

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**HETEROPHASE POLYMERIZATION OF PYRROLE AND THIENYL END
CAPPED ETHOXLATED NONYL PHENOL BY IRON (III) CHLORIDE**

M.Sc. THESIS

Görkem ÜLKÜ

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Assoc.Prof. Dr. Nesrin KÖKEN

MAY 2015

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**POLİPİROL İLE TİYENİL SONLU ETOKSİLE NONİL FENOLÜN DEMİR
(III) KLORÜR VARLIĞINDA HETEROFAZ POLİMERİZASYONU**

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To my family,

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ABBREVIATIONS

PPy	: Polypyrrole
ENP	: Ethoxylated Nonyl Phenol
ThC	: Thiophenecarbonyl
SEM	: Scanning Electron Microscope
FTIR	: Fourier Transform Infrared Spectroscopy
NMR	: Nuclear Magnetic Resonance
PTSA	: p-toluene sulfoic acid

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HETEROPHASE POLYMERIZATION OF PYRROLE AND THIENYL END CAPPED ETHOXYLATED NONYL PHENOL BY IRON (III) CHLORIDE

SUMMARY

Polypyrrole (PPy) is one of the most investigated conducting polymers, due to its easy synthesis and good conductivity. However synthetically conductive PPy is insoluble and infusible which restricts its processing and applications. PPy is a hard, brittle, and nonprocessable solid that is insoluble in common solvents.

This study presents synthesis of novel block copolymers of thienyl end capped ethoxylated nonyl phenol and pyrrole via chemical oxidative polymerization, by iron (III) chloride (FeCl_3). 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. The images of polymer samples were produced by using a Jeol JSM-5410 scanning electron microscope (SEM). The samples were coated with platinum (Pt) for SEM.

Results showed that with the addition of ENP-ThC groups, the average particle size of PPy was decreased from 1000 nm to 200 nm. The reduction of conductivity was expected due to the ENP-ThC group which is non-conductive, but conductivities of copolymers were still high. Also, ENP-ThC group increased the solubility of PPy in various organic solvents. This research could help the processability problem of PPy and open new research areas.

POLİPİROL İLE TİYENİL SONLU ETOKSİLE NONİL FENOLÜN DEMİR (III) KLORÜR VARLIĞINDA HETEROFAZ POLİMERİZASYONU

ÖZET

İletken polimerler metallere ait elektrik, elektronik ve optik özellikleri taşımanın yanında kendi türüne ait işlenebilme ve güçlü mekanik özellikleri bünyesinde taşır. İletken polimer alanındaki yeni çalışmalar konjuge polimerlerin dizaynı ve sentezi üzerine yoğunlaştı, böylece polimerin elektriksel özelliklerinden fedakarlık etmeden aynı zamanda işlenebilir bir malzeme elde edilebilir.

Polipirol, iyi bir iletkenlik gösteren ve hava etkisine dayanıklı , kullanışlı bir iletken polimerdir. İkincil piller, elektrokromik görüntü cihazları, ışık yayan diyotlar (LEDs), kapasitörler, sensörler, membranlar ve enzim elektrotlar gibi geniş kullanım alanlarında kendine yer buldukça, polimerin özellikleri ile ilgili çalışmalar/iyileştirmeler yapılmaya başlandı.

Herhangi bir malzemenin elektrik iletkenliğini arttırmanın bir yolu, dopant adı verilen anyonik yapıli malzemelerin polimer matriksiyle etkileşime girmesiyle olabilir. Polipirol için de iletken polimer ve anyonik bileşik arasındaki redoks etkileşimi ile elektrik iletkenliği arttırılabilir. Bu amaçla klorür (Cl⁻) , perklorat (ClO₄⁻) , tetrafloroborat (BF₄⁻) , p-toluen sülfonat (PTS) , dodecylbenzen sülfonat (DBS) ve polistiren sülfonat iletken malzemedeki katyon yükünü dengelemek için kullanılabilir.

Polipirol, pirol monomerinin kimyasal redoks polimerizasyonu ile üretilebilir. Redoks polimerizasyonu için oksidant seçimi ve çözücü seçimi çok önemlidir. Potasyum persülfat (K₂S₂O₈) , hidrojen peroksit (H₂O₂) , demir (III) ve seryum (IV) tuzları en sık kullanılan oksidantlar arasındadır. DMF (dimetil formamide) ve DMSO (dimetilsülfoksit) gibi yüksek donör numaralı solventler dışında protik ve aprotik bir çok solvent bu reaksiyonda kullanılabilir. Bu yöntemle yapılan deneylerde en yüksek değer , solvent olarak metanol seçildiğinde ve oksidant olarak demir (III) klorür seçildiğinde 220 S/cm olarak bulunmuştur.

Alkil fenol ailesinden nonil fenol yüzey aktif özellik taşır ve bu özelliğiyle deterjanlarda, antioksidantlarda , makina yağlarında ve çözünürlük arttırıcı malzemelerde kullanılır. Genellikle etoksile halde kullanılır ve etoksile yapısının miktarı malzeme için önemlidir. İnsanlar ve diğer memelilerde hormonal dengesizliklere yol açtığı için kullanımı sınırlıdır.

Bu çalışmanın amacı, büyük tanecik boyutları ve birçok çözücüde çözünmemesinden dolayı işlenemeyen polipirolün kopolimerini yaparak daha küçük tanecik boyutunda, işlenebilir ve çözünebilir bir polimer elde etmektir. Bu amaçla , tiyenil sonlu etoksile nonil fenol ile polipirol'ün demir (III) klorür varlığında

heterofaz polimerizasyonu incelenmiştir. Etoksile nonil fenol 2-tiyofenkarbonil klorür ile reaksiyona girerek tiyenil sonlu bir makromonomer haline gelmiştir. Tiyenil grubunun amacı ileride yapılacak blok kopolimer yapısında iletken (polipirol kısmı) ve iletken olmayan (etoksile nonil fenol kısmı) arası köprü görevi görmek ve malzemenin kimyasal yükseltgenme potansiyelini arttırarak demir (III) klorür oksidantı için uygun hale getirmektir. 24 saat süren reaksiyon sonucu tiyenil uçlu etoksile nonil fenol (ENP-ThC) elde edilmiş ve reaksiyonun başarıyla sonuçlandığı FTIR ve NMR sonuçlarıyla kanıtlanmıştır.

Tiyenil sonlu etoksile nonil fenol ile pirol monomerinin kopolimerizasyonu demir (III) klorür varlığında , oda sıcaklığında gerçekleşmiştir. Polipirol'ü iletken olmayan başka bir blok ile birleştirdiğimiz için iletkenlik kaybı beklenebilirdi. Bunu önlemek için p-toluensülfonik asit dopant olarak kullanıldı ve bu kayıp minimize edilmeye çalışıldı. Reaksiyon ortamı olarak saf su kullanıldı. Reaksiyonun verimine ve ürünün iletkenliğine etki eden bazı parametreler (monomer mol oranları , süre , dopant etkisi vb.) incelendi ve optimum koşullar bulunmaya çalışıldı. Elde edilen ürünler FTIR ve NMR gibi spektroskopik yöntemlerde karakterize edildi ve SEM görüntüleri ile morfolojik olarak incelendi.

Yapılan deneylere göre, tiyenil sonlu etoksile nonil fenol'ün (ENP-ThC) kullanılan pirol monomer miktarına molce oranı arttıkça iletkenliğin azaldığını fakat polimerizasyon veriminin arttığını gözlemlemiş olduk. Tiyenil sonlu etoksile nonil fenol grubu ne kadar fazla polipirol yapısına eklenirse o kadar düşük ortalama parçacık boyutu elde edildi. Bu, yüksek parçacık boyutundan dolayı kolay proses edilemeyen polipirol için önemli bir gelişmedir.

Reaksiyon süresi de kimyasal oksidatif redoks polimerizasyonu için önemli bir kavramdır. Deneyler esnasında üç farklı süre (1 saat , 2 saat ve 24 saat) çalışıldı ve elde edilen sonuçlara göre süre arttıkça reaksiyon verimi artıyor , fakat iletkenlik git gide azalıyor. Maksimum iletkenliğin 1 saatlik deneyde elde edilmesinin sebebi dopant iyonlarının anlık etkisi olabilir.

Kimyasal oksidatif polimerizasyonda kullanılan oksidant cinsinin son ürüne etkisi de deneyler esnasında araştırıldı. Seryum amonyum nitrat (CAN) ve demir (III) klorür ile çalışıldı ve en yüksek iletkenlik değerleri demir (III) klörür ile elde edildi. Demir (III) klörür aynı zamanda malzemenin homolitik zincir yapısını korumayı sağladığı için daha sonraki deneyler demir (III) klörür ile yapıldı.

Dopant kullanımı beklendiği üzere iletkenliklerde ve verimde ciddi bir artış sağladı. Ayrıca polipirol homopolimerinde ve blok kopolimerinin FTIR sonuçlarında p-toluen sülfonik asitten kaynaklı pikler tespit edildi ve dopant iyonlarının polimerin yapısına da katıldığı gösterilmiş oldu.

Kimyasal oksidatif polimerizasyon aynı zamanda bir heterofaz polimerizasyonu çeşidi olan emülsiyon polimerizasyonuydu. Çözücü olarak su kullanılmıştır ve düşük vizkozitesi oluşan ürünün elde edilmesini kolaylaştırmıştır.

Polipirol işlenebilirliğindeki bir diğer engel organik çözücülerde çözünememesidir. Deney sonuçlarına göre tiyenil sonlu etoksile nonil fenol sayesinde malzemelede çözünürlük artışı gözlemlenmiştir, fakat henüz tam olarak çözündüğü

söylenememektedir. Malzemelerden belirli bir miktarda alınan örnekler çözücülerde ayrı ayrı çözülmüş ve bir gece bekletildikten sonra süzgeç kağıdı ile süzölmüştür. Bu iki miktar arası fark gözlemlenmiş ve kopolimerlerin organik çözücülerde " biraz çözüdür " olduđu belirlenmiştir.

Sonuç olarak, tiyenil uçlu etoksi nonil fenol grubunun etkisiyle polipirol ortalama tanecik boyutlarında azalma olduđunu ve organik solventlerde çözüdürlüđünün homopolimer haline kıyasla daha da arttıđını gözlemledik. Kopolimerizasyon işlemleri sırasında beklenen iletkenlik kaybını da minimum düzeyde tutarak, işlenebilir ve yüksek iletkenlikli bir polipirol kopolimeri elde etmiş olduk.

1. 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].

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 [32-34] 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 using methanol as solvent and FeCl_3 as oxidant [26].

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) [35] 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 [36].

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), as described in Fig 1.1.

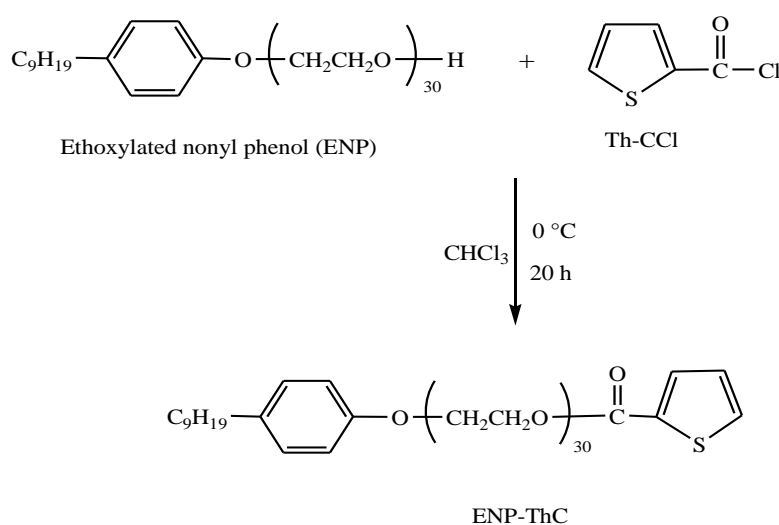


Figure 1.1. Synthesis of ENP-ThC.

Then copolymers of ENP-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant, the reaction mechanism can be seen in Fig 1.2.

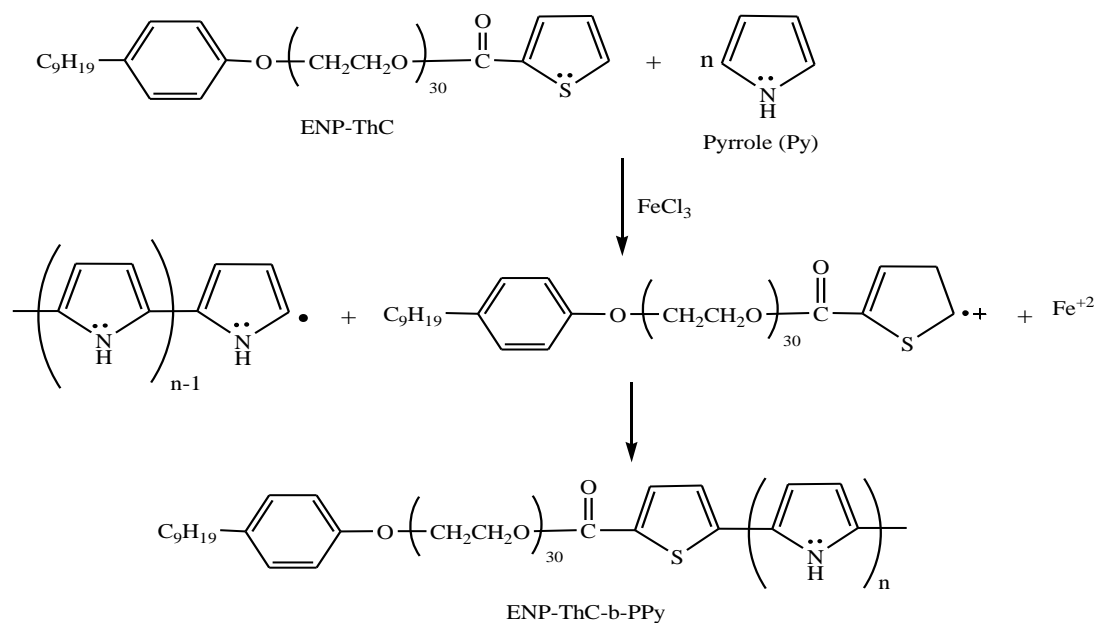


Figure 1.2. Synthesis of ENP-ThC-b-PPy copolymer.

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. The obtained samples were also characterized morphologically by Scanning Electron Microscope (SEM).

2. THEORY

2.1 Heterophase Polymerization

Any heterophase polymerization is characterized by changing heterogeneity and dispersity during almost the entire reaction. Heterogeneity means the coexistence of different phases and is a qualitative feature, which implies that phase boundaries are of importance. Contrary, dispersity is a quantitative measure that characterizes the degree of division of the heterophase system. It is defined as the reciprocal average characteristic length scale. Generally, the coexistence of two immiscible phases requires a balanced relation between lyophilic and lyophobic interactions or between hydrophilic and hydrophobic interactions as in the particular case of aqueous heterophase polymerizations. Heterogeneity and dispersity together cause an energetic characterization of a dispersed system that is the existence of an interfacial tension between coexisting phases and an interfacial free energy (interfacial tension times interfacial area). It is straightforward that with increasing dispersity interfacial effects become more and more important. Also, the interface is responsible for all peculiarities, for all pro's and con's of heterophase polymerizations. In this sense both the hydrophilicity and the hydrophobicity of all recipe components are crucial for an understanding of aqueous heterophase polymerizations. Hydrophobic substances are defined as only sparingly soluble or insoluble in water [37] and hence, keeping them in a dispersed state requires a proper stabilization by hydrophilic components, which can be either surface active molecules, or hydrophilic polymers, or hydrophilic parts in the polymer chains arising from initiator residues, comonomers, or chain transfer reagents [38].

In heterophase polymerization processes, the polymer phase separates in the very early stages of the reaction. The morphology of the polymer particles depends on the characteristics of the polymer phase such as its degree of crystallinity and "amorphousness", its compatibility with the monomer and solvents and whether the polymerization temperature is higher or lower than the glass temperature of the polymer [39,40].

Two main advantages of heterophase polymerizations are, firstly, the ease of removing the polymerization heat through the continuous phase of low viscosity and, secondly, the possibility, in the case of feeding procedures, to polymerize most of the time at a maximum polymerization rate [41]. The complete exploitation of these advantages requires knowledge of the polymerization kinetics up to very high conversions, i.e. the change of the rate of polymerization during the whole polymerization period, the so called reaction rate profile (RRP). The overall rate of polymerization of a heterophase polymerization is given by Eq. 2.1.

$$r_p = k_p * N * C_M * \bar{n} \quad (2.1)$$

Eq. 2.1 describes with the assumptions that after the nucleation period (Interval I) the particle concentration, N ($\text{mol}\cdot\text{cm}^{-3}$), as well as the mean number of radical per particle, \bar{n} , and the monomer concentration in the particle, C_M ($\text{mol}\cdot\text{cm}^{-3}$) are almost constant at constant reaction polymerization rate, as long as a free monomer phase is present.

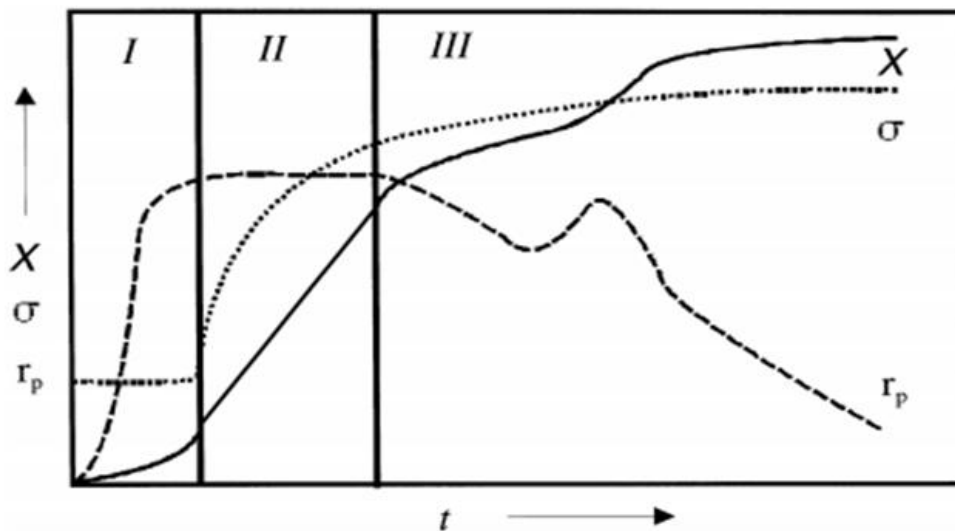


Figure 2.1. Schematic description of emulsion polymerization for Styrene polymerization with respect to time.

Fig 2.1 shows the change of main reaction parameters (r_p , rate of polymerization; X , monomer conversion; σ , latex surface tension) with respect to time. During interval I the rate of polymerization increases due to increasing values of N , C_M and \bar{n} . In

contrast, during interval III (monomer starvation) the rate of polymerization decreases due to a decreasing value of C_M . As the decrease in C_M leads to an increasing viscosity inside the polymer particles a Norrish [42] or Trommsdorff [43] or gel effect frequently occurs leading to a temporary increase in r during interval III. Fig. 1.1 sketches the time development of the rate of polymerization, the conversion, and the latex surface tension, respectively, for a batch styrene emulsion polymerization with a weak gel effect at an emulsifier concentration above the critical micelle concentration (CMC) according to the classical assumptions of Harkins [44] and Smith/Ewart [45]. But it is also known that for more water soluble monomers the observed RRP strongly deviate from that classical picture. For example, the RRP of a methyl methacrylate (MMA) emulsion polymerization is characterized by the absence of a period with a constant r_p and by a very strong gel effect [46,47].

The use of polymers in heterophase polymerizations is especially in industrial processes limited to the application of polymeric stabilizers. Examples are protective colloids in suspension polymerizations [48], block copolymers as stabilizers in emulsion polymerization [49], and mainly homopolymers as stabilizers in dispersion polymerization [50]. The use of polymeric stabilizers imparts to the particles an additional electrolyte stability up to the molar concentration range of monovalent ions and makes these dispersions much less sensitive to process fluctuations.

In several research groups there has been done a great deal over the last years with respect to the development of polymeric initiators for free radical polymerizations and also for heterophase polymerizations [51-55]. The special feature of the use of polymeric radicals is the formation of block copolymers in a free radical polymerization. The block copolymer structure, i.e. the formation of diblock copolymer, triblock copolymers, or multiblock copolymers depends on the number of radicals per polymer chain as well as on the termination mode during the free radical polymerization of the particular monomer. In heterophase polymerizations this leads to the development of a special particle morphology due to microphase separation depending on the particular conditions [46].

Another possible application of polymers in heterophase polymerizations is their use as dispersion media. This is a similar procedure to modifications of polymers by polymerization of a second monomer in a reaction extruder [56,57].

2.2. Conducting Polymers

Conducting polymers have been studied most intensively due to their easy synthesis, high conductivity, environmental stability, cost effectiveness and unique electrochemical redox properties. The first conjugated polymer, polythiazyl (SN)_x was discovered in 1975, which is exhibited metallic conductivity as well as superconductivity at 0.29 K [58]. In 1977, Shirakawa et al. have demonstrated the variation of electrical conductivity with doping in trans-polyacetylene [59]. Conducting polymers rendered conduction through a conjugated bond system along the polymer backbone. The various electronic properties of the CPs result from the various types of charge carriers in these materials, which is entirely different from that of conventional semiconductors. The polymer chain is distorted when electrons or holes are injected at the electrodes and the charge carriers couple with the polymer chain distortion to form a mobile polaron/ soliton [60,61].

Conducting polymers are synthesized mainly using either chemical oxidative polymerization (OP) or electrochemical polymerization (EP) [62]. OP is preferred when polymer is required in large quantity and it yields product in powdered form. Polymer synthesized via OP are generally in high conducting oxidized state. In comparison, EP offers many unique advantages such as no catalyst required, reproducibility, uniform thickness and direct deposition as thin film that makes it more suitable for DSSCs applications. EP can be done either by galvanostatic or potentiostatic method [63]. Conducting polymers are attractive, because they have good intrinsic conductivity in the range from a few S/cm to 500 S/cm in the doped state [64,65]. Conducting polymers are not only exhibiting conduction properties, but also have specific electronic, magnetic, wetting, optical, mechanical and microwave-absorbing properties. They combine the electronic and optical properties of semiconductors with the mechanical and physical properties of polymers. Conducting polymers such as polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), poly(p-phenylenevinylene) (PPV), poly(3,4-ethylene dioxythiophene) (PEDOT), polyfuran (PF), polyvinylidene fluoride (PVDF) and other polythiophene (PTh) derivatives, have drawn special attention. They can be used as thin film transistors [66], polymer light emitting diodes (LEDs) [67], corrosion resistance materials [68], electromagnetic shielding [69], sensor technology [70], molecular

electronics [71], supercapacitors [72], electrochromic devices [73] and others [74].

2.2.1. Polyaniline

Polyaniline (PANI) is considered one of the conducting polymers most used as an anticorrosion coating. It has the following advantages over other conducting polymers: (1) it can be synthesized easily via chemical or electrochemical means, (2) it can be doped and dedoped easily by treatment with aqueous acid and base, (3) it cannot be degraded easily, and (4) the aniline monomer is relatively cheap [75]. First report of its synthesis dates back to 1862 [76] and its primary application was as textile dye. It was only during the 1960s that the electrical property of PANI was realized [77]. PANI can be synthesized either chemically or electrochemically. Chemical synthesis of PANI involves the oxidation of aniline in acidic medium with an oxidizing agent such as ammonium persulfate and tetrabutyl ammonium periodate [78,79]. First report of electrochemical oxidation of aniline was done by Letheby and was later extended to polymerize alkyl, alkoxy, and dimethoxy-substituted aniline[80]. It has been proven that chemical oxidation of aniline yields linear PANI, while electrochemical oxidation of aniline yields a cross-linked polymer network[81,82]. PANI can exist in a number of well-defined oxidation states.[83] PANI can either be fully reduced (leucoemeraldine), fully oxidized (pernigraniline), or partially oxidized (protoemeraldine, emeraldine, nigraniline). None of these are conducting. PANI becomes moderately conducting when the partially oxidized states, specifically the emeraldine base, are protonated by adding an aqueous acid solution.

2.2.2. Polypyrrole

Polypyrrole is an example of heterocyclic conductive polymer. The earliest report of its synthesis was in 1968 [84]. Electrochemical synthesis of polypyrrole in sulfuric acid yielded a black conducting film, which is stable under ambient conditions and even at temperatures above 200°C [85]. Electrical and mechanical properties of the electropolymerized polypyrrole film depend heavily on the counter-ion used. Using perchlorate instead of oxalate can increase its conductivity by 10 times [86,87]. Commercially available polypyrrole films with tosylate counter-ions are highly conductive (15 S/cm) and are very stable under ambient conditions (conductivity only decreased by 15% after 1 year) [88].

To increase the processability of polypyrrole, soluble forms were synthesized by adding flexible side chains along the ring. Addition of various functionalities at the nitrogen can also improve its solubility; however, the conductivity of the resulting film can be reduced drastically because of the strong steric interactions of the substituent at the nitrogen and the hydrogens at the 3- and 4-positions of the adjacent pyrrole rings. The adjacent rings are forced out of the plane, which results in loss of conjugation and ultimately drastic reduction of its conductivity [89,90]. Recently, Gonzalez et al. studied the electropolymerization of pyrrole in the presence of nitrate and molybdate anions and evaluated the anticorrosion property of the resulting film [91]. They reported that only the film electropolymerized potentiostatically has the strong adhesion on the stainless steel substrate and can completely prevent the pitting corrosion in chloride solution. It has also been suggested that the presence of nitrate and molybdate provided the polymer coating with fixed negative charge, which prevents the diffusion of the negative chloride ions through the polymer matrix. Mrad et al. found out that addition of hydroxyquinoline or molybdate anions drastically changes the morphology and the thickness of the electropolymerized polypyrrole and moderates the resistance of the coating against pitting corrosion of the aluminum alloy [92]. Hybrid coating comprising polypyrrole and titania nanotubes has been recently studied by Herrasti et al [93]. They reported that addition of titania nanotubes increases the polymerization rate of pyrrole because the nanotubes act as nucleation sites. Also, the hybrid coating improved the corrosion resistance of stainless steel by 400 times as compared to the uncoated steel, and by twice as compared to the stainless steel coated with just polypyrrole.

2.2.3. Polythiophene derivatives

Polythiophene is similar to polypyrrole, but with sulfur in place of the nitrogen in the aromatic ring. Chemical synthesis of polythiophene can be performed by mixing thiophene monomer and sulfuric acid to yield a dark insoluble material or by using a Grignard type coupling of 2,5-dibromothiophene. A highly conducting form of polythiophene is composed of monomers linked at the 2- and 5-positions. Defects like 2,4- and 2,3-linkages reduce the degree of conjugation and, in effect, reduce the conductivity of the resulting film [94]. In terms of processability, addition of flexible side chains at the 3- and/or 4-position can improve the solubility of polythiophene. Electropolymerization of thiophene monomer is rarely done because it requires high

oxidation potential (2.07 vs. SCE). Instead, thiophene oligomers, such as bi-thiophenes and terthiophenes with oxidation potentials of 1.05 and 1.31V versus SCE, respectively, are used [95]. In terms of anticorrosion property, poly(thiophene) was recently used as part of a polymer alloy that was used as a coating on mild steel.[96] It has been shown that the resulting polymer alloy coating has very high heat resistance and is stable at 380 °C.

Poly(3,4-ethylenedioxythiophene) is extensively investigated as CE for dye sensitized solar cells (DSSCs). PEDOT is developed by Jonas and Schrader[97] and the CEs had a high room temperature conductivity, electrochemical reversibility and significant thermal and chemical stabilities. The electrocatalytic property of PEDOT is first reported by Yohannes and Inganäs[98]. When doped with a polyanion such as polystyrenesulfonate (PSS), PEDOT had better compatibility with polar group polymer and it exhibited good device performance with aqueous electrolytes. Among all the conducting polymers, PEDOT exhibits highest electrocatalytic activity towards redox couple in DSSCs [99].

Conducting (or electro-active) polymers are a special type of polymer with extensive π -electron delocalization along their backbones that give rise to interesting optical properties and allows them to become good electrical conductors (typically when oxidized or reduced). Having a conjugated backbone and/or a backbone that has low oxidation potential is necessary, but not sufficient for the polymer to be conductive [100]. Conjugation provides the orbital system that allows the charge carriers to move because of the continuous overlapping of the Π -orbitals along the backbone. Most organic polymers, including some conjugated polymers, do not have intrinsic charge carriers. Charge carriers can be introduced by partial oxidation (p-doping) of the polymer chain with electron acceptors or by partial reduction (n-doping) with electron donors[101]. Such doping processes mostly introduce charged defects (e.g., polaron, bipolaron, and soliton) along the polymer backbone. There are several ways to introduce charge carriers or to dope the conjugated polymer to become conducting, but the most widely used are electrochemical and chemical oxidation/reduction. Electrochemical doping offers advantages over other doping techniques: doping level can be precisely controlled by controlling the amount of current passed, and doping and dedoping processes can be done simply by changing the applied potential[102]. Partial oxidation of the conjugated polymer converts the

polymer into its cationic salt form, while partial reduction yields the anionic salt form. Both forms are conducting; however, cationic salt form is more stable [103].

2.2.4.Doping

Conjugated organic polymers are either electrical insulators or semiconductors. Those that can have their conductivity increased by several orders of magnitude from the semiconductor regime are generally referred to as "electronic polymers" and have become of very great scientific and technological importance since 1990 because of their use in light emitting diodes [104]. An increase in electrical conductivity of many orders of magnitude which can be obtained by doping.

The concept of doping is the unique, central, underlying, and unifying theme which distinguishes conducting polymers from all other types of polymers [105]. During the doping process, an organic polymer, either an insulator or semiconductor having a small conductivity, typically in the range 10^{-10} to 10^{-5} S/cm, is converted into a polymer which is in the "metallic" conducting regime (about 1 to 10^4 S/cm). The controlled addition of known, usually small (lower than 10%) non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical, and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer backbone. Both doping and undoping processes, involving dopant counterions which stabilize the doped state, may be carried out chemically or electrochemically [106]. Transitory doping by methods which introduce no dopant ions are also known [107].

By controllably adjusting the doping level, a conductivity anywhere between that of the non-doped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer can be easily obtained. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator), whose conductivity can be adjusted by varying the relative proportions of each polymer, can be made [108]. This permits the optimization of the best properties of each type of polymer.

Since the initial discovery in 1977, that polyacetylene $(CH)_x$, now commonly known as the prototype conducting polymer, could be p- or n-doped either chemically or electrochemically to the metallic state, [106, 109, 110] the development of the field of conducting polymers has continued to accelerate at an unexpectedly rapid rate and a variety of other conducting polymers and their derivatives have been

discovered.[106][107] This rapid growth rate has been stimulated by the field's fundamental synthetic novelty and importance to a cross-disciplinary section of investigators-chemists, electrochemists, biochemists, experimental and theoretical physicists, and electronic and electrical engineers and to important technological emerging applications of these materials.

2.2.4.1.Redox Doping

All conducting polymers (and most of their derivatives), for example, poly-(para-phenylene) (1), poly(phenylenevinylene) (2), polypyrrole (3), polythiophene (4), polyfuran (5), by chemical and/or electrochemical processes during which the number of electrons associated with the polymer backbone changes.[108,109] Selected examples of the different types of doping are shown below in Fig 2.2.

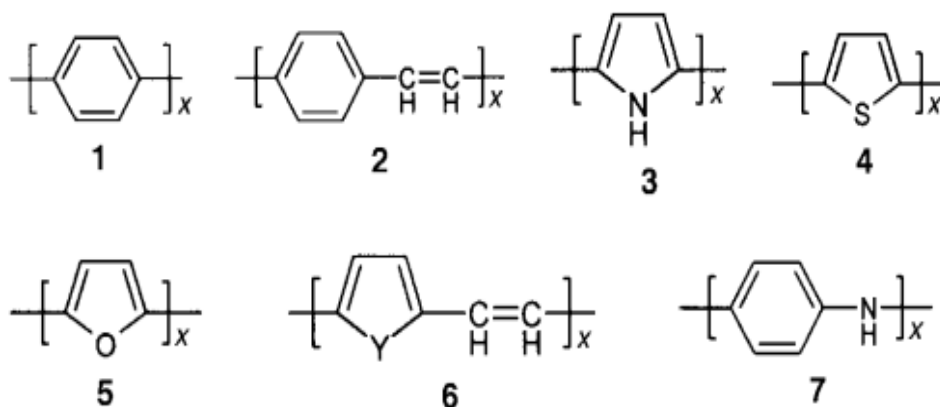
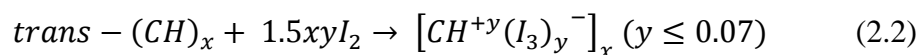


Figure 2.2. Typical examples of conducting polymers.

Chemical and electrochemical p-doping

Doping, that is, partial oxidation of the p backbone of an organic polymer, was first discovered by treating $\text{trans}-(\text{CH})_x$ with an oxidizing agent such as iodine,[110] as described in Eq 2.2.



This process was accompanied by an increase in conductivity from about 10^{-5} S/cm to about 10^3 S/cm. If the polymer is stretch-oriented five- to six-fold before doping, conductivities parallel to the direction of stretching up to around 10^5 S/cm can be obtained.[108,109]

Approximately 85% of the positive charge is delocalized over 15 CH units (depicted in Fig 2.3. for simplicity over only five units) to give a positive soliton.

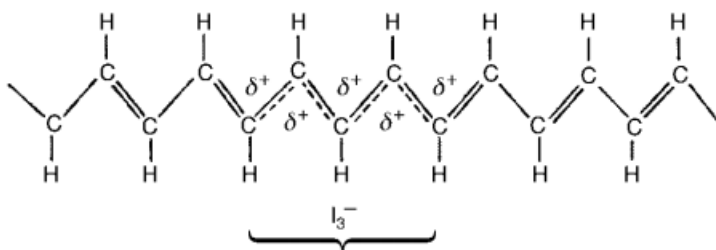


Figure 2.3. The delocalized five units of CH group.

Chemical and electrochemical n-doping

n-Doping, that is, partial reduction of the backbone p system of an organic polymer, was also discovered using $\text{trans}-(\text{CH})_x$ by treating it with a reducing agent such as liquid sodium amalgam or preferably sodium naphthalene [108].

The antibonding p-system is partially populated by this process which is accompanied by an increase in conductivity of about 10^3 Scm^{-1} .

n-Doping can also be carried out by electrochemical cathodic reduction[111] by immersing a $\text{trans}-(\text{CH})_x$ film in, for example, a solution of LiClO_4 , dissolved in tetrahydrofuran and attaching it to the negative terminal of a DC power source, the positive terminal being attached to an electrode also immersed in the solution.

In all chemical and electrochemical p- and n-doping processes discovered for $(\text{CH})_x$ and for the analogous processes in other conducting polymers, counter "dopant" ions are introduced which stabilize the charge on the polymer backbone. In each case, spectroscopic signatures, for example, those of solitons, polarons, bipolarons, etc., are obtained characteristic of the given charged polymer. However, the doping phenomena concept extends considerably beyond that given above to "doping" processes where no counter dopant ion is involved, that is, to doping processes in which transitory "doped" species are produced, which have similar spectroscopic signatures to polymers containing dopant ions. This type of doping can provide information not obtainable by chemical or electrochemical doping. Examples of such types of redox doping which can be termed "photo-doping" and "charge-injection doping" are given below.

Photo doping

When $\text{trans}-(\text{CH})_x$ for example, is exposed to radiation of energy greater than its band gap, electrons are promoted across the gap and the polymer undergoes "photo-doping". Under appropriate experimental conditions, spectroscopic signatures characteristic of, for example, solitons can be observed [112], as it is seen in Fig 2.4.

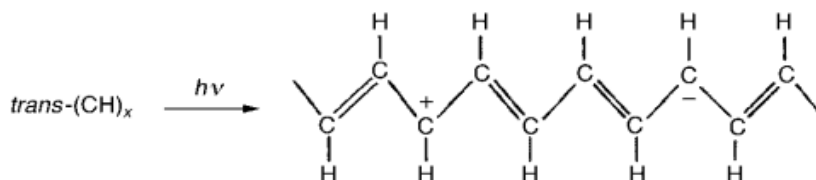


Figure 2.4. An example of photo doping process.

The positive and negative solitons are here illustrated diagrammatically for simplicity as residing only on one CH unit; they are actually delocalized over about 15 CH units. They disappear rapidly because of the recombination of electrons and holes when irradiation is discontinued. If a potential is applied during irradiation, then the electrons and holes separate and photoconductivity is observed.

Charge-Injection Doping

Charge-injection doping is most conveniently carried out using a metal/insulator/semiconductor (MIS) configuration involving a metal and a conducting polymer separated by a thin layer of a high dielectric strength insulator. It was this approach, which resulted in the observance of superconductivity in a polythiophene derivative, as described previously. Application of an appropriate potential across the structure can give rise, for example, to a surface charge layer, the "accumulation" layer which has been extensively investigated for conducting polymers [108,113]. The resulting charges in the polymer, for example, $(\text{CH})_x$ or poly(3-hexylthiophene), are present without any associated dopant ion. The spectroscopic properties of the charged species so formed can therefore be examined in the absence of dopant ion. Using this approach, spectroscopic studies of $(\text{CH})_x$ show the signatures characteristic of solitons and the mid-gap absorption band observed in the chemically and electrochemically doped polymer. However, coulombic interaction between charge on the chain and dopant ion is a very strong interaction and one that can totally alter the energetics of the system.

2.2.4.2. Non-redox doping

This type of doping differs from redox doping described above in that the number of electrons associated with the polymer backbone does not change during the doping process. The energy levels are rearranged during doping. The emeraldine base form of polyaniline was the first example of the doping of an organic polymer to a highly conducting regime by a process of this type to produce an environmentally stable polysemiquinone radical cation. This was accomplished by treating emeraldine base with aqueous protonic acids and is accompanied by a nine to ten order of magnitude increase in conductivity (up to around 3 S/cm) to produce the protonated emeraldine base, as shown in Fig 2.6. [114-116] Protonic acid doping has subsequently been extended to systems such as poly(heteroaromatic vinylenes) [117].

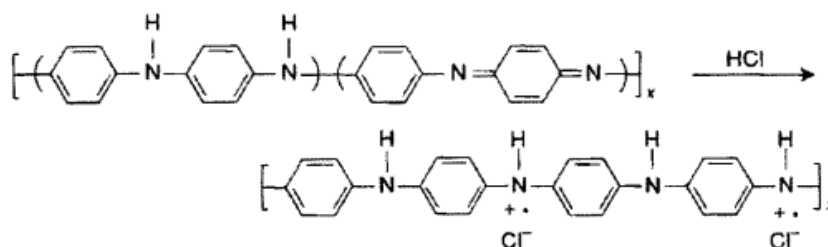


Figure 2.5. Doping with aqueous protonic acid.

2.3. Conducting Block Copolymers

There is a significant and continuing need in the art for conducting polymers that exhibit improved processability and mechanical and physical properties. Having a block copolymer of a polymer which have heteroaromatic nature can be the solution of this problem.

The chemically different blocks of the copolymer are covalently bonded to each other in alternating fashion through an appropriate linkage group. The poly(heteroatomic) block may exist in its neutral or oxidized form, and when in the oxidized form, it associates with organic or inorganic counter-anions to balance the charge. The poly(heteroatomic) polymer is an intrinsically conducting polymer (ICP) and when in the oxidized form it is electrically conducting. In case of the ICP block or blocks are in the doped form, the block copolymer is also electrically conducting. Preferably the conducting block copolymers have conductivities in the

range of 10^{-6} - 10^3 Scm^{-1} . The resulting copolymers are generally soluble or dispersible in water, an organic solvent, or a mixture thereof.

Due to their extended π conjugation, conducting polymer chains behave like rigid rods, have poor flexibility, and so do not flow or melt. Moreover, because of the strong ionic interactions among polymer chains and counterions, most conducting polymers do not dissolve in either aqueous or organic solvents and, as a result, can not be processed from solution. The poor processability is a major impediment to their commercial use.

The non-conducting block is modified at one end or at both ends with a linkage group that undergoes oxidation under the conditions used to polymerize the heteroaromatic monomer. Linkage groups include among others aliphatic acid, aromatic amino groups, phenols, substituted thiophenes, furan species and their derivatives, carbonyl compounds, thiols and the other species that undergo oxidation.

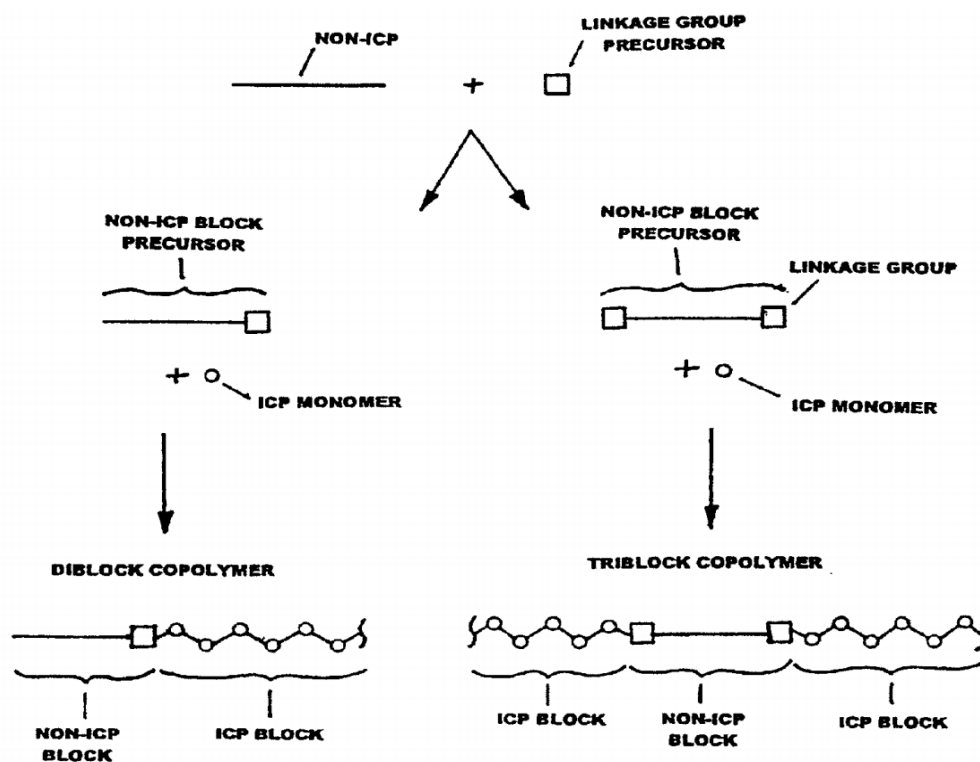


Figure 2.6. Types of block copolymers (AB or ABA) with a non-conductive linkage group.

As it can be seen in Fig 2.6., the linkage group is bonded to the non-conducting polymer during the first step of the synthesis, preferably through a covalent bond. The covalent bond between the non-conducting block and the linkage group may be an ester, thioester, amide, ether, carbon-carbon, anhydride, urethane or thiourea linkage.

The modified non-conducting block (with one or more terminal linkage groups) is then copolymerized with one or more heteroaromatic monomers (second step of the synthesis). Copolymerization occurs by chemical or electrochemical oxidation of the monomers. For chemical polymerization, it can be performed in the presence of an oxidizing agent comprising one or more of the following; hydrogen peroxides, persulfates, peroxyacids, bromates, chlorates, organic or inorganic salts of iron (III), chromium (IV), manganese (VII), lead (IV), mercury (II), copper (II), also gases such as oxygen, ozone, chlorine, bromine, SO_2 , SO_3 , NO_2 . The polymerization reaction is carried out in a solvent or mixture of solvents which can include water, alcohols, ketones, esters, ethers, amides, hydrocarbons and aromatic solvents and mixtures thereof.

2.4.Redox Polymerization Systems

Polymerizations initiated by a reaction between an oxidizing and a reducing agent are called redox polymerizations. The essence of redox initiation is a reduction-oxidation process. In this process an oxidant, i.e., Ce(IV) or Iron (III) forms initially a complex by reacting simply with organic molecules which then decomposes unimolecularly to produce free radicals that initiate polymerization. Commonly used oxidants include peroxides, persulphates, peroxydiphosphate, and the salts of transition metals. These oxidants form effective redox systems with various reducing agents like alcohols, aldehydes, amines, thiols for the aqueous polymerization of vinyl monomers. The essential features of components constituting a redox pair for aqueous polymerization are their solubility in water and fairly fast and steady liberation of active radicals [118]. Apart from the fact that low temperatures can be employed with redox systems, the reaction rate is easy to control by varying the concentration of metal ion or peroxide [119].

The synthesis of block copolymers by redox systems exerts a number of technical and theoretical advantages over other methods. Because of the applicability at low temperatures, side reactions are minimized [120]. This method has found wide

applications in initiating various polymerization reactions [121,122] and with industrial importance, e.g. low-temperature emulsion polymerizations [123,124].

There are still some problems with this redox system, namely a poor solubility of such inorganic salts in organic medium (for example acrylic resin), the formation of slightly colored products and an expected short pot-life due to the fact that polymerization may occur already at ambient temperature [125].

Various redox systems, such as ceric, manganese, copper, iron, vanadium ion, and hydrogen peroxide, have been used as catalysts for synthesis block copolymers via redox polymerization.

2.4.1. Iron ion redox polymerization system

Polymers containing hydroperoxy groups at chain ends with Fe^{+2} were used as redox macro initiators for the block copolymerization of vinyl monomers [126-132]. Catula et al. [133,134] in mid seventies prepared the hydroperoxide terminated poly(styrene) by a reaction sequence as shown below. Reacting polymeric hydroperoxide with ferrous sulphate in the presence of a second monomer afforded block copolymers as in Fig 2.7.

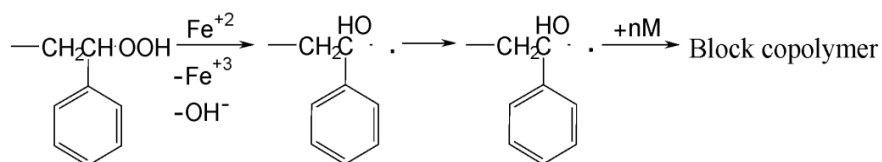


Figure 2.7. An example of ferric ion redox polymerization system.

The redox system ferric salt/acyl hydrazide had been used to obtain a poly(aminotriazole-block-acrylonitrile) block copolymer in 1962 The formation of free radicals by the reaction of terminal acyl hydrazide groups of poly(aminotriazole) RCONHNH_2 and Fe(III) was studied [135].

Block copolymers by redox polymerization of vinyl chloride can be prepared, optionally comonomers and ferrous sulphate in the presence of the peroxides $\text{HO}_2\text{CR}_1\text{R}_2\text{O}_2\text{R}_3\text{R}_4\text{CO}_2\text{H}$ ($\text{R } 1-4 = \text{H}$ or alkyl groups) to give peroxides having terminal vinyl chloride polymers and block polymerization with comonomers by thermal decomposition of the peroxides [124].

Fenton's reagent, the combination of H_2O_2 and ferrous salt has been applied to the oxidation of many organic compounds including alcohols, glycols, aldehydes, ethers,

esters, and amines [125]. As shown in Fig 2.8, a mechanism for the reaction between hydrogen peroxide and ferrous ion involves single-electron transfer from the ferrous ion to the peroxide with the dissociation of oxygen–oxygen bond and generation of a hydroxyl radical and a hydroxyl ion [126,127]. In the presence of sufficient monomer, all the generated OH radicals can initiate polymerization.

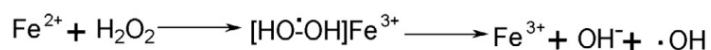
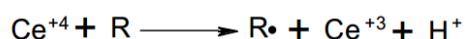


Figure 2.8.Combination of H₂O₂ and ferrous salt.

2.4.2.Ceric ion redox polymerization systems

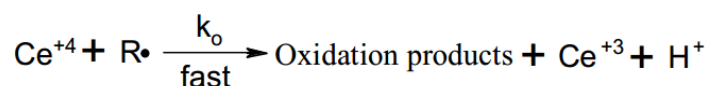
Ceric ions in acidic media are well-known oxidizing agents for various organic substrates [128]. Also, these ions, either by themselves or in combination with reducing agents function as initiators for vinyl polymerization [129-136]. A first attempt to initiate polymerization by Ce(IV) in organic solvents was performed in 1979 by Singh et al. [137] who observed that the solvent (toluene) inhibits the redox initiating process for the polymerization of acrylonitrile. The suitable reducing agents reported in the literature are alcohols [138], polyols [139], ketones [140], acids [141], amines [142], thiols [143], and thiourea [144]. Based on the experimental results, the following kinetic reaction schema are proposed by Nagarajan et al. [145] for vinyl radical polymerization.

I. (a) Reaction of ceric ion with reducing agent:

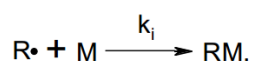


where, R is reducing agent and R· is the organic free radical formed from the reducing agent.

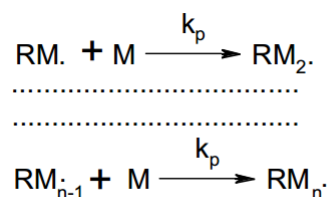
(b) Reaction of the radical with Ce⁺⁴ to give the oxidation products:



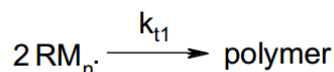
II. Initiation of polymerization by reaction of the free radical with monomer:



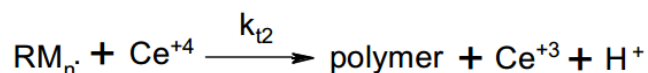
III. Propagation



IV. (a) Mutual termination



(b) Linear termination by Ce^{+4}



2.4.3. Manganese ion redox polymerization systems

Mn(III) in the form of pyrophosphate [146], sulphate [147], perchlorate [148] and acetate [149] has received attention as an oxidant in the presence of a number of organic substrates such as malonic acid, isobutyric acid, cyanoacetic acid, glycerol [150], and ethylene glycol [151] for the polymerization of various monomers in aqueous media, Mn(III) reacts with simple organic molecules to form a complex that decomposes unimolecularly to produce a free radical that initiates polymerization [152].

2.5. Nonyl Phenol and Derivatives

Nonylphenols and nonylphenol ethoxylates are both groups of chemicals, members of the large families of alkyl phenols (AP) and alkyl phenol ethoxylates (APE), respectively. Nonylphenols (NP) have a phenolic ring on which a nine carbon alkyl chain is attached. The various nonylphenols are differentiated by the position in which the alkyl chain is attached to the phenolic ring and also by the structure of the alkyl chain (linear or branched), it can be seen in Fig 2.9. Nonylphenol ethoxylates (NPE) are chemicals that have surface-active properties that make them useful as surfactants, wetting agents, emulsifiers and dispersant.

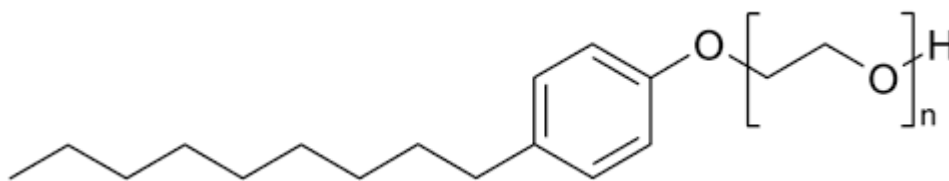


Figure 2.9. Ethoxylated Nonyl Phenol structure.

Nonylphenol ethoxylates are produced by reacting nonylphenol and ethylene oxide with potassium hydroxide as catalyst shown in Fig 2.10. The ratio of ethylene oxide to nonylphenol determines the molecular weight of the product or the length of the molecule produced. The degree of ethoxylation for commercially available ranges from four moles of ethoxylates (NPE4) to eighty moles of ethoxylates (NPE80). Depending on the degree of ethoxylation, products are obtained that exhibit different hydrophile–lipophile balance values, which enables a wide range of applications at relatively low costs.

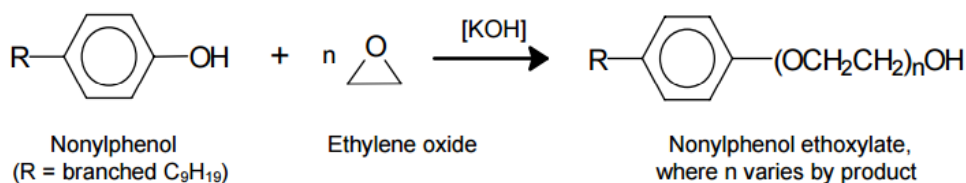


Figure 2.10. Synthesis of Nonyl Phenol Ethoxylate.

Nonylphenol ethoxylates are primarily used in industrial applications. Use of nonylphenol ethoxylates in household and consumer applications is declining.

The market applications for these products fall into the four basic categories listed below:

- Industrial – agriculture, leather processing, metal working, oil field, pulp and paper, textile processing, water treatment
- Emulsions and coatings – paints and coatings, emulsion polymerization, adhesives
- Industrial and institutional cleaning – hard-surface cleaners, circuit-board cleaners, industrial laundry/dry-cleaning detergents, metal cleaning, food and dairy
- Household cleaning – detergents, laundry prewash, hard-surface cleaners, air fresheners

The widespread use of products containing NPEs leads to a large discharge into different environmental compartments; major vectors for the entry of NPEs and NPs into receiving aquatic environments (rivers, lakes, seas and their sediments) are the effluents of industrial and municipal wastewater-treatment plants but also direct discharge such as through pesticide application. Also if toxicity of NPEs to aquatic organisms tends to decrease with increasing degree of ethoxylation, on the other hand their solubility increases linearly. Due to the high aquatic toxicity, since 2003 the European Commission has published marketing and use restrictions of NPEs and NPs ; moreover, several political initiatives have banned or restricted the use of NP(E) in Europe, and in some countries the use of NPEs is almost completely phased out. Nevertheless, the occurrence of NPEs and their degradation products is still well documented in many regions across the world; indeed nonylphenolic compounds are ubiquitous and have been found at significant level in environmental samples taken from freshwater, saltwater, groundwater, sediment, soil and aquatic biota. There is strong evidence from the literature that nonylphenolic compounds represent substances of very high concern for contamination of aquatic environment and may pose a significant risk to aquatic fauna.

Nonylphenol ethoxylates are extensively biodegraded in laboratory screening tests, but do not meet the stringent criteria for classification as "readily biodegradable." These substances are inherently biodegradable to carbon dioxide and water, and numerous studies have shown that under conditions where sufficient oxygen, nutrients, and microorganism concentrations occur, such as in soils, surface waters, and well-functioning sewage treatment plants, the substances are extensively biodegraded. Treatment efficiencies vary, although most facilities typically remove between 80 and 90% (through a combination of biodegradation and adsorption). Small amounts of various metabolites have been detected in effluents from sewage treatment plants, including low molecular weight nonylphenol ethoxylates, ether carboxylates and nonylphenol. Nonylphenol is a minor metabolite in aerobic systems, although higher levels can be formed during anaerobic treatment of sewage biosolids (sludges).

3. EXPERIMENTAL

3.1 Materials

Chloroform(CHCl_3), Hydrochloric Acid (HCl), Sodium Bicarbonate (NaHCO_3), Dichloromethane (DCM), and Pyridine were all reagent-grade chemicals of the highest purity, so they were used without further purification.

Iron (III) Chloride (FeCl_3) and Pyrrole was product of Sigma-Aldrich.

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.

3.2. 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.

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.

The images of polymer samples were produced by using a Jeol JSM-5410 scanning electron microscope (SEM). The samples were coated with platinum (Pt) for SEM.

3.3. Conductivity Measurements

Thin pellets with typical sample diameter of 13 mm were prepared by compaction of the polymer powders under 10 tons of pressure. Conductivity measurements of polymers were performed by the four probe technique and calculated from the following equation 3.1

$$\sigma = V^{-1} * I * (\ln 2 / \pi d_n) \quad (3.1)$$

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

3.4. Synthesis of Etoxyated Nonyl Phenol-Thiophene Carbonyl Compound (ENP30-ThC)

Ethoxylated nonyl phenol (ENP) was reacted with 2-thiophenecarbonyl chloride 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.



Figure 3.1. Experimental set-up for ENP-ThC synthesis

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.

3.5. Synthesis of Blank Polypyrrole (PPy)

Polypyrrole was synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant and p-toluene sulfonic acid as a dopant. Reaction medium was selected as pure water.

First, 2.53 g p-toluene sulfonic acid (PTSA) was dissolved in 20 mL water and put on the magnetic stirrer. Then, 0.3 mL pyrrole monomer (0.0043 mol) was added to the reaction mixture. The mol ratio of oxidant to pyrrole ($n_{\text{oxidant}}/n_{\text{Py}}$) is an important parameter, for all reactions this ratio was accepted as 2,4. Finally, 1,673 g FeCl₃ which dissolved in 35 mL water was added to the reaction medium dropwise, by a dropping funnel. The color of the reaction mixture was turned from yellowish to black while oxidant addition. The reaction took place at 25 ° C and lasted about 24 hours.

At the end of the reaction, black powders were observed. The product was filtered with filter paper, washed with water, methanol and acetone, in order to eliminate any unreacted parts including remaining iron (III) chloride and oligomers. The resultant polymer was dried at 45 ° C in vacuum oven.

Different parameters (such as oxidant type, dopant) were investigated during the experiments and this was tabulated in Table 3.1.

Table 3.1. The parameters of PPy synthesis.

Sample No	Monomer	Ox ₁	nOxidant/ nPy	[PTSA] (mol/l)	Time(h)
Blank -1	Py	CAN	1,25	-	1
Blank-2	Py	CAN	1,00	-	1
Blank-3	Py	CAN	0,50	-	1
Blank-4	Py	CAN	0,33	-	1
Blank-5	Py	CAN	0,25	-	1
Blank-6	Py	CAN	1,00	0,267	24
Blank-7	Py	CAN	0,5	0,267	24
Blank-8	Py	FeCl ₃	2,4	-	24
Blank-9	Py	FeCl ₃	2,4	0,267	24

3.5. Synthesis of Thienyl End-capped Ethoxylated Nonyl Phenol-b-Polypyrrole Copolymer (ENP-ThC-b-PPy)

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 increase 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 mol) 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 ($n_{\text{FeCl}_3}/n_{\text{Py}}=2.4$). 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. Experimental set-up can be seen in Fig 3.2.



Figure 3.2. Experimental set-up for chemical oxidative polymerization.

At the end of the reaction, black powders were observed. The product was filtered with filter paper, washed with water, methanol and acetone, in order to eliminate any unreacted parts including remaining iron (III) chloride and oligomers. The resultant polymer was dried at 45 °C in vacuum oven.

During the experiments, different molar ratios of pyrrole to ENP30-ThC were investigated and it is shown in Table 3.2. Also, the effect of copolymerization on electrical conductivity was examined by blank experiments without using ENP30-ThC.

Table 3.2. The investigation of the effect of mol ratio (nPy/nENP-ThC).

Sample No	Monomer		Ox ₁	nPy/nENP-ThC	nOx ₁ /nPy	[PTSA] (mol/l)	Time (h)
Blank-9	-	Py	FeCl ₃	-	2,4	0,267	24
b-1	ENPTh	Py	FeCl ₃	50	2,4	0,267	24
b-2	ENPTh	Py	FeCl ₃	40	2,4	0,267	24
b-3	ENPTh	Py	FeCl ₃	30	2,4	0,267	24
b-4	ENPTh	Py	FeCl ₃	20	2,4	0,267	24
b-5	ENPTh	Py	FeCl ₃	10	2,4	0,267	24
b-6	ENPTh	Py	FeCl ₃	5	2,4	0,267	24

Time has an important effect on the copolymerization, so reaction time was accepted as a parameter. The experimental data was shown in Table 3.3.

Table 3.3. The investigation of the effect of time on copolymerization and conductivities.

Sample No	Monomer		Ox ₁	nPy/nENP-ThC	nOx ₁ /nPy	[PTSA] (mol/l)	Time (h)
b-5	ENPTh	Py	FeCl ₃	10	2,4	0,267	24
b-7	ENPTh	Py	FeCl ₃	10	2,4	0,267	1
b-8	ENPTh	Py	FeCl ₃	10	2,4	0,267	2

The effect of using p-toluene sulfonic acid (PTSA) as a dopant was investigated by comparing the reactions whether the presence of PTSA, the experimental data can be seen in Table 3.4.

Table 3.4. The investigation of the effect of dopant.

Sample No	Monomer		Ox ₁	nPy/nENP-ThC	nOx ₁ /nPy	[PTSA] (mol/l)	Time (h)
b-5	ENPTh	Py	FeCl ₃	10	2,4	0,267	24
b-9	ENPTh	Py	FeCl ₃	10	2,4	-	24

At the same conditions and procedures, ethoxylated nonyl phenol (ENP) was used in order to observe the effect of thienyl group. This data can be found in Table 3.5.

Table 3.5. The investigation of the effect of thienyl group.

Sample No	Monomer		Ox ₁	nPy/ nENP- ThC	nOx ₁ / nPy	[PTSA] (mol/l)	Time (h)
b-5	ENPTh	Py	FeCl ₃	10	2,4	0,267	24
b-10	ENP	Py	FeCl ₃	10	2,4	0,267	24

Lastly, at the same conditions and procedures, cerium ammonium nitrate(CAN) was used as an oxidant, to compare the results with that of FeCl₃ , which can be seen in Table 3.6.

Table 3.6. The investigation of the effect of oxidant type.

Sample No	Monomer		Ox ₁	nPy/ nENP- ThC	nOx ₁ / nPy	[PTSA] (mol/l)	Time (h)
b-5	ENPTh	Py	FeCl ₃	10	2,4	0,267	24
b-11	ENPTh	Py	CAN	10	1,0	0,267	24

4. RESULTS AND DISCUSSION

4.1. Thienyl End Capped Ethoxylated Nonyl Phenol (ENP-ThC)

Ethoxylated nonyl phenol (ENP) was reacted with 2-thiophenecarbonyl chloride in order to synthesize a macromonomer containing thienyl end-group (ENP-ThC). The reaction scheme is shown in Fig 4.1.

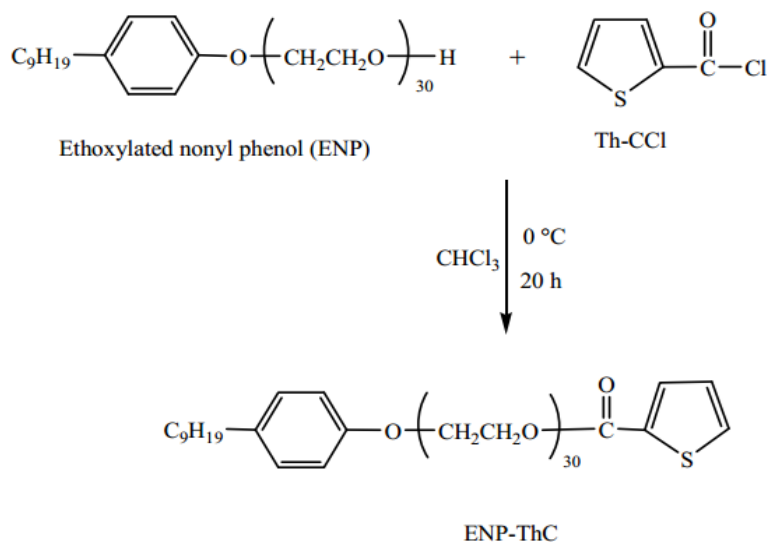


Figure 4.1. Synthesis of ENP-ThC

The ¹H NMR spectrum of thiophenecarbonyl end-capped ethoxylated nonyl phenol (ENP-ThC) is shown in Fig 4.2. Chemical bonds and corresponding peaks show that the esterification reaction between ethoxylated nonyl phenol and 2-thiophenecarbonyl chloride was completed successfully. The 1H-NMR spectrum of the ENP-ThC showed peak at 7.6 and 7.8 ppm due to protons in the 3- and 2, 4-positions of the Th ring and 6.8 and 7.2 ppm due to protons of the benzene ring . This situation can be also seen in ¹³C NMR spectrum, Fig 4.3.

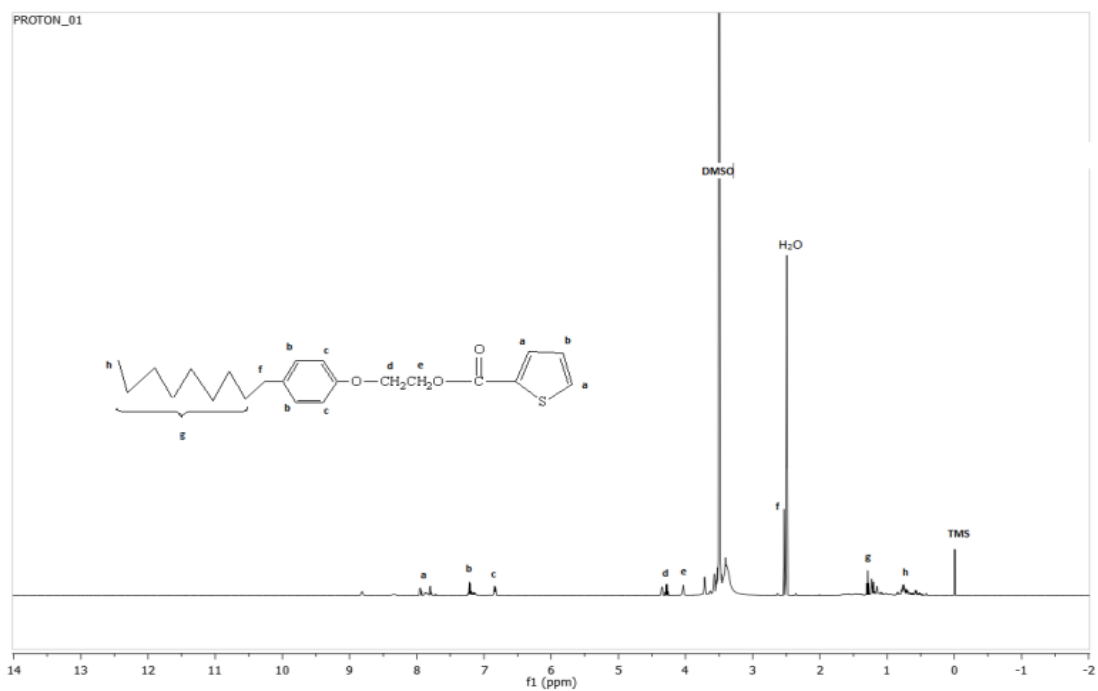


Figure 4.2. ^1H NMR spectrum of ENP-ThC

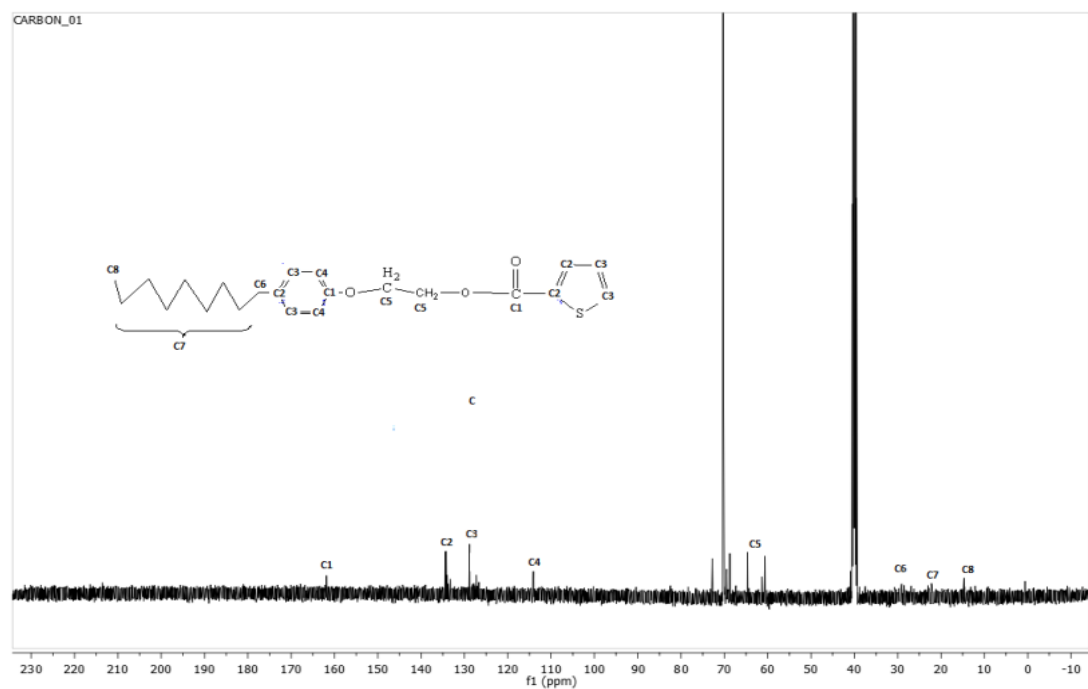


Figure 4.3. ^{13}C NMR spectrum of ENP-ThC

The FTIR spectrum of ENP-ThC was shown in Fig 4.4. At 2800 cm^{-1} , there is an aliphatic proton peak can be observed. Also, the carbonyl group which comes from thienyl (thiophenecarbonyl) group has a narrow peak about 1700 cm^{-1} , and this shows reaction is completed successfully.

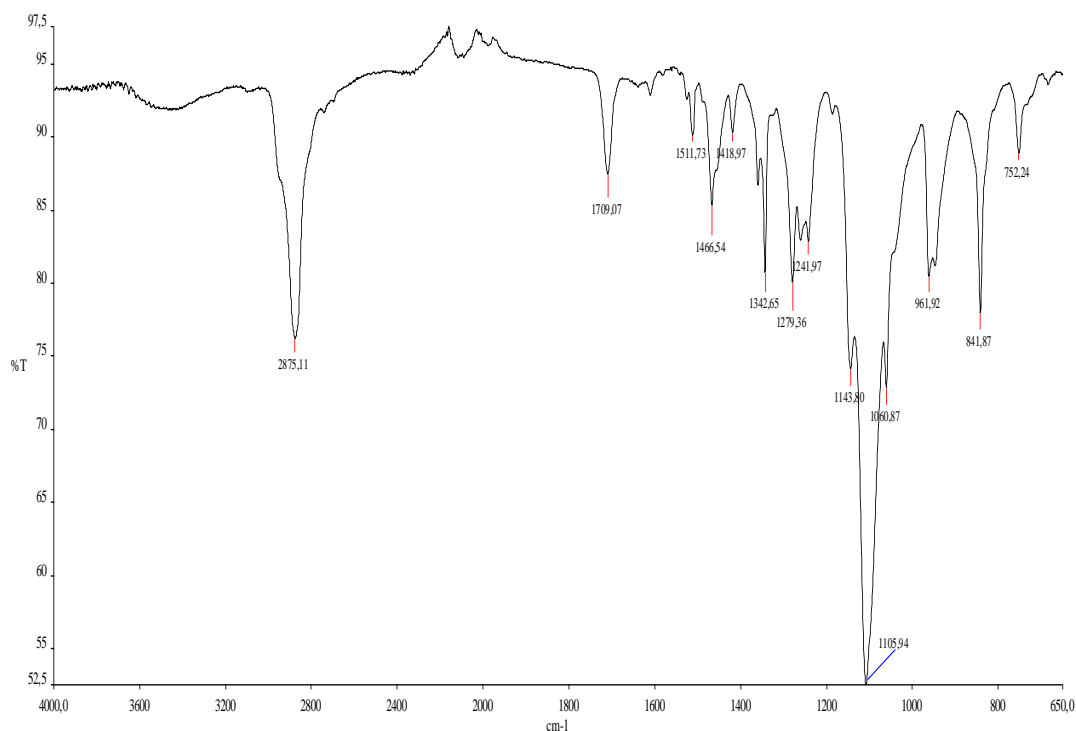


Figure 4.4. FTIR results of ENP-ThC.

4.2. Blank Polypyrrole (PPy)

Polypyrrole homopolymer was synthesized via chemical oxidation polymerization with cerium ammonium nitrate (CAN) and iron (III) chloride (FeCl_3), in case of comparison. Unlike the experiments carried out cerium salts, experiments which carried out with iron (III) chloride had better conductivities and polymerization yield. Also, the difference between Blank-8 and Blank 9 shows using p-toluene sulfonic acid (PTSA) as a dopant increased the conductivity and yield, as expected. This results can be seen in Table 4.1.

Table 4.1. Experimental results of PPy synthesis.

Sample No	Ox ₁	nOxidant/nPy	[PTSA] (mol/l)	Time	Conductivity (S/cm)	Yield	
						Gr	%
Blank-1	CAN	1,25	-	1	0,73	0,1819	63
Blank-2	CAN	1,00	-	1	0,80	0,1369	47
Blank-3	CAN	0,50	-	1	1,10	0,0617	21
Blank-4	CAN	0,33	-	1	1,13	0,0348	12
Blank-5	CAN	0,25	-	1	0,55	0,0298	10
Blank-6	CAN	1,00	0,267	24	0,09	0,1805	62
Blank-7	CAN	0,5	0,267	24	0,05	0,0945	33
Blank-8	FeCl ₃	2,4	-	24	0,14	0,2690	93
Blank-9	FeCl ₃	2,4	0,267	24	5,63	0,3696	127

Polypyrrole (PPy) homopolymers have some difficulties in the applications, because of its large particle size. The scanning electron microscope (SEM) analysis of Blank-9 with 20000x zoom can be seen in Fig 4.5. Average particle size of polypyrrole is 1 μm .

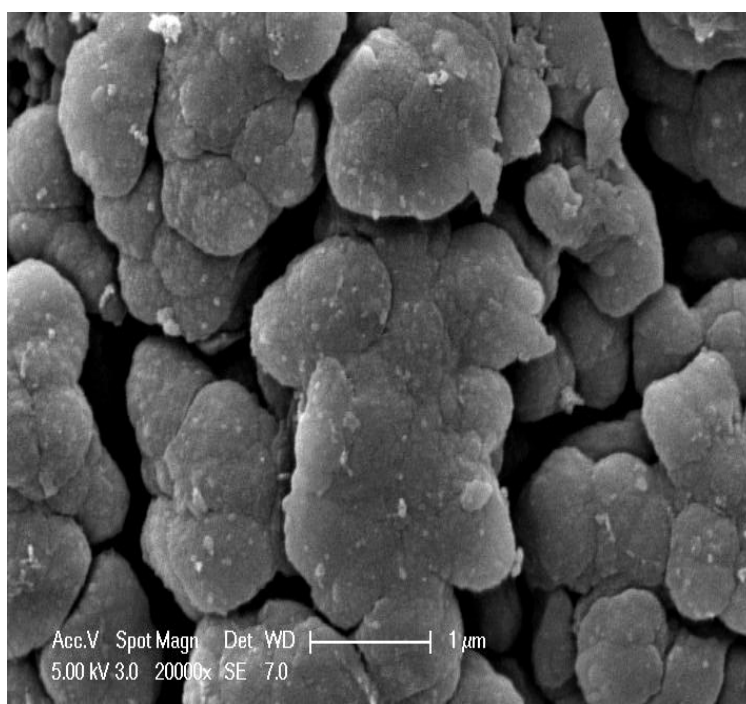


Figure 4.5. SEM image of blank PPy.

4.3. Block Copolymers of Thienyl End Capped Ethoxylated Nonyl Phenol and Polypyrrole (ENP-ThC-b-PPy)

Copolymers of ENP-ThC and pyrrole were synthesized by chemical oxidative polymerization using iron (III) chloride as an oxidant. The reaction scheme is shown in Fig 4.6. ENP-ThC served both as a macromonomer and an emulsifier for pyrrole with poor solubility in water.

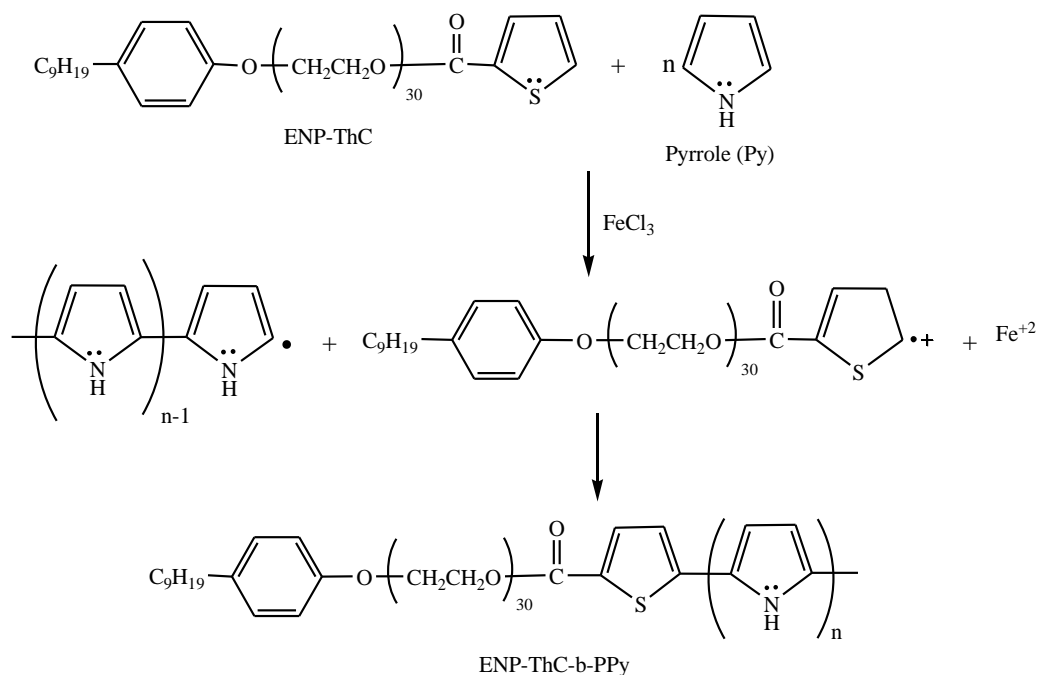


Figure 4.6. Synthesis of ENP-ThC-b-PPy copolymer.

FTIR spectra of the copolymer composed of ethoxylated nonyl phenol with thiophenecarbonyl end capped and polypyrrole is shown in Fig 4.7. The absorbance of S-O stretching at 1066 cm⁻¹ of PTSA also appeared. The strong ν(C-H) bands at 2850 and 2920 cm⁻¹ proved the presence of ENP in the products of the emulsion polymerizations. The peaks at 1544 and 1407 cm⁻¹ could be attributed to C-N and C-C asymmetric and symmetric ring-stretchings, respectively. Additionally, the strong peaks near 1066 and 891 cm⁻¹ present the doping state of polypyrrole.

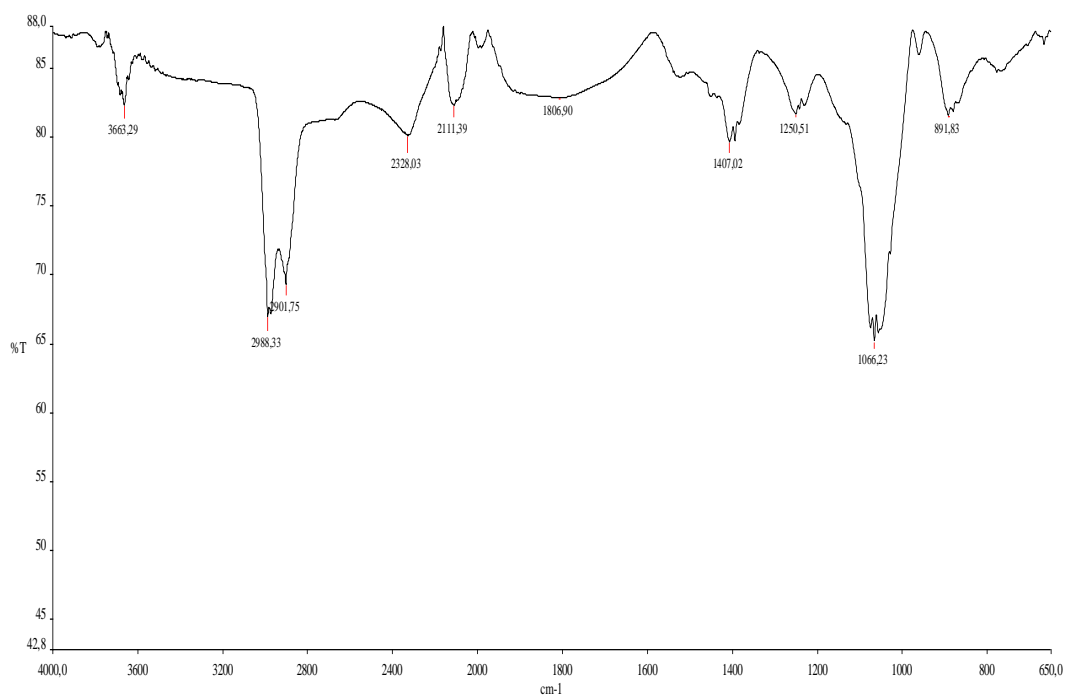


Figure 4.7. FTIR spectra of ENP-ThC-b-PPy copolymer (b-5)

4.3.1. Effect of Mol Ratio ($n_{\text{ENPThC}}/n_{\text{Py}}$)

The mol ratio of ENP group to pyrrole ($n_{\text{ENPThC}}/n_{\text{Py}}$) has important effect on the conductivity and yield. As it is seen in Table 1, conductivity of blank PPy showed the highest value (which shown with red square, 5.63 S/cm) and with the addition of ENPThC group, this value began to decrease as expected, this situation can be seen in Fig 4.8. Because, even ENP-ThC group brings numerous advantageous on polypyrrole processability and solubility issues, it is non-conductive in nature. A reasonable drop of conductivity is accepted and the resultant conductivities are still moderate. Results are tabulated in Table 4.2.

Table 4.2. The effect of mol ratio on conductivity and yield

Sample No	Monomer		Ox ₁	$n_{\text{ENP-ThC}}/n_{\text{Py}}$	Conductivity (S/cm)	Yield	
		Py				Gr	%
Blank-9	-	Py	FeCl ₃	-	5,63	0,3696	127
b-1	ENPTh	Py	FeCl ₃	0,02	2,51	0,3086	77
b-2	ENPTh	Py	FeCl ₃	0,025	0,57	0,3530	82
b-3	ENPTh	Py	FeCl ₃	0,033	1,12	0,3303	70
b-4	ENPTh	Py	FeCl ₃	0,05	1,29	0,3556	63
b-5	ENPTh	Py	FeCl ₃	0,1	1,4	0,3140	37
b-6	ENPTh	Py	FeCl ₃	0,2	0,36	0,3630	28

[PTSA]=0.267 M

Time= 24 hours

$n_{\text{Oxidant}}/n_{\text{Py}}=2.4$

Effect of Mol Ratio ($n_{\text{ENPThC}}/n_{\text{Py}}$) on Conductivity

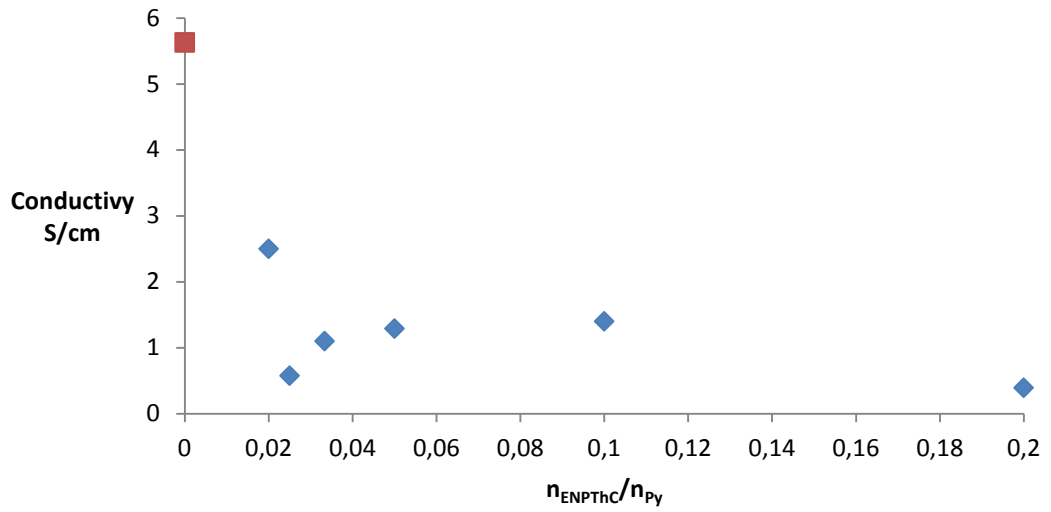


Figure 4.8. The effect of mol ratio on conductivity

As the mol ratio increases , the yield of polymerization was decreased.This situation can be seen in Fig 4.9.

Effect of Mol Ratio ($n_{\text{ENPThC}}/n_{\text{Py}}$) on Polymerization Yield

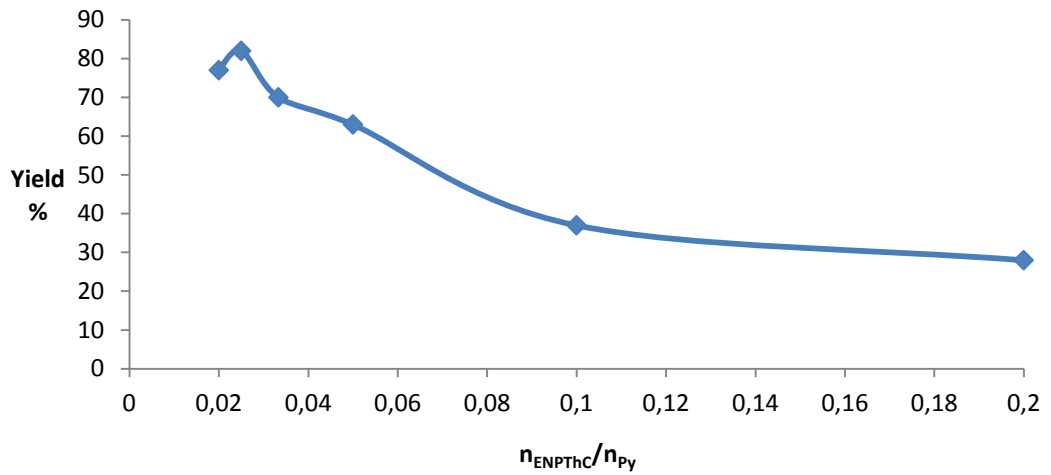


Figure 4.9. The effect of mol ratio on polymerization yield

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. The average particle size of PPy particles were decreased as the mol ratio of $n_{\text{ENP-ThC}}/n_{\text{PPy}}$ increased. So, the more ENP-ThC groups added to Py structure, the less particle size have obtained. The SEM images of ENP-ThC-b2-PPy, ENP-ThC-b3-PPy and ENP-ThC-b4-PPy can be seen in Fig 4.10. , Fig 4.11. and Fig 4.12. , respectively.



Figure 4.10. SEM image of ENP-ThC-b2-PPy copolymer.

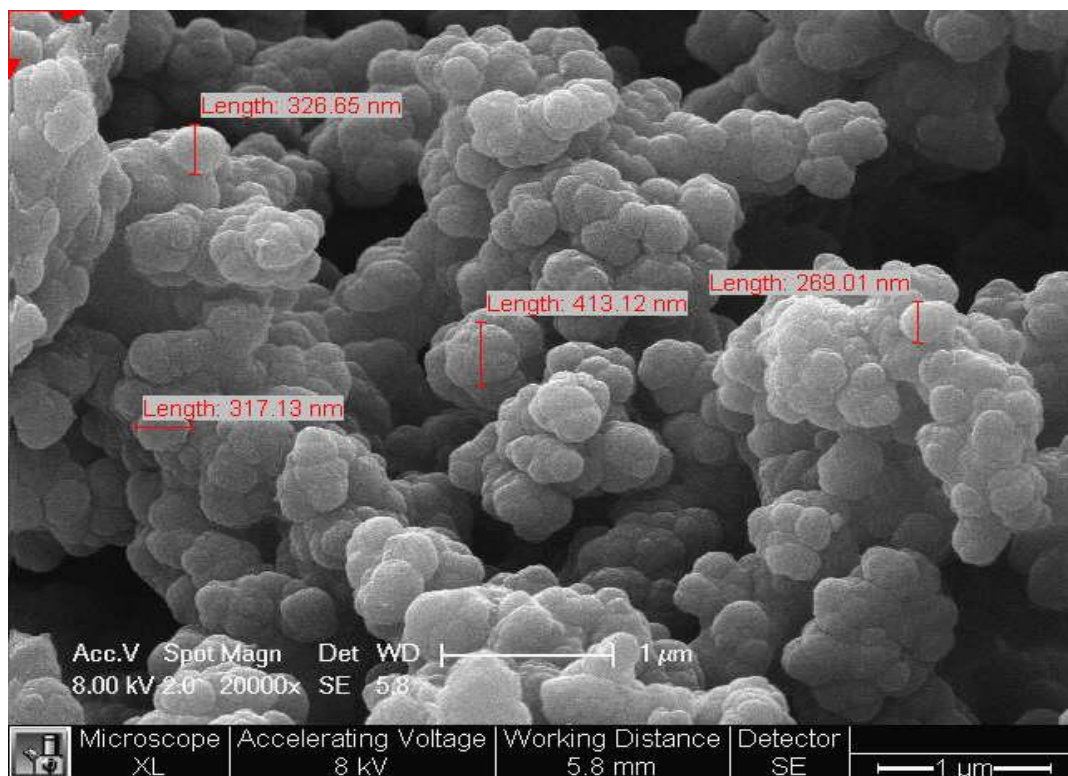


Figure 4.11. SEM image of ENP-ThC-b3-PPy copolymer.



Figure 4.12. SEM image of ENP-ThC-b4-PPy copolymer.

With the same 20000x zoom, the average particle size for b-2 copolymer ($n_{\text{ENPThC}}/n_{\text{Py}}=0.025$) was 410 nm, while the b-3 copolymer ($n_{\text{ENPThC}}/n_{\text{Py}}=0.033$) had a particle size of 357 nm. Average particle size of b-3 copolymer was bigger than that of b-4 copolymer ($n_{\text{ENPThC}}/n_{\text{Py}}=0.05$), which had more ENP-ThC groups on its structure than the others. Also, these three copolymer had lower average particle size than PPy homopolymer, which was 1 μm . This situation also shown in Fig 4.11.

The effect of mol ratio on average particle size

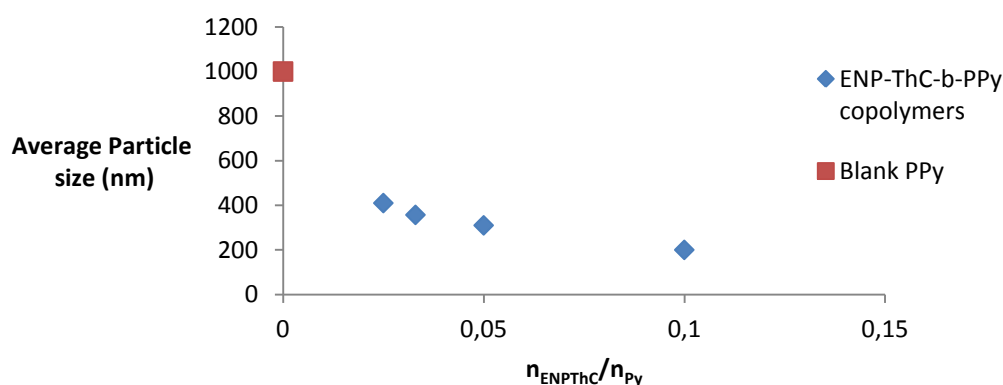


Figure 4.13. The effect of mol ratio on average particle size.

4.3.2. Effect of Time

As the reaction time increases, the conductivity of material was decreased, as it can be seen in Fig 4.12. Contrary, time had positive effect on the polymerization yield, as the time increases the polymerization rate increases, shown in Fig 4.13. Experimental results were tabulated in Table 4.3.

Table 4.3. Effect of time on conductivity and yield.

Sample No	Monomer		Ox ₁	Time (h)	Conductivity (S/cm)	Yield	
						Gr	%
b-5	ENPTh	Py	FeCl ₃	24	1,4	0,3140	37
b-7	ENPTh	Py	FeCl ₃	1	29,87	0,1714	20
b-8	ENPTh	Py	FeCl ₃	2	18,92	0,2590	30

[PTSA]=0.267 M

$n_{\text{Py}}/n_{\text{ENP-ThC}}=10$

$n_{\text{Oxidant}}/n_{\text{Py}}=2.4$

Time Effect on Conductivity

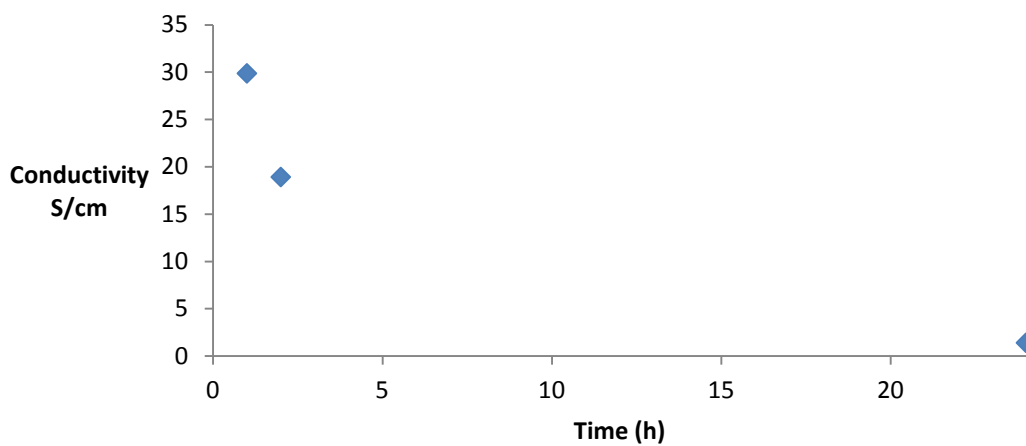


Figure 4.13. Time effect on copolymers' conductivity.

Time Effect on Polymerization Yield

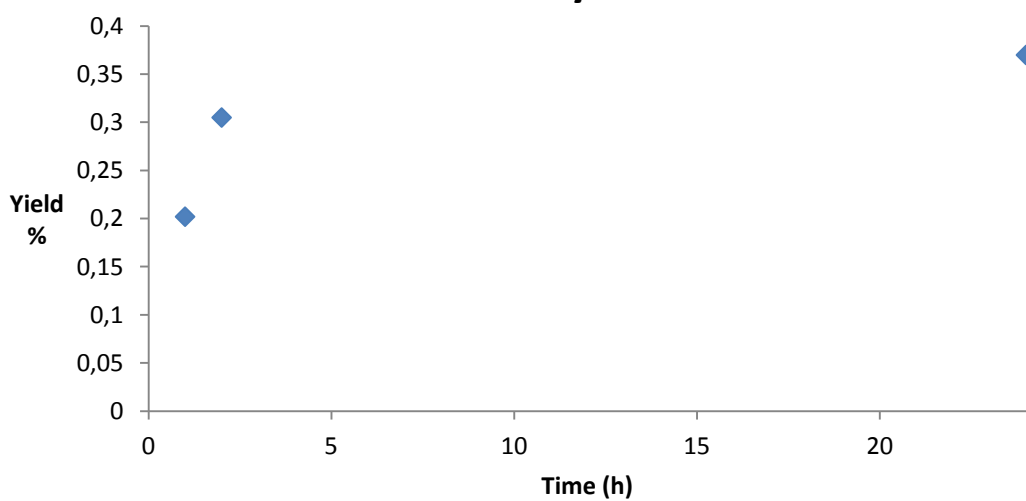


Figure 4.14. Time effect on copolymers' polymerization yield.

4.3.3. Effect of Dopant

Like the PPy homopolymer case, using p-toluene sulfonic acid (PTSA) increased the conductivity of PPy and yield of the polymerization, as expected. The results were tabulated in Table 4.4.

Table 4.4. Effect of using dopant on conductivity and yield.

Sample No	Monomer		Ox ₁	[PTSA] (mol/l)	Conductivity (S/cm)	Yield	
						Gr	%
b-5	ENPTh	Py	FeCl ₃	0,267	1,4	0,3140	37
b-9	ENPTh	Py	FeCl ₃	-	0,05	0,1755	21

$$n_{\text{Oxidant}}/n_{\text{Py}}=2.4$$

$$t=24 \text{ h}$$

$$n_{\text{Py}}/n_{\text{ENPThC}}=10$$

4.3.4. Effect of Thienyl Group

Thienyl (thiophenecarbonyl) group acted like a linkage compound between a non-conductive (ENP) and a conductive (PPy) side. It increased the chemical oxidative potential of material and enabled to be oxidized with iron (III) chloride. As it was shown in Table 4.5., when compared to ENP30-b-PPy copolymer, thiophenecarbonyl group increased the conductivity of copolymer (ENP30-ThC-b-PPy).

Table 4.5. Effect of thienyl group on conductivity.

Sample No	Monomer		Ox ₁	nPy/nENP groups	nOx ₁ /nPy	Conductivity (S/cm)	Yield	
							Gr	%
b-5	ENPTh	Py	FeCl ₃	10	2,4	1,4	0,3140	37
b-10	ENP	Py	FeCl ₃	10	2,4	0,009	0,2818	35

$$[\text{PTSA}]=0.267 \text{ M}$$

$$t=24 \text{ h}$$

4.3.5. Effect of Oxidant Type

As it is tabulated in Table 4.6., using FeCl₃ instead of CAN has increased the conductivity and yield.

Table 4.6. Effect of oxidant type.

Sample No	Monomer		Ox ₁	nPy/nENP-ThC	nOx ₁ /nPy	Conductivity (S/cm)	Yield	
							Gr	%
b-5	ENPTh	Py	FeCl ₃	10	2,4	1,4	0,3140	37
b-11	ENPTh	Py	CAN	10	1,0	0,055	0,1764	21

$$[\text{PTSA}]=0.267 \text{ M}$$

$$t=24 \text{ h}$$

4.4. Solubility in organic solvents

Since Polypyrrole (PPy) is insoluble in most solvents, its application areas are limited and researchers study to make PPy soluble by tailoring its properties. Block copolymers of PPy with a non-conductive, but emulsifier group can be a solution and as it is seen in Table 4.7. , PPy solubilities in various organic solvents has slightly increased with addition of ENP-ThC groups on its structure.

Table 4.7. Solubility of polymers in various solvents

Sample No	Solvents				
	DMSO	DMF	Chloroform	Acetone	THF
Blank-8	insoluble	slightly soluble	insoluble	insoluble	insoluble
b-1	insoluble	slightly soluble	insoluble	insoluble	insoluble
b-2	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble
b-3	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble
b-4	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble
b-5	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble
b-6	slightly soluble	slightly soluble	slightly soluble	slightly soluble	slightly soluble

5. CONCLUSION

Since polypyrrole (PPy) homopolymers have some difficulties in the applications, soluble and conductive copolymers of PPy may overcome these difficulties and open new application areas. For this purpose, thienyl 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.

Conductivity at blank PPy is the highest value, and with the addition of ENPThC group, this value began to decrease as expected. Because, even ENP-ThC group brings numerous advantages on polypyrrole processability and solubility issues, it is non-conductive in nature. A reasonable drop of conductivity is accepted and the resultant conductivities are still moderate.

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.

Thienyl group acts as a linkage group between conducting and non-conductive blocks. When compared to ENP30-b-PPy copolymer, thiophenecarbonyl group increased the conductivity of copolymer (ENP30-ThC-b-PPy).

These soluble and conductive copolymers may overcome difficulties in the applications of PPy homopolymers and open new application areas. Therefore, the copolymers may find a number of new application areas as well as existing PPy applications.

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PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- **Ülkü G.**, Köken N., Güvel, E. A., Kızılcın N., 2015: Heterophase Polymerization of Pyrrole and Thienyl End Capped Ethoxylated Nonyl Phenol by Iron (III) Chloride. *XIII. International Conference on Polymer (ICP 2015) - WASET*, February 23-24, 2015 Paris, France.
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