17].

G. Ulku is with the Polymer Science and Technology Department, Istanbul Technical University, Maslak, Turkey (phone: +90-554-453-7283; e-mail: gorkemulku@gmail.com).

E.A. Güvel is with the Chemistry Department, Istanbul Technical University, Maslak, Turkey (phone: +90-535-641-2858; e-mail: esinatess@gmail.com).

N. Köken is with the Chemistry Department, Istanbul Technical University, Maslak, Turkey (phone: +90-212-285-7103; e-mail: nesrin@itu.edu.tr).

N. Kızılcın is with the Chemistry Department, Istanbul Technical University, Maslak, Turkey (phone: +90-212-285-3242; e-mail: kizilcan@itu.edu.tr).

The improvement of the electrical conductivity is typically based on incorporation with an anionic compound, normally called “dopant”, into the polymer matrix. The mechanism of improvement in the electrical conduction in PPy has been attributed to a redox interaction between the conducting polymer and the dopant [18], [19]. A variety of anionic dopants have been investigated, including Cl^- , ClO_4^- , BF_4^- [20], p-toluenesulfonate (PTS), dodecylbenzene sulfonate (DBS) [21], and polystyrene sulfonate (PSS) [22], all of which function to balance the cationic charge of the conductive polymer [23].

A wide variety of oxidants is feasible in the polymerization of pyrrole: $\text{K}_2\text{S}_2\text{O}_8$ [24], H_2O_2 [25], iron(III) and cerium (iv) salts [26]–[31] or halogens [32]–[35] are well-established reagents. A lot of protic and aprotic solvents can be used with exception of those with high donor numbers like dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The highest conductivity (220 S/cm) for polypyrrole (PPy) prepared by chemical oxidative polymerization was measured by [26] using methanol as solvent and FeCl_3 as oxidant [36].

Ethoxylated nonyl phenols (ENPs) and ceric ammonium nitrate redox systems have been used for the polymerization of vinyl and acrylic monomers. In that case ENP acted as an organic reducing agent in the presence of Ce (IV) salt and a radical was formed. The polymers obtained with that redox system contained ENP chain ends because the radicals are formed on the reducing molecules. Similar copolymer synthesis have been reported using poly (ethylene oxide) [37] instead of its nonyl phenol terminated derivative, ENP. Copolymers of poly (ethylene oxide) and conducting polymers synthesized by ferric ions were produced in two steps. Firstly, heteroatoms (pyrrole, thiophene etc.) were attached to the poly (ethylene oxide) chains then copolymerization with heterocyclic monomers was carried out [38].

In this work, ethoxylated nonyl phenol (ENP) was reacted with 2-thiophenecarbonyl chloride in order to synthesize a macromonomer containing thienyl end-group (ENP-ThC). Then copolymers of ENP-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. ENP-ThC served both as a macromonomer and an emulsifier for pyrrole with poor solubility in water. The synthesized block copolymers (ENP-ThC-b-PPy) were characterized by spectroscopic analysis and the electrical conductivities were investigated with 4-point probe technique.

II. EXPERIMENTAL

A. Materials

Pyrrole (Py), Chloroform, Hydrochloric Acid (HCl), Sodium Bicarbonate (NaHCO_3), Dichloromethane (DCM), Pyridine, Cerium Ammonium Nitrate (CAN) and Iron (III) Chloride (FeCl_3) were all reagent-grade chemicals of the highest purity, so they were used without further purification.

Ethoxylated Nonyl Phenol (ENP30) was product of Henkel chemical company and its molecular weight is 1180 g/mol, the number 30 represents the amount of ethoxylate group in the component.

2-Thiophenecarbonyl chloride (ThCCl) was product of Sigma Aldrich with a molecular weight of 146.59 g/mol.

B. Analysis

Infrared spectra were recorded on an FTS-6000 Excalibur FTIR, using Varian Resolutions Pro as software. $^1\text{H-NMR}$ measurements were performed on Varian Mercury 400 spectrometer at room temperature, using CDCl_3 as deuterated solvent.

C. Conductivity Measurements

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.

$$\sigma = V^{-1} * I * (\ln 2 / \pi d_n) \quad (1)$$

where V is the potential (Volt), I is current (Amper) and d_n is the thickness of the samples (cm).

D. Synthesis of Ethoxylated Nonyl Phenol-Thiophene Carbonyl Compound (ENP30-ThC)

In this work, ethoxylated nonyl phenol (ENP) was reacted with 2-thiophenecarbonyl chloride (Fig. 1) in order to synthesize a macromonomer containing thienyl end-group (ENP-ThC).

For this purpose, firstly 20 g ENP (0.017 mol) was dissolved in 35 ml Chloroform to form a homogenous mixture. Then, Pyridine (1.8 ml, 0.0232 mol) was added in order to eliminate chloride part, which comes from 2-thiophenecarbonyl chloride. During calculations, the molar ratio of ThCCl to ENP30 was accepted as 1,1 ($n_{\text{ThCCl}}/n_{\text{ENP30}}=1,1$) and the molar ratio of pyridine to ThCCl was accepted as 1,2 ($n_{\text{Pyridine}}/n_{\text{ThCCl}}=1,2$). So, 2 ml ThCCl dissolved in 5 ml chloroform was added to reaction mixture by a dropping funnel, about 30 minutes. Since ThCCl and ENP30 were reacted violently, the temperature of reaction medium was kept at 0°C with ice. The reaction was ended after 20 hours. When proceeding the colour of reaction mixture was changed from onionskin to opaque.

After reaction, hot DCM was added in order to eliminate pyridium chloride for purification. Then, reaction mixture was extracted by 5% HCl solution and 10% NaHCO_3 solution,

respectively. In order to recrystallize, the extracted solution was washed with hot ethanol. Finally, the product was dried at 60°C in vacuum oven. The resultant polymer was in white color.

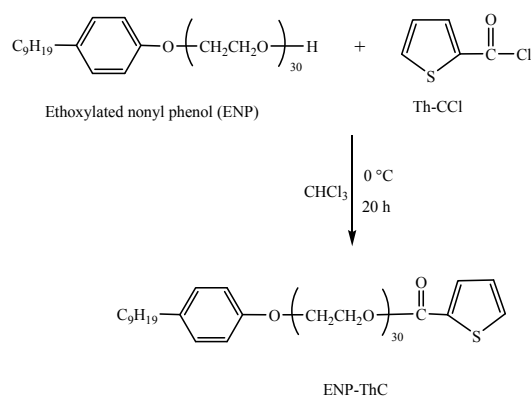


Fig. 1 Formation of ENP-ThC

E. Preparation of Thienyl End-capped Ethoxylated Nonyl Phenol-b-Polypyrrole Copolymer

Copolymers of ENP-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant (Fig. 2). ENP-ThC served both as a macromonomer and an emulsifier for pyrrole with poor solubility in water.

First, ENP30-ThC polymer (0.11 g, 0.00086 mol) was dissolved in 20 ml pure water. In order to alter the electrical properties of copolymer, 2.53 g p-toluene sulfonic acid (PTSA) dissolved in 20 ml pure water, as a dopant. Then, 0.3 ml pyrrole monomer (0.0043 mole) was added to the reaction mixture. For calculations, the molar ratio of pyrrole to ENP30-ThC was selected as 50 ($n_{\text{Py}}/n_{\text{ENP30-ThC}}=50$) and the molar ratio of iron (III) chloride to pyrrole was selected as 2.4 ($n_{\text{FeCl}_3}/n_{\text{Py}}=1,2$). Next step was adding the 1.673 g iron (III) chloride solution dissolved in 15 ml water to reaction mixture, via a dropping funnel, about 10 minutes. The reaction took place at 25°C and lasted about 24 hours.

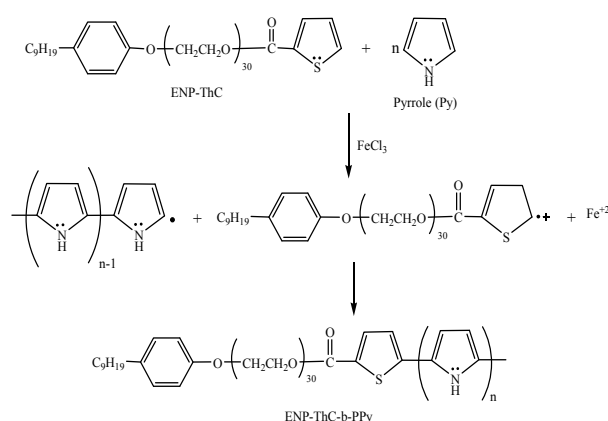


Fig. 2 Synthesis of ENP-ThC-b-PPy

At the end of the reaction, black powders were observed. The product was filtered with filter paper, washed with water,

methanol and acetone respectively. The resultant polymer was dried at 45°C in vacuum oven.

During the experiments, different molar ratios of pyrrole to ENP30-ThC were investigated. Also, the effect of copolymerization on electrical conductivity was examined by blank experiments without using ENP30-ThC. Lastly, at the same conditions and procedures, Cerium Ammonium Nitrate(CAN) was used as an oxidant, to compare the results with that of FeCl₃.

III. RESULTS AND DISCUSSIONS

TABLE I
EXPERIMENTAL RESULTS

#	Polymer	Ox	n _{py} /n _{ENP}	n _{Ox} /n _{py}	[PTSA]	Yield (%)	σ (S/cm)
1	ENP	CAN	10	1,00	0,24	23	0,013
2	ENPTh	CAN	10	1,00	0,24	21	0,055
3	ENPTh	FeCl ₃	50	2,40	0,24	77	2,5
4	ENPTh	FeCl ₃	10	2,40	0,24	37	1,4
5	-	CAN	-	0,5	0,24	33	0,087
6	-	CAN	-	1,00	0,24	21	0,055
7	-	FeCl ₃	-	2,40	-	93	0,14
8	-	FeCl ₃	-	2,40	0,24	127	5,63

A. The Effect of Oxidant Types and Dopant

PPy was obtained by chemical oxidation of Py monomer, with different oxidants namely Cerium Ammonium Nitrate (CAN) and Iron (III) Chloride (FeCl₃). Also, the effect of dopant (p-toluene sulfonic acid) was investigated. As it is stated in Table I, polypyrroles with using FeCl₃ have higher conductivities than that with performed by CAN.

Using p-toluene sulfonic acid (PTSA) increased the conductivity of PPy, as expected. The results can be seen in Table I, with the same oxidant amount and mole ratio.

B. The Effect of Thiophenecarbonyl Group

As it is seen in Table I, when compared to ENP30-b-PPy copolymer, thiophenecarbonyl group increased the conductivity of copolymer (ENP30-ThC-b-PPy).

C. The Effect of Molar Ratio

The molar ratio of Pyrrole to ENP group (n_{py}/n_{ENP}) had important effect on the conductivity and yield. As this ratio increases, the conductivity and yield also increases, which is shown in Table I.

D. Spectroscopic Study

FTIR spectra of the copolymer composed of Ethoxylated nonyl phenol with Thiophenecarbonyl end capped and Polypyrrole is shown in Fig. 3. The peaks about 2900 cm⁻¹ was due to aliphatic parts of material and proves that copolymerization reaction is completed.

The 1H NMR spectrum of Thiophenecarbonyl end-capped Ethoxylated Nonyl Phenol (ENP-ThC) is shown in Fig. 4. Chemical bonds and corresponding peaks show that the esterification reaction between Ethoxylated Nonyl Phenol and 2-Thiophenecarbonyl Chloride was completed successfully. This situation can be also seen in 13C NMR spectrum, Fig. 5.

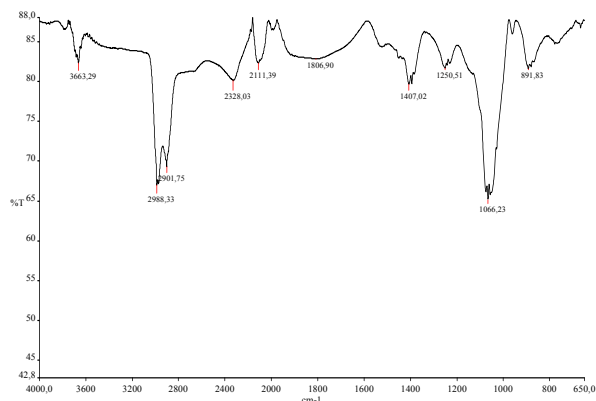


Fig. 3 FTIR results of ENP30-ThC-b-PPy copolymer

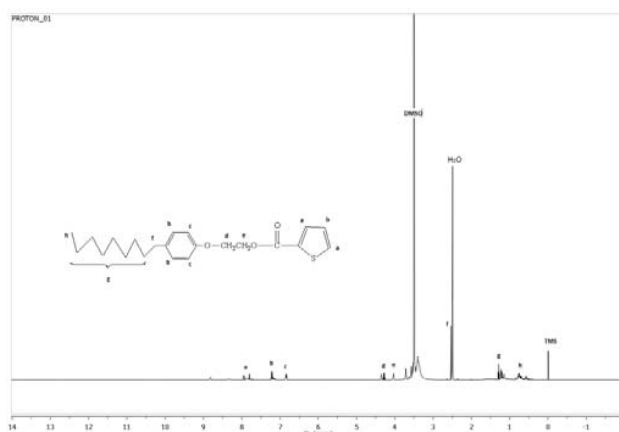


Fig. 4 ¹H NMR results of ENP-ThC

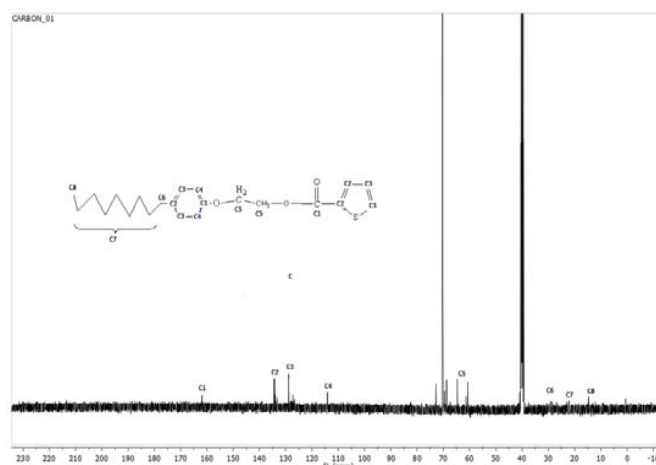


Fig. 5 ¹³C NMR results of ENP-ThC

IV. CONCLUSION

Since polypyrrole (PPy) homopolymers have some difficulties in the applications, soluble and conductive copolymers of PPy may overcome this difficulties and open new application areas. For this purpose, Thieryl End-Capped Ethoxylated Nonyl Phenol proposed a way to change the PPy's

properties, by means of Iron (III) chloride (FeCl_3), as an oxidizing agent. Thienyl group increased the conductivity of copolymer, but had no significant effect on the yield of polymerization.

Also, the molar ratio of Pyrrole to ENP group ($n_{\text{P}}/n_{\text{ENP}}$) had important effect on the conductivity and yield. As this ratio increases, the conductivity and yield also increases.

Some dopants can be used to enhance the high conductivity. For this purpose, p-toluene sulfonic acid (PTSA) was used to investigate the effect on conductivity. As expected, with PTSA, PPy had 40 times higher conductivity than that which had no dopant.

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Görkem Ülkü was born in Istanbul, Turkey, in 1990. He received the BSc degree in Chemical Engineering from Ege University, Izmir, Turkey in 2013. Recently, he is a MSc student at Polymer Science and Technology Department, Istanbul Technical University. His research interests are polymer processing, polymeric membranes and conductive

polymers.



Nesrin Köken was born in Istanbul, Turkey, in 1967. She is currently a Lecturer and Researcher in the Organic Chemistry group in Chemistry Department, and Polymer Science and Technology Programmers at Istanbul Technical University. She obtained her BSc in Chemistry Department in 1989, her MSc and PhD degrees in chemistry at the same university in 1992 and 1997, respectively.

Köken has published 11 research papers and 13 national and 14 international presentations. She was 5 completed research project coordinators, 1 PhD thesis supervisors, 6 MSc thesis supervisors. She specializes in emulsion polymerization, conducting polymer and copolymers.

Assos. Prof. Dr. Nesrin Köken is a member of Deutscher Akademischer Austausch Dienst German Academic Exchange Service (DAAD) and Turkish Chemical Society.



Esin Ateş Güvel was born in Razgrad, Bulgaria, in 1979. She is currently a doctoral student with the Chemistry Programme at Istanbul Technical University. She obtained her BSC degree in chemistry from Trakya University in 2002 and MSc degree in chemistry program at Istanbul Technical University 2005, respectively.

A. Güvel has published 4 research papers, 8 national and 4 international presentations.



Nilgün Kızılcan was born in İstanbul, Turkey, in 1965. She is currently a Lecturer and Researcher in the Organic Chemistry group in Chemistry Department and Polymer Science and Technology Programmers at Istanbul Technical University. She obtained her BSc in Chemical Engineering Department in 1986, her MSc and PhD degrees in chemistry at the same university in 1990 and 1995, respectively.

Kızılcan has published 44 research papers and 48 national and 47 international presentations. She was 16 completed research project coordinators, 5 PhD thesis supervisors, 18 MSc thesis supervisors. She wrote book chapters in 2 books. She is on the Editorial Advisory Board of ISRN Polymer Science. She specializes in resins, conducting polymer and copolymers.

Professor N. KIZILCAN is a member of Turkish Chamber of Chemical Engineers.