MICROWAVE INITIATED POLYMERIZATION OF TRIHALOPHENYLENEOXIDE AND ANILINE

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ABSTRACT

MICROWAVE INITIATED POLYMERIZATION OF TRIHALOPHENYLENEOXIDE AND ANILINE

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The aim of the study is to synthesize poly(dibromophenyleneoxide) and polyaniline separately applying different microwave energies (90-900 watt), water amounts (1-5 ml) and time intervals (2-10 min) and investigate the effects of these parameters on the percent conversion of the polymers. The synthesis of poly(dibromophenyleneoxide) (P), radical ion polymer (RIP) and crosslinked polymer (CLP) were achieved by using tribromophenol (TBP) and $Ca(OH)_2$ via microwave energy in a very short time interval.

P and RIP were characterized by ATR-FTIR, ^{1}H-NMR, ^{13}C-NMR, TGA-FTIR, ESR, GPC, UV-VIS, DLS and SEM. Crosslinked polymers were characterized by ATR-FTIR and TGA-FTIR and polyaniline was characterized by ATR-FTIR.

Keywords: Microwave energy, poly(dibromophenyleneoxide), polyaniline, crosslinked polymer, radical ion polymer.

ÖZ

MİKRODALGA İLE TRİHALOFENOLOKSİTİN
VE ANİLİNİN POLİMERLEŞMESİ

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Yüksek Lisans, Polimer Bilimi ve Teknolojisi
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Bu çalışmanın amacı, poli(dibromofenilenoksit) ve polianilini 90 ile 900 watt arasında değişen mikrodalga enerjisi, 1 ile 5 ml arasında değişen su miktarları ve 2 ile 10 dakika arasında değişen sürelerde ayrı ayrı sentezlemek ve bu parametrelerin yüzde dönüşüme ve polimer sentezine etkilerini incelemekir. Poli(dibromofenilenoksit) (P), iyon radikal (RIP) ve çapraz bağlı (CLP) polimerlerin sentezi mikrodalga enerjisi ile TBP ve $Ca(OH)_2$ kullanılarak çok kısa sürede gerçekleştirildi.

Poli(dibromofenilenoksit) ve radikal iyon polimerleri ATR-FTIR, ^{1}H-NMR, ^{13}C-NMR, TGA-FTIR, ESR, GPC, UV-VIS, DLS and SEM ile karakterize edildi. Çapraz bağlı polimerler ATR-FTIR ve TGA-FTIR ile, polianilin ATR-FTIR ile karakterize edildi.

Anahtar Kelimeler: Mikrodalga enerjisi, poli(dibromofenilenoksit), polianilin, çapraz bağlı polimer, iyon radikal polimer.

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ABBREVIATIONS

TBP: Tribromophenol

P: Poly(dibromophenyleneoxide)

RIP: Radical Ion Polymer

CLP: Crosslinked Polymer

PANI: Polyaniline

WL: Weight Loss

CHAPTER 1

INTRODUCTION

1.1. Microwave Irradiation

In organic and polymer chemistry, use of microwave ovens as a common device, has started at the end of 1980s. From that time microwave ovens have been mostly preferred in all fields of chemistry since it is less time consuming method than other conventional heating methods. Although numerous experiments were done with domestic microwave ovens, nowadays commercial microwave ovens are mostly preferred because of its controllable temperature and pressure properties [1].

Besides reducing the reaction times, other important advantages of microwave radiation are decreasing side reactions, increasing yields and reproducibility. These properties make microwave irradiation more popular than conventional heating methods like oil bath, Bunsen burner, electric plate heater and heating jacket. Conventional heating results in temperature variations within the material while microwave irradiation provides uniform heating throughout the material which decreases decomposition and side product formation possibilities [2].

In electromagnetic spectrum microwave irradiation covers a range between infrared radiation and radio frequencies. The wavelength range of microwave region is between 1mm – 1m and the frequency region is between 0.3 – 300

GHz. Radar transmissions (1-25 cm) and telecommunications (25-100 cm) are also found in the microwave region. In order to prevent any interference with these uses, domestic and commercial microwave heaters are performed at 12.2 cm which corresponds to 2.45 GHz [3].

Microwave irradiation mechanism depends on dielectric heating which can be defined as the ability of converting electromagnetic radiation energy into heat. Electromagnetic radiation composes of two parts namely; electric field and magnetic field components. Electric field component which is closely related with dielectric heating, is also affected by dipolar polarization mechanism and ionic conduction mechanism.

1.1.1. Dipolar Polarization Mechanism

Molecules which have dipole moment are able to absorb microwave energy and convert it into heat. When an electric field is applied, dipoles will attempt to align themselves in this field by rotation. (Figure 1.1.)

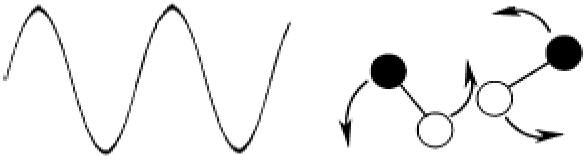

Figure 1.1. Dipolar molecules align with electromagnetic field

In this mechanism, ability of dipoles to align with the electromagnetic field depends on the frequency and viscosity of the liquid. In low frequency, molecules rotate to align however, conversion of energy into heat becomes small. In high frequency there is not enough time for molecules to follow the electrical field. Therefore, no rotation is observed. In microwave frequency region dipoles in the molecule start to re-orientate by following the field while field changes. As a result, phase difference occurs and some energy is given to the medium. Heat is generated with the help of this energy losts [4].

Gases are not suitable for microwave irradiation since the distance of rotating molecules is long to follow the electric field. Liquids are more suitable however depends on the frequency factor as mentioned above.

1.1.2. Ionic Conduction Mechanism

Another part of electric field conduction mechanism, is directly related to the ions in a molecule. Under the electric field charged particles in the sample moves through the solution by increasing the collision rate. As a result, kinetic energy is converted into heat. This mechanism involves much stronger interaction than dipolar polarization method. (Figure 1.2.)

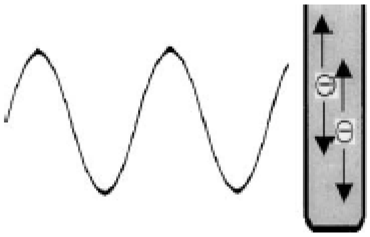

Figure 1.2. Moving ions in the applied electric field

1.1.3. Loss Tangent

Loss tangent which is in tangent form of loss angle, determines the ability of substance to convert electromagnetic energy into heat.

$$\tan \delta = \varepsilon''/ \varepsilon' \qquad \textbf{(1)}$$

ε'' is called loss factor that refers to the efficiency of converting electromagnetic energy into the heat. ε' is called dielectric constant that indicates the ability of material to store electrical potential energy under applied electrical field. For effective microwave absorption high loss tangent value is needed. When dielectric constant and loss tangent values of the solvents are close to each other, loss factor value becomes important to compare the abilities of different substances to convert electromagnetic energy into heat. Moreover, solvents that do not have dipole moment can be used in microwave ovens by adding polar additives like ionic liquids [4].

1.1.4. Superheating Effect

Important thermal property of the microwave irradiation is superheating effect of solvents at atmospheric pressure. This phenomena is described as an increase in the boiling point of solvents ca. 13 - 26 ^{0}C higher than their normal boiling points. Therefore, rapid increasing heating rates are observed. Superheating effect in microwaves causes hot spots in the solution. Hot spots which are named as "false microwave effect", form mostly because of the inhomogeneity of the medium [5].

1.2. Literature Survey Of Microwave Polymerization

Kısakurek et.al. studied polymerization and characterization of poly(dihalophenyleneoxide)s with different techniques; namely; electroinitiated polymerization [6-11], thermal decomposition in solution [12-17], thermal decomposition in solid state [18-22] and microwave assisted polymerization [23-24]. Except microwave assisted polymerization technique, other techniques include decomposition of metal complexes containing different amine ligands. It was seen that different types of transition metal, ligand and halogen affected the polymer structure, molecular weight and the yield. As a transition metal, copper, cobalt and nickel were preferred. Copper was used mostly since its complexes decompose faster than other metals. As a ligand, ethylenediamine, pyridine and TMEDA (N,N,N′,N′-tetramethylethylenediamine) were generally used. It was observed that lower molecular weight polymers were synthesized electrochemically, on the other hand higher molecular weight polymers were synthesized with thermal decomposition and microwave method.

In 1997, Correa, Gonzalez and Dougar carried out emulsion polymerization under both microwave heating and conventional heating using potassium persulfate as the initiator and sodium lauryl as the emulsifier. Time for styrene polymerization with microwave heating is 70 times shorter than that of conventional heating. It was also reported that under microwave heating, molecular weight of polystyrene (M_w = 350.000) was about 1.2 times higher than that of under conventional heating [25].

In 2001, Porto, Sadicoff, Amorim and Mattos experimented microwave free radical bulk-polyaddition reactions of vinyl acetate, styrene, methyl methacrylate and acrylonitrile with the use of AIBN in domestic microwave oven. The polymerizations were carried out to observe the rate of polymerizations with respect to the change of monomer, time and power. As a result; irradiation with low power and time, led to high molecular weight polymers [26].

In 2004, Cheng, Zhu X., Zhou, Zhu J., and Zhang studied polymerization of styrene by atom transfer radical polymerization (ATRP) and reverse atom transfer radical polymerization (RATRP) under microwave irradiation and conventional heating with the use of 1-PEBr/CuCl/PMDETA or AIBN/$CuCl_2$/PMDETA initiators. It was observed that under microwave irradiation, polymerization rate was faster than that of conventional heating (oil bath). On the other hand, PDI is narrow for both microwave and conventional heating conditions [27].

In 2006, Ritter and coworkers studied 2,5-dibutoxy-1,4-phenylenevinylene (PPV) polymerization under microwave irradiation by Heck polycondensation which is a kind of homogeneous metal catalyzed reaction. To compare the results, polymerization was done both with microwave irradiation and thermal heating (oil bath). It is seen that; 1000 g/mol higher number average molecular weight polymer was synthesized in 1 hour under microwave irradiation.

Furthermore, it was observed when 2-phenyl-2-oxazoline was polymerized under microwave conditions, reaction rates was about 3 times faster than with oil bath conditions [28].

Microwave irradiation was also used in coating of iron fibers which were covered with polymeric materials with channel structures. Methyl methacrylate (monomer), ethylene glycol dimethacrylate (crosslinker), AIBN (initiator) and toluene (solvent) were used to prepare polymeric material on the surface of iron fibers. This method which is not suitable with conventional heating methods, is used for medical purposes and protection from corrosion [28].

In 2006, being dialkyl fumarates as hardly polymerized monomers; Cortizo, Laurella and Alessandrini investigated dialkyl fumarate polymerization under microwave irradiation by free radical polymerization. Four different dialkyl fumarate monomers were polymerized to compare the conversion percents, molecular weights and polydispersity index. It was observed that DIPF(diisopropyl fumarate) and DCHF(dicyclohexyl fumarate) were more reactive than DEHF(di-2-ethylhexyl fumarate) and DPEF(di-2-phenylethyl fumarate). DIPF and DCHF reactions showed higher conversion yields at low watts, whereas; DEHF and DPEF showed lower conversion yields at low watts. Weight average molecular weights and polydispersity indexes were almost same for both microwave irradiation and thermal conditions [29].

In 2007, Lü, Liang, Luo and Dong studied copolymerization of 1-1′-(1,4-butamethylene)bis(imidazole) with 1,2-dibromoethane and used this copolymer as phase transfer catalyst (PTC) in the fluorination of chloronitrobenzene under microwave irradiation. Having good chemical and thermal stability and high ionic conductivity, polymer imidazole salts have played remarkable roles [30].

In 2007, Gong, Zhang and Liao reported the polymerization of trimethylene carbonate (TMC) by microwave assisted ring opening polymerization in the presence of ethylene glycol as the initiator in the absence of catalyst. PTMC has important properties like low toxicity, biocompatibility, high toughness and tensile strength. It required 10 minutes to polymerize completely under microwave irradiation. Otherwise, 24 h or longer times are needed to complete the polymerization in an oil bath [31].

In 2008, Schubert and coworkers studied living cationic ring opening polymerization of fluorinated 2-phenyl-2-oxazolines under microwave irradiation using nitromethane as the solvent and methyl tosylate as the initiator. Fluorinated and non-fluorinated monomers were synthesized in a microwave oven. According to the result, almost all monomers were polymerized with 100 % yield in 3 hours. It was also observed that, polymerization of fluorinated oxazoline monomers were faster than unsubstituted oxazoline monomers [32].

In 2008, Chauveau, Marestin, Martin and Mecier studied the synthesis of polyarylimidazoles with polycondensation reaction using α-diketone and aromaticdialdehyde monomers. Using different dialdehyde monomers, various poly(arylimidazole)s were obtained and at the end of the experiment it was reported that high molecular weight polyimidazoles were synthesized under microwave conditions, on the other hand; only low molecular weight polyarylimidazoles were recovered under conventional heating [33].

In 2008, Costa, Santos, Fortuny, Araujo and Sayer experimented emulsion polymerization of methyl methacrylate (MMA) and butyl acrylate (BuA) under both microwave irradiation and conventional heating. For MMA, 93 % conversion was obtained in 6 minutes with microwave oven, while; same conversion percent was obtained in 10 minutes with a thermostatic bath. For BuA, there was almost no change in conversion and reaction times for both methods. Another important point is that for both MMA and BuA polymerizations under microwave irradiation, polymer particles were smaller in size than the ones obtained with conventional heating [34].

In 2009, Malik, Trathnigg and Kappe investigated anionic opening polymerization of butene oxide and hexane oxide under microwave irradiation with the use of 1-alkanols and PEG-MME 1100 as the initiators to see the effects of reaction parameters on the polymers and obtained purified block copolymers without side products [35].

In 2009, Zhu and coworkers studied poly(ε-caprolactone) synthesis with industrial microwave oven by microwave assisted ring opening polymerization (ROP) with large scale mass of ε-caprolactone ranging from 750 g to 2450 g using $Sn(Oct)_2$ as the catalyst. It was seen that shorter reaction times and higher yields (93%) were obtained with microwave technique [36].

1.3. Phenols

Phenols are monomers that are composed of hydroxyl groups attached to benzene ring. They are colorless and generally stored at 50-60^{0}C in liquid phase [37]. Phenols can form strong hydrogen bonding due to their hydroxyl group on the benzene ring. With this property, they have higher boiling and melting points than alcohols and toluene. Moreover, phenols are slightly soluble in water due to its ability to form hydrogen bond with water molecules. They are generally soluble in polar solvents (ketones, ethers, esters, pyridine), but less soluble in nonpolar aliphatic hydrocarbons. In addition to these properties, phenols are more acidic than alcohols because of the resonance stability of the phenoxide ions. Acidity increases as negative groups replace hydroxyl group while decreases as alkyl group replace hydroxyl group.

Phenols are mostly used in the production of phenolic resins. They are also used in the ε-caprolactam synthesis which is used in nylon-6 polymerization. Plasticizers, wood preservatives, disinfectants, insecticides, detergents, dyes, stabilizers, explosives and petroleum refineries are the other area of uses of phenols [37].

Many polymers are synthesized with the use of phenols where reactions occur generally at orto and para positions of the benzene ring or through hydroxyl group. Polysulfones, polyesters, nylon-6 and polyphenyleneoxides are common polymers synthesized from phenols.

Phenols are oxidized with the use of different phenols, solvents and catalysts. As a catalyst, different copper salts are used in the reaction. Tetraalklyldiphenoquinones (1), polyphenyleneoxides (2) and o-benzoquinone (3) are the example products (shown in Figure 1.3.) that synthesized by the oxidation of different phenols [38].

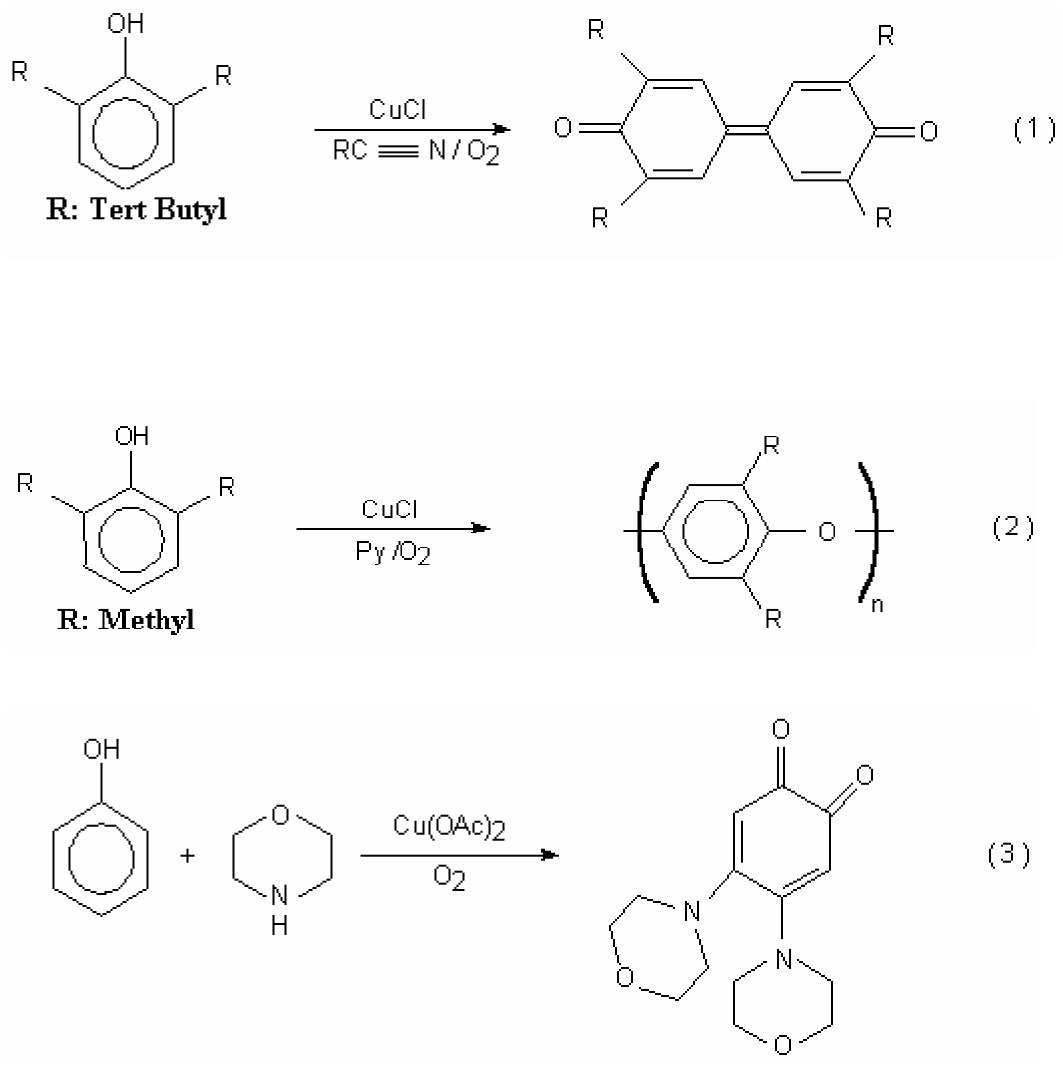

Figure 1.3. Phenolic products obtained by oxidation

1.4. Monomers

1.4.1. 2,4,6 Tribromophenol (2,4,6 TBP)

2,4,6 Tribromophenol is a white coloured solid monomer with a molar mass 330.8 g/mol, melting point of 94 ^{0}C and boiling point of 244 ^{0}C. As bromine number increases on benzene ring, solubility and vapor pressure decrease. 2,4,6 Tribromophenol does not decompose quickly and is synthesized in non-aqueous medium. At the end of synthesis it is obtained in melt form and stored as pellets after cooling.

2,4,6 Tribromophenol is used as an intermediate for flame retardancy. It is also used as wood preservative which is done by the synthesis of sodium tribromophenol salt from 2,4,6 tribromophenol and sodium hydroxide [39].

1.4.2. Aniline

Aniline ($C_6H_5NH_2$) is known as primary aromatic amine that amino group is linked to benzene ring. Anilines are firstly synthesized by distilling indigo. Now, the common production method of aniline is reduction of nitobenzenes with the use of metal (tin, iron or zinc) and acid (hydrochloric acid or acetic acid).

Anilines are colorless oils and when they expose to light and air, they become dark. They are soluble in alcohols, ethers and benzenes but slightly soluble in water. Anilines are weaker bases than aliphatic amines because of the resonance effect. They are used in the production of dyes, polymers, rubber, agricultural compounds and photographic chemicals [40].

1.5. Polyaniline (PANI)

Polyaniline is one of the known conducting polymers like polyacetylene, polyparaphenylene, polythiophene, polypyrrole, polyfuran, poly(p-phenylenevinylene). The chemical formula is shown below: (Figure 1.4.)

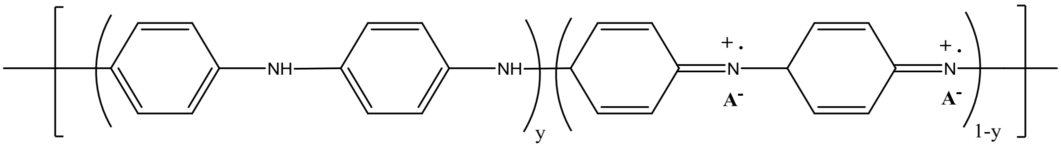

Figure 1.4. General formula of PANI

Polyaniline has three different oxidation states namely, leucoemeraldine, emeraldine and pernigraniline oxidation states with different y values [41].

PANI can be synthesized chemically or electrochemically by oxidative polymerization of aniline in the aqueous medium of HCl. Polyaniline salt is firstly synthesized by using strong oxidizing agent; $(NH_4)_2S_2O_8$, ammonium persulfate. Then polyaniline base form can be synthesized by reacting the salt with NH_4OH.

As a conductive polymer, PANI is environmentally stable, inert and it is preferred mostly by the advantages of having low costs, easy production and stability of the conductive forms. It is used in rechargable batteries, in cell phones and biosensors [42].

1.6. Polyphenyleneoxide (PPO)

Polyphenyleneoxides are classified in polyether group where there is an oxygen linkage between aromatic groups. One of the most known and commercial polyphenylene oxide is poly(2,6-dimethylphenyleneoxide) or poly(oxy-(2,6-dimethyl-1,4-phenylene). Trade name of this polymer is Noryl (General Electric Co.). Poly(2,6-dimethylphenyleneoxide) thermoplastic resin was introduced at 1964 [37].

Other known polymer is poly(dibromophenyleneoxide). Its commercial name is Firemaster TSA (Velsicol Chemical Corporation)[43]. Poly(dibromophenyleneoxide) is synthesized by the oxidation of 2,4,6 Tribromophenol (monomer) with the help of oxidizing agents (PbO_2 or $K_3[Fe(CN)_6$) in basic medium or by microwave irradiation.

PPO is a white powder and stored as pellets. Since the polymer contains 63-65.5 % bromine, its softening range is between 200 and 230 ^{0}C. PPO is soluble to a certain extent in water, acetone, ethanol, toluene, methylenechloride and perchloroethylene.

One of the important properties of poly(dibromophenyleneoxide)(s) is thermal stability. Thermal Gravimetry Analysis (TGA) proves the thermal stability of this polymer in that, even at 568 ^{0}C 75 % weight loss is obtained where HBr is evolved during the analysis.

Another important property of PPO is flame retardancy. PPO is blended with glass fiber reinforced nylons and thermoplastic polyesters due to its flame retardant property in addition to its thermal stability. Moreover, low molecular weight polydibromophenylene oxides are used to increase flow property of the polymer blends [44].

Poly(dibromophenyleneoxides) can differ by the oxygen position of linkage i.e.; ortho- , para- or both. If the oxygen linkage is at para position, then the polymer is called poly(1,4dibromo-phenyleneoxide) (Figure 1.5a). If the oxygen linkage is at ortho position, the polymer is called poly(1,2-dibromophenyleneoxide) (Figure 1.5b). Both 1,2 and 1,4 additions can exist on the same polymer chain (Figure 1.5c).

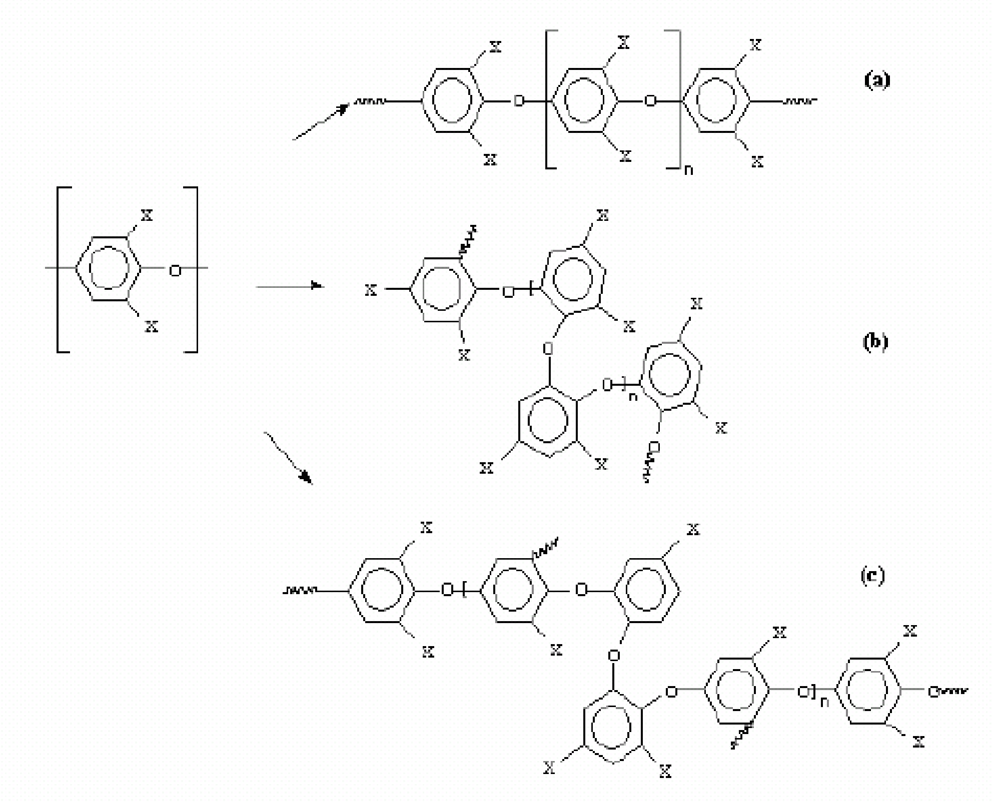

Figure 1.5. Poly(dihalophenyleneoxide) structures (X : Br, Cl, I)

a) 1,4 addition
b) 1,2 addition and
c) Both 1,2 and 1,4 addition

1.7 Crosslinked Polymers

As being different from linear polymers crosslinked polymers are insoluble where chains are linked to each other at multiple points with covalent bonds resulting in polymer networks [45]. (Figure 1.6)

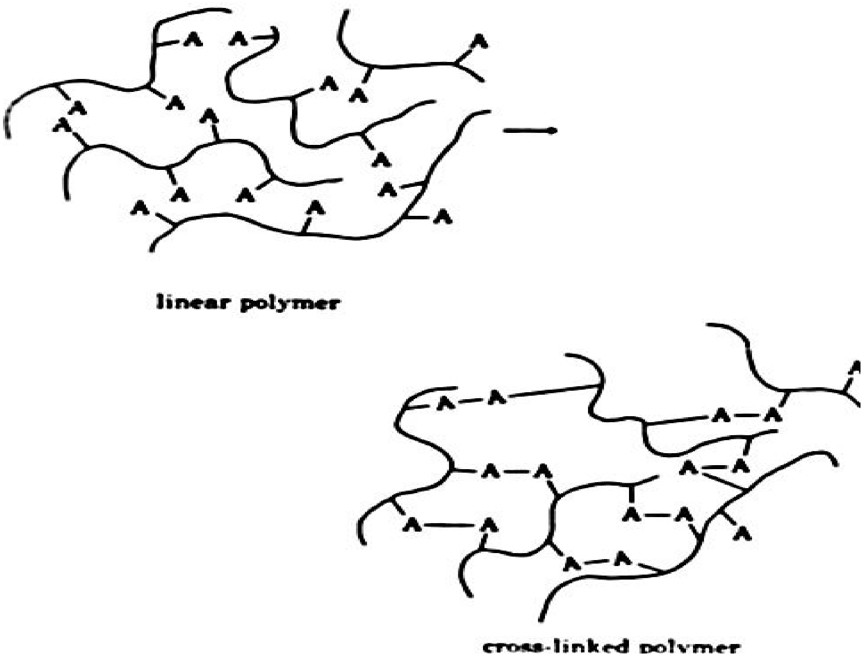

Figure 1.6 Linear and Crosslinked Polymeric Structure

Uncrosslinked or lightly uncrosslinked polymers (elastomers) are softer and flexible above their glass transition temperatures while crosslinked polymers are harder and brittle. Moreover, crosslinked polymers are solid because of the restriction of the motion, on the other hand; linear or branched polymers tend to flow. Light crosslinked polymers have good elastic properties to be used as rubbers, high crosslinked polymers have high dimensional stability and high rigidity properties [45].

Crosslinking mechanism occurs either during or after polymerization process as a separate step (post-polymerization). During the polymerization process, polyfunctional monomers are used to obtain crosslinked polymer via step polymerization and chain polymerization. In post-polymerization step, firstly linear or branched polymers are synthesized, then they are crosslinked.

Novalacs and resols are examples of crosslinking process as a second step. Novalacs are firstly prepolymerized then crosslinked by adding hexamethylene tetramine catalyst. Resoles are crosslinked by heating after prepolymerization. Moreover, epoxy and hydroxyl groups are responsible from crosslinking of epoxy resins. Crosslinking occurs by reacting the polymer with amines like diethylenetriamine and triethylenetetramine. In addition, unsaturated polyesters are crosslinked with monomers containing vinylic group using peroxide crosslinking agent. Methyl ethyl ketone peroxide is an example of crosslinking agent. Vulcanization of rubber is another crosslinking process. Stiff rubber is obtained in order to use it in the places where high mechanical strength is needed [46].

CHAPTER 2

EXPERIMENTAL

2.1. Chemicals

2.1.1. 2,4,6 – Tribromophenol (TBP) and Aniline

Analytical grade 2,4,6 – tribromophenol and aniline were provided from Merck and was used without further purification.

2.1.2. Calcium Hydroxide $Ca(OH)_2$, Potassium Hydroxide (KOH)

$Ca(OH)_2$ was obtained from J.T. Baker and used in the polymerization. KOH was purchased from J.T. Baker and used in the microwave production of polyaniline.

2.1.3. Toluene

Toluene was provided from Sigma Aldrich and used as the solvent for the polymer.

2.1.4. Ethyl Alcohol

Ethyl alcohol was commercially available as technical grade and used as the non-solvent for the polymers for precipitation.

2.1.5. Hydrochloric Acid

It was provided from Merck and used to dissolve the byproduct salts formed during polymerization. It was also used in the chemical synthesis of polyaniline.

2.1.6. Deuterated Chloroform ($CDCl_3$)

$CDCl_3$ was used as the solvent to obtain NMR spectra of the polymers.

2.2. Apparatus and Instruments

2.2.1. Microwave Oven

Domestic microwave oven (BOSCH) works at 2.45 MHz. It has several time intervals (2-10min) and microwave energies (90-900 watt) and was used for polymerization.

2.2.2. Attenuated Total Reflection-Fourier Transform Infrared Spectrophotometer (ATR-FTIR)

Infrared spectra of the samples were obtained on a Nicolet IS 10 Thermo Scientific ATR-FTIR spectrometer.

2.2.3. NMR Spectrophotometer

^1H NMR and ^{13}C NMR spectra of poly(dibromophenyleneoxide) were recorded on a Avance III Bruker NMR spectrometer (400 MHz) in deutorated chloroform with respect to TMS as the internal reference.

2.2.4. Thermogravimetry Analysis and Fourier – Transform Infrared Spectrophotometer (TGA/FTIR)

Weight losses of the polymers were determined by Perkin Elmer STA 6000 TGA-FTIR thermogravimetric analyzer. Samples were heated from 30 ^{0}C to 800 ^{0}C with a heating rate of 10 C/min under nitrogen atmosphere.

2.2.5. Light Scattering

Weight average molecular weight, radius of gyration, and virial coefficient of polymers were determined using multi-angle light scattering spectrometer (Malvern 5000). The ALV/CG –3 Goniometer system is designed to perform dynamic and static light scattering analysis simultaneously.

2.2.6. GPC

Mw/Mn values were measured at 30 ^{0}C with PL-GPC 220 Gel Permeation Chromatography in THF.

2.2.7. ESR

ESR spectra of the products were recorded by Bruker Xepr ELEXSY–580 spectrometer in quartz cell at room temperature where diphenylpicrylhydrazine was the reference.

2.2.8. SEM

Analysis of the surface morphology of the polymer was done by using Quanta 400F (Fei) scanning electron microscope.

2.2.9. UV-Vis

UV-Visible spectra of the samples were obtained on Cary 100 UV-Visible Spectrophotometer in the 800 – 200 nm region.

2.3. Procedure

Tribromophenol (TBP), calcium hydroxide ($Ca(OH)_2$) and water were used as the starting materials for the microwave-assisted polymerization. For aniline polymerization, $(NH_4)_2S_2O_8$ is used the oxidizing agent in chemical synthesis.

2.3.1. Synthesis of Polymers

Microwave initiated polymerizations were performed at several time intervals (2-10 min), in different ranges of microwave energy (90-900 watt) and in various amounts of water (1-5 ml). Tribromophenol and $Ca(OH)_2$ were mixed by grinding and wetting by deionized water. Polymerization was performed in a Pyrex glass holder, loosely covered with a lid, inserted in a microwave oven working at 2.45 MHz. At the end of the reaction time intervals, the simultaneously resulting products were dissolved in 100 ml toluene by vigorous stirring. The insoluble part, crosslinked polymer (**CLP**), were removed by filtration and washed several times by triple distilled hot water for purification. The toluene soluble part, poly(dibromophenylene oxide) (**P**) or radical ion polymer (**RIP**), were precipitated in ethanol. All the recovered precipitates were dried to a constant weight under vacuum.

For aniline polymerization, chemical synthesis and microwave synthesis were studied. In chemical synthesis, 0.1 M aniline and 0.1 M $(NH_4)_2S_2O_8$ were reacted and stirred for 1 minute. Salt was then neutralized with ammonium hydroxide. The salt and the base then filtrated and were dried to a constant weight under vacuum. In microwave synthesis, aniline and HCl solution (with different concentrations) were reacted at different watts.

2.3.2. Characterization of the Polymers

Soluble part (P and RIP) was characterized by ATR-FTIR, 1H-NMR, 13C-NMR, TGA/ FTIR, SEM, ESR, GPC, UV-Vis and light scattering. Insoluble part (CLP) was characterized by TGA-FTIR and ATR-FTIR.

CHAPTER 3

RESULTS AND DISCUSSION

Microwave-assisted polymerization of tribromophenol (TBP) were performed at constant microwave energy and water amount at different time intervals ranging from 2 to 10 min; or at constant time intervals and constant amount of water with the variation of microwave energy ranging from 90 to 900 watt or at constant time intervals and constant microwave energy with varying amounts of water ranging from 1 to 5 ml. Percentage conversion values of each product (P, RIP and CLP) were calculated using the following equation:

$$\text{Conversion (\%)} = \frac{\text{Weight of product}}{\text{Initial weight of monomer}} \times 100 \qquad \textbf{(2)}$$

Triboromophenol polymerization was carried out in three parts by changing tribromophenol and calcium hydroxide amount to observe the changes in molecular weight and percentage of conversion. Moreover, polyaniline synthesis was studied in both chemically and in microwave oven.

3.1. Synthesis of Polymer with a 1:1 Ratio of TBP and $Ca(OH)_2$

In the first experimental part, 0.02 mol TBP and 0.02 mol $Ca(OH)_2$ were reacted for polymerization in microwave oven with different time intervals, different watts and different amounts of water. Insoluble crosslinked polymer (CLP), toluene soluble polymer (P) and radical ion polymer (RIP) were synthesized at the end of the experiments. The effect of water amount (1ml-5ml), microwave energy (90 watt-900 watt) and time (2 min to 10 min) for the polymerization were shown in the Table 3.1. % Conversion and to % Weight Loss (WL) were also shown in the table.

Table 3.1. % Conversion and % Weight Loss Values for Polymers at Different Watts, Times and Water Amounts

90 Watt	**1 ml water** **10 min**	**3 ml water** **10 min**	**5 ml water** **10 min**
% CLP	84.3	90.2	97.7
% RIP	15.2	-	0.9
% P	-	1.1	-
% WL	20.4	8.7	1.3
180 Watt	**1 ml water** **7 min**	**3 ml water** **7 min**	**5 ml water** **7 min**
% CLP	55.2	36.7	55.6
% RIP	19.0	24.6	18.6
% P	-	-	-
% WL	25.8	38.7	25.8
360 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	44.6	45.5	56.0
% RIP	15.6	12.2	23.6
% P	-	-	-
% WL	39.8	42.3	20.4
600 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	26.6	32.0	36.6
% RIP	-	-	-
% P	28.4	28.4	23.6
% WL	45.0	36.7	39.8
900 Watt	**1 ml water** **2 min**	**3 ml water** **2 min**	**5 ml water** **2 min**
% CLP	19.5	21.2	22.3
% RIP	35.5	-	-
% P	-	32.2	30.3
% WL	45.1	46.6	47.3

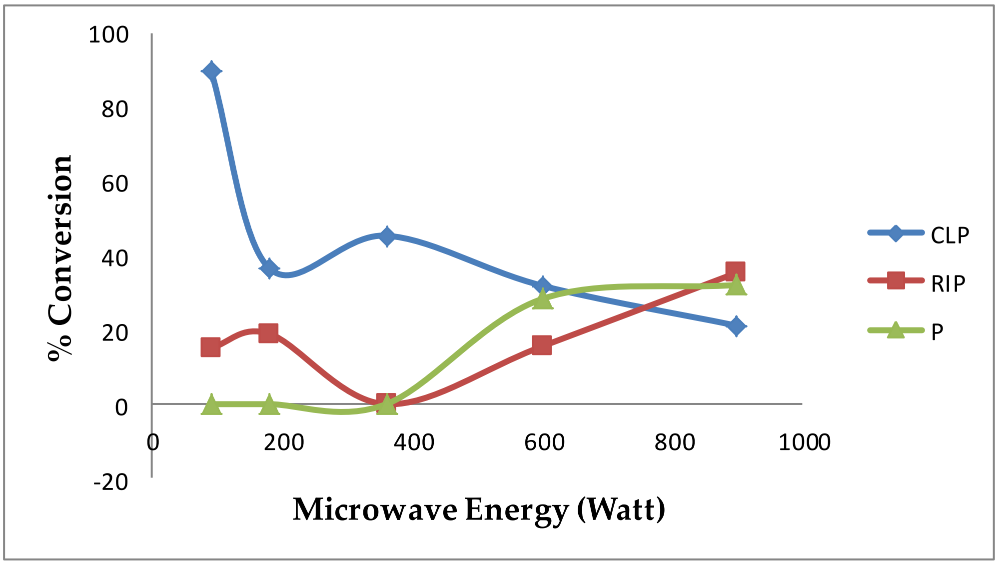

Figure 3.1. Change in % Conversion with Microwave Energy

Figure 3.1. shows the change in % conversion of polymers with microwave energy by keeping water amount constant to show the optimum conditions of P, RIP and CLP.

As seen in Table 3.1., optimum condition for CLP is 90 watt for 10 min in 5 ml water. It can be observed from the graph that % conversion of CLP decreases as microwave energy increases. On the other hand, the result is different for RIP and P. According to the Figure 3.1., % conversion of RIP and P increases as the microwave energy increases. The optimum condition for RIP is 900 watt for 2 min. in 1 ml water, for P is 900 watt for 2 min. in 3 ml water.

Moreover, synthesized CLP amount is high at low watts while; RIP and P amounts are high at high watts. It is also possible to say that weight loss percents are higher at high watts since the medium temperature becomes very high in a short time.

3.1.1. Characterization

According to the Figure 3.1.1.; ATR-FTIR spectra of P and RIP (Figure 3.1.1a and 3.1.1b) show that peak at 3070 cm^{-1} (at both polymer) is due to aromatic C-H stretching and peaks at 1420-1590 cm^{-1} are related with C=C ring stretching. Peaks at 1110-1230 cm^{-1} correspond to C-O stretching. Moreover, peaks at 920-1065 cm^{-1} are due to C-O-C stretching. Out of plane C-H stretching is at 855 cm^{-1}.

According to the Figure 3.1.1c, ATR-FTIR spectrum of CLP shows similar peaks with P and RIP. However, the peak at 1065 cm^{-1} (C-O-C stretching) shifts to 1170 cm^{-1}.

In the ^{1}H-NMR spectrum of P shows that peak at 7.6 ppm is due to the protons of 2,4-dibromo-1,6-phenylene oxide units (1,2 addition) and peak at 7.2 ppm is due to protons of 2,6-dibromo-1,4-phenylene oxide units (1,4 addition). The broad peaks at higher fields indicate both 1,2 and 1,4 addition on the same unit. (Figure 3.1.2.)

According to the ^{13}C-NMR spectrum of P, peaks at 120 ppm are due to C-Br bonds both from 1,2 addition and 1,4 addition of PPO and C=C bonds from 1,4 addition of PPO. Peaks at 126-130 ppm are related to C=C bond due to 1,2 addition of PPO. Peaks at 130-140 ppm are related to C-O bond due to both 1,2 and 1,4 additions (Figure 3.1.3.).

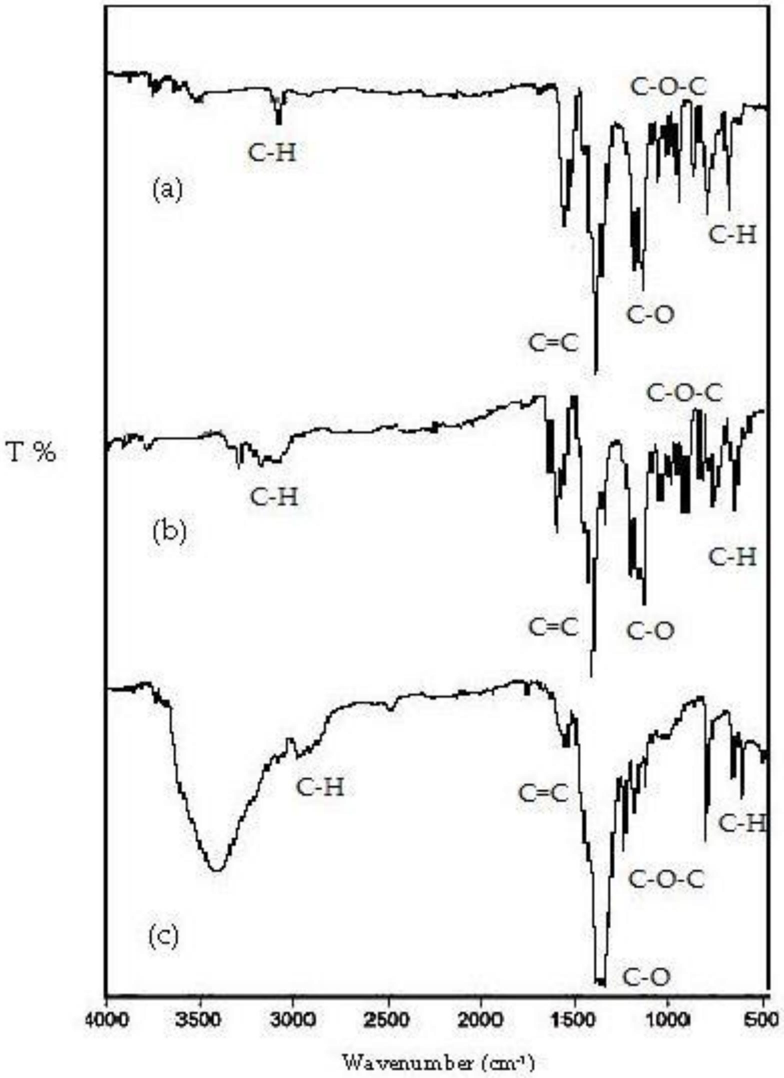

Figure 3.1.1. ATR-FTIR spectrum of **(a)** P, **(b)** RIP and **(c)** CLP

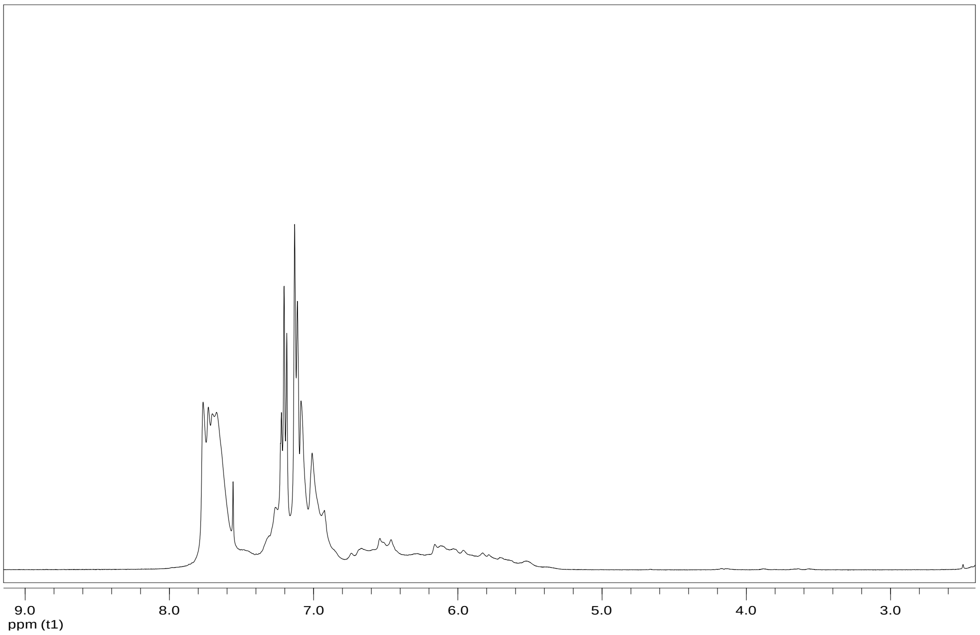

Figure 3.1.2. ^{1}H-NMR spectrum of P

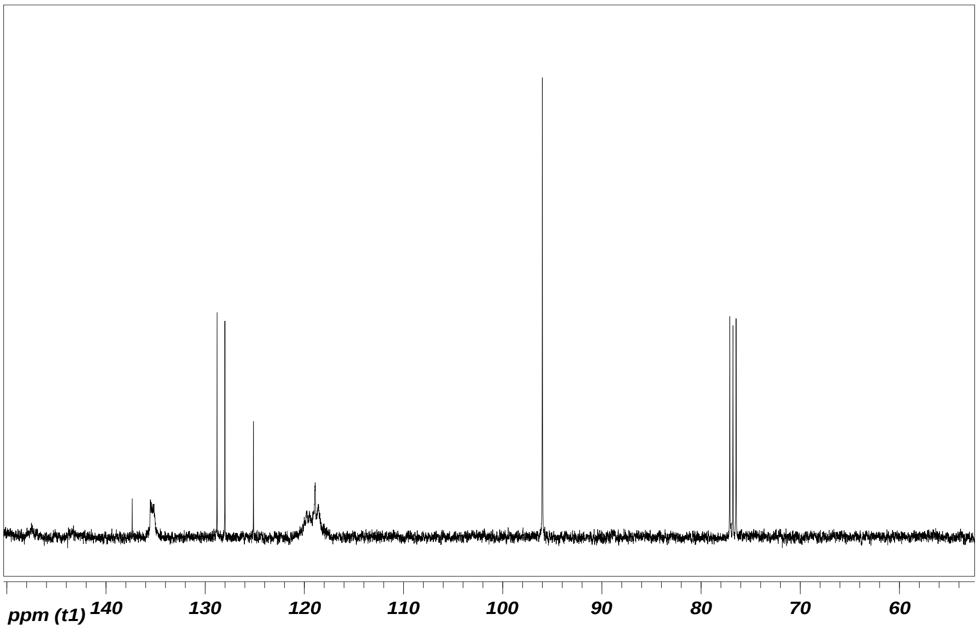

Figure 3.1.3. ^{13}C-NMR spectrum of P

In the TGA thermogram of P, it is seen that weight loss started at about 380 ^{0}C revealing that the polymer was stable up to nearly 350 ^{0}C. When the temperature reached 700 ^{0}C, about 90 % of sample was lost (Figure 3.1.4.). During the thermal degradation FTIR spectrum of evolved gases was obtained (Figure A-1). According to the TGA-FTIR spectrum of P, it was observed that at 2400 and 630 cm^{-1} CO_2 gas was evolved. At around 2100 cm^{-1} CO gas was evolved. Moreover, HBr gas evolution was seen between 2400-2700 cm^{-1}. Vinyl bromide gas evolution was obtained as given by the peaks between 600-3000 cm^{-1}.

TGA thermogram of RIP shows similar case with P (Figure 3.1.5.). Polymer degradation started at about 380 ^{0}C and around 90 % of the polymer degraded at 700 ^{0}C. Evolved gases during the thermal degradation were observed in the FTIR spectrum. Vinyl bromide (600-3000 cm^{-1}), HBr (2400-2700 cm^{-1}), CO (2100 cm^{-1}) and CO_2 (630 and 2400 cm^{-1}) gas evolutions were observed during degradation (Figure A-2).

TGA thermogram of CLP is shown in Figure 3.1.6. It is seen that CLP is more stable than P and RIP. Main degradation started at about 450 ^{0}C and about 50 % of polymer was lost at 700 ^{0}C. According to TGA-FTIR spectrum of CLP, at 3600 cm^{-1} and peaks at between 2000-1400 cm^{-1} H_2O evolution was seen. Moreover, CO_2, CO, HBr and C_2H_3Br gas evolutions were observed in the TGA-FTIR spectrum of CLP (Figure A-3).

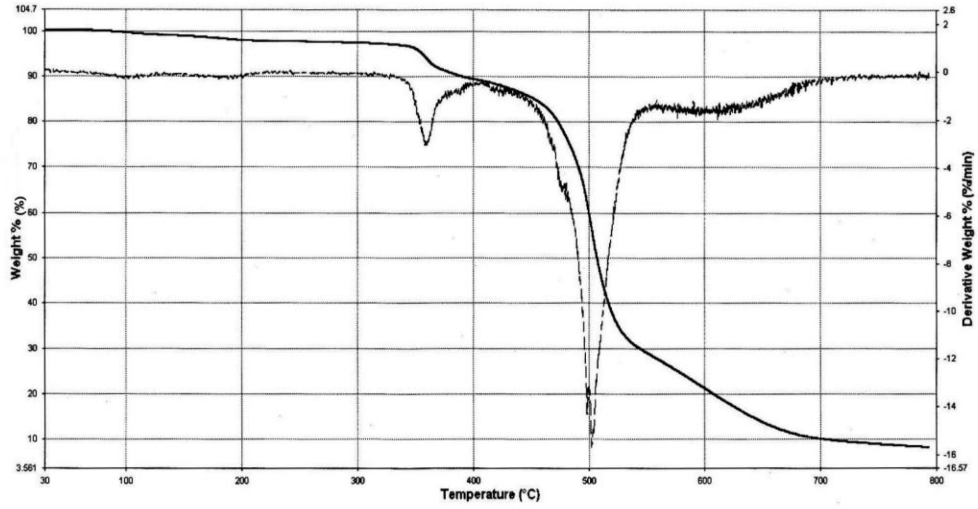

Figure 3.1.4. TGA thermogram of P

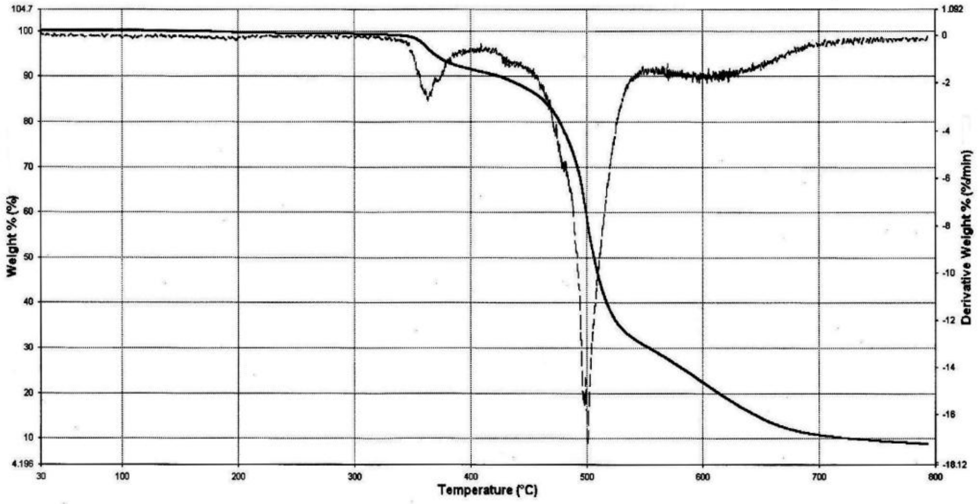

Figure 3.1.5. TGA thermogram of RIP

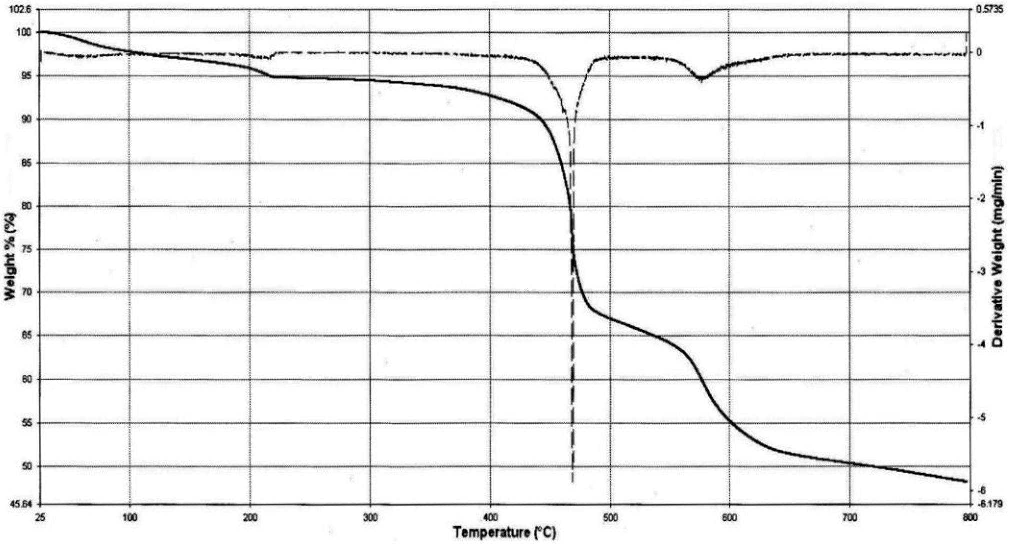

Figure 3.1.6. TGA thermogram of CLP

ESR spectrum which is taken at room temperature was used in order to show the presence of radicals in the polymer. According to the ESR spectrum of RIP (Figure 3.1.7.), radical can be on the CH group on benzene ring which yields as a doublet.

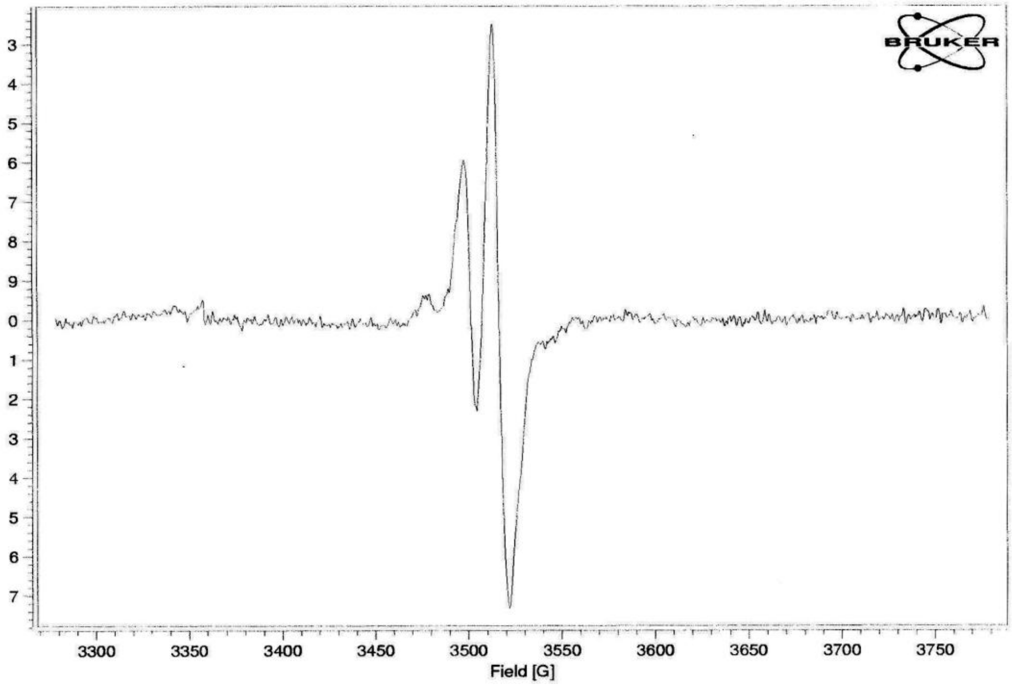

Figure 3.1.7. ESR spectrum of RIP

Figure 3.1.8. shows UV-VIS absorption spectrum of P and RIP. According to the graph absorption maxima at about 320 nm (both P and RIP) arising from π-π* absorption, is related with the absorption of aromatic rings.

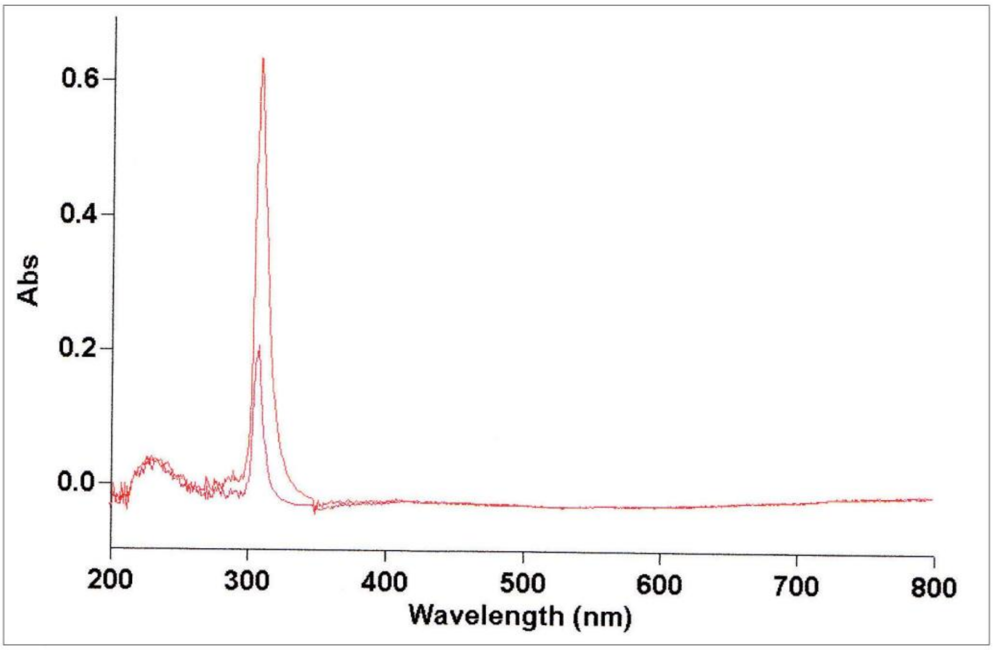

Figure 3.1.8. UV-VIS absorption spectra of P and RIP

As in Table 3.1.1., weight average molecular weight ($\overline{M}_w$), radius of gyration (R_g) and second virial coefficients (S^2) of P and RIP are shown and are carried out by DLS. According to the Table 3.1.1., $\overline{M}_w$ of P is higher than RIP.

Table 3.1.1. $\overline{M}_w$, R_g and S^2 of P and RIP

	P	**RIP**
$\overline{M}_w$ (g/mol)	3.4×10^4	1.5×10^4
R_g (nm)	3.4×10^1	3.7×10^1
S^2 (mol.dm^3/g^2)	5.1×10^{-7}	4.2×10^{-8}

3.2. Synthesis of Polymer with 1:2 Ratio of TBP and $Ca(OH)_2$

In the second experimental part, 0.01 mol TBP and 0.02 mol $Ca(OH)_2$ were reacted in microwave oven with different time intervals, different watts and different amount of water. Insoluble CLP, toluene soluble P and RIP were synthesized at the end of the experiments. The effects of microwave energy, water amount and polymerization time are shown in Table 3.2.

Table 3.2. % Conversion and % Wieght Loss Values for Polymers at Different Watts, Times and Water Amounts

90 Watt	**1 ml water** **10 min**	**3 ml water** **10 min**	**5 ml water** **10 min**
% CLP	82.5	96.0	98.2
% RIP	-	-	-
% P	-	1.2	-
% WL	18.5	2.8	1.8
180 Watt	**1 ml water** **7 min**	**3 ml water** **7 min**	**5 ml water** **7 min**
% CLP	63.5	73.2	97.6
% RIP	24.6	19.3	1.3
% P	-	-	-
% WL	11.9	7.5	1.1
360 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	70.3	73.3	75.6
% RIP	13.0	24.8	0.5
% P	-	-	-
% WL	16.7	1.9	23.9
600 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	62.5	75.6	77.2
% RIP	-	-	-
% P	37.5	20.3	14.1
% WL	-	4.1	8.7
900 Watt	**1 ml water** **2 min**	**3 ml water** **2 min**	**5 ml water** **2 min**
% CLP	90.0	92.2	92.8
% RIP	8.7	-	-
% P	-	5.1	1.7
% WL	1.3	2.7	5.5

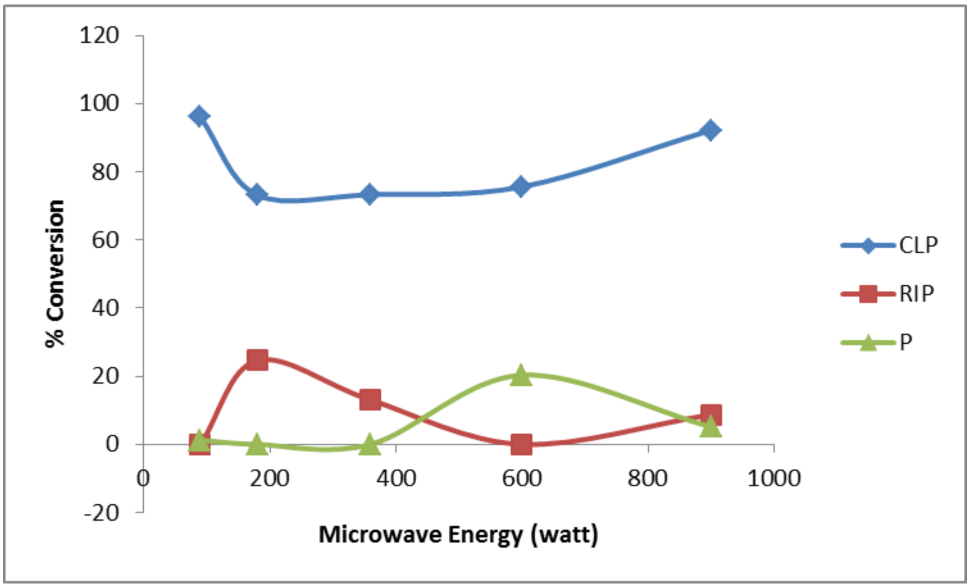

Figure 3.2. Change in % Conversion with Microwave Energy

Figure 3.2. shows the change in % conversion of polymers with microwave energy by keeping water amount constant to show the optimum conditions of P, RIP and CLP.

As in Table 3.2., % CLP synthesis is generally high in almost all watts. It shows that % CLP conversion is high when $Ca(OH)_2$ amount is increased. On the other hand % P and % RIP conversions decreased compared to the results of 1:1 ratio of TBP and $Ca(OH)_2$. According to Figure 3.2., optimum condition for CLP is 90 watt for 10 min in 5 ml water. The optimum condition for RIP is 360 watt for 5 min. in 3 ml water and then % conversion amount of RIP decreased. For P, optimum condition is 600 watt for 5 min. in 1 ml water.

3.2.1. Characterization

In Figure 3.2.1., ATR-FTIR spectra of P (Figure 3.2.1a), RIP (Figure 3.2.1b) and CLP (Figure 3.2.1c) shows that peaks at about 3000 cm^{-1} is related to aromatic C-H stretching and peaks at 1420-1590 cm^{-1} are related to C=C ring stretching. Peaks at 1110-1230 cm^{-1} are due to C-O stretching. Moreover, peaks at 920-1065 cm^{-1} are due to C-O-C stretching. Out of plane C-H stretching is due to the peak at 855 cm^{1}.

^{1}H-NMR spectrum of P (Figure 3.2.2.) shows that peak at 7.6 ppm is due to the protons of 2,4-dibromo-1,6-phenylene oxide units (1,2 addition) and peak at 7.2 ppm is due to protons of 2,6-dibromo-1,4-phenylene oxide units (1,4 addition). The broader peaks at higher fields indicate both 1,2 and 1,4 addition on the same unit. Similar peaks on ^{1}H-NMR was observed for RIP.

^{13}C-NMR spectrum of P (Figure 3.2.3.) indicates the peaks at 120 ppm are due to C-Br bonds both from 1,2 addition and 1,4 addition of PPO and C=C bonds from 1,4 addition of PPO. Peaks at 126-130 ppm are related to C=C bond from 1,2 addition of PPO. Peaks at 130-140 ppm are related to C-O bond from both 1,2 and 1,4 addition of PPO (Figure 3.2.3.). It is proved that both 1,2 and 1,4 additons are present on the same monomeric unit as given by both ^{1}H-NMR and ^{13}C-NMR.

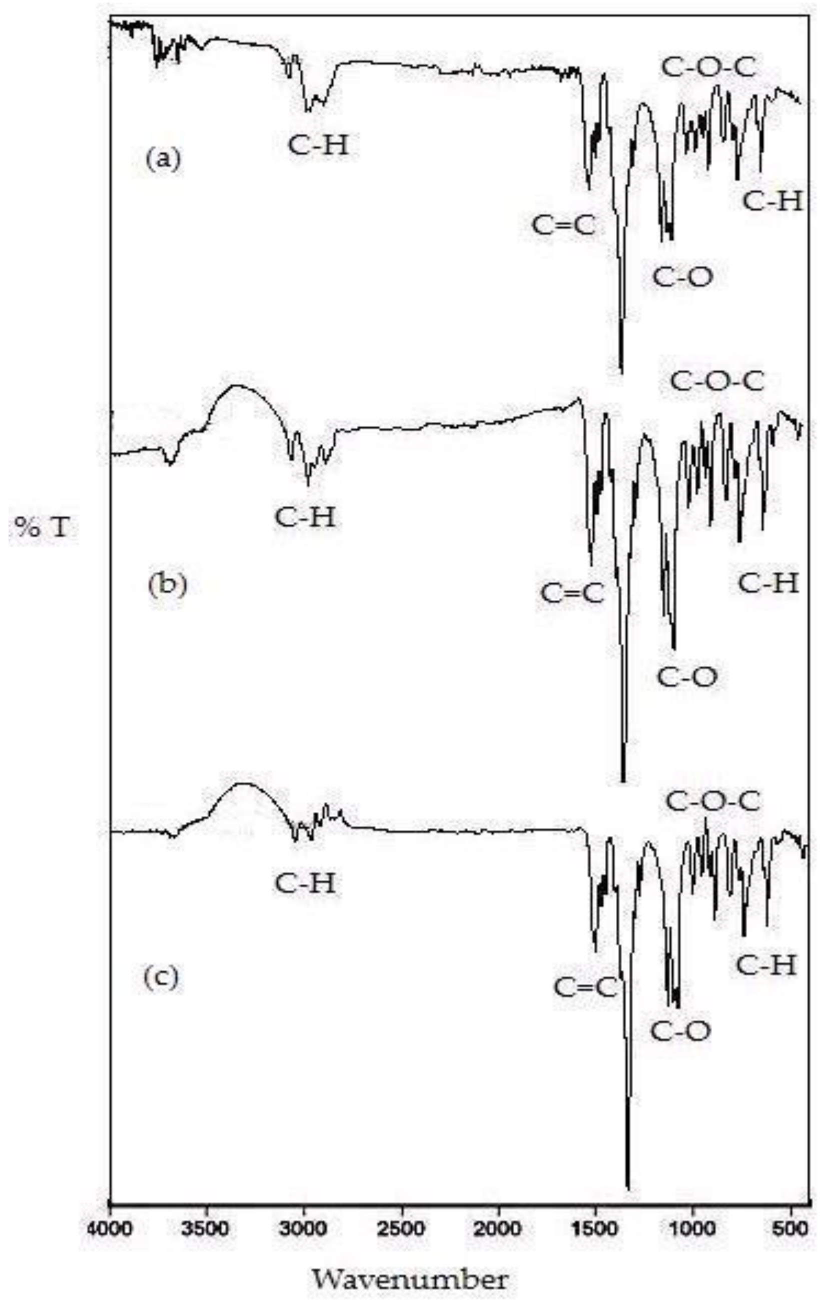

Figure 3.2.1. ATR-FTIR spectrum of a)P, b) RIP and c) CLP

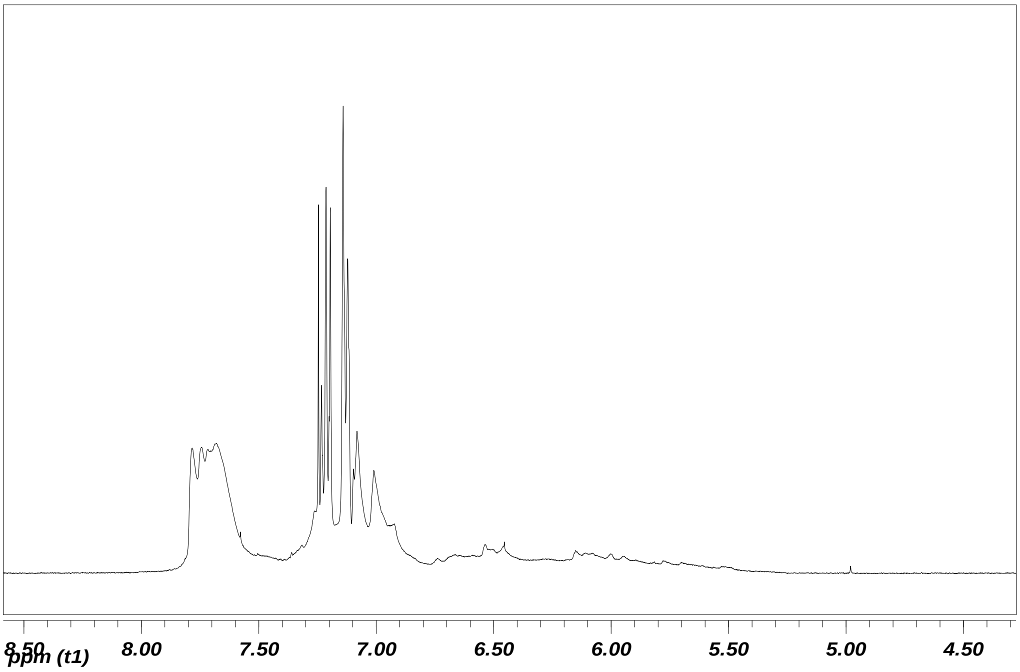

Figure 3.2.2. ^{1}H-NMR spectrum of P

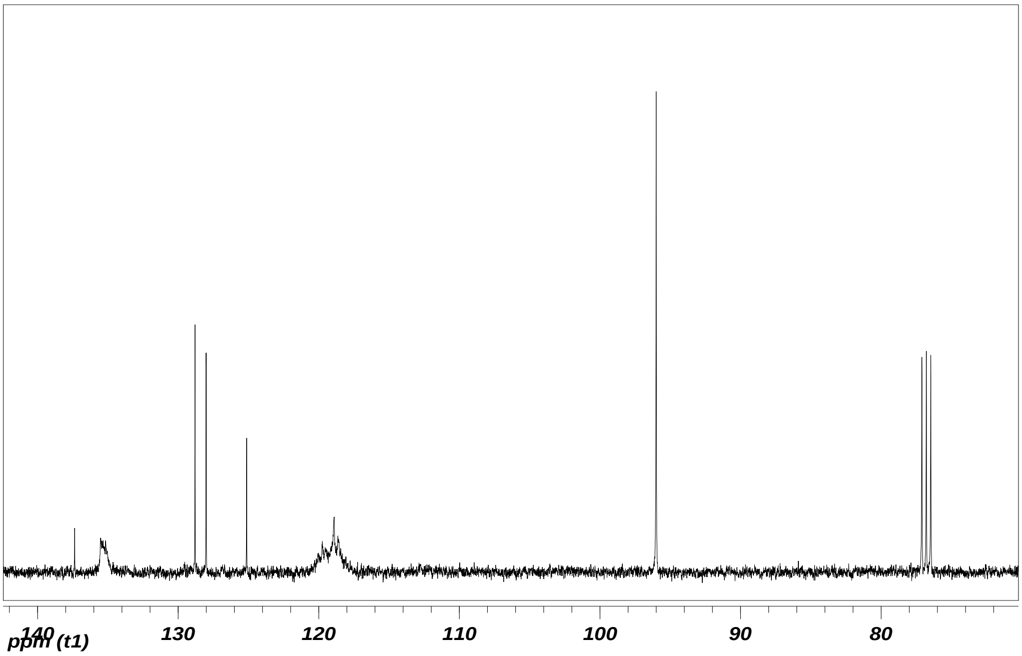

Figure 3.2.3. ^{13}C-NMR spectrum of P

GPC results of polymers (P and RIP) at constant water amount (3ml) with varying microwave energy (180W, 360W, 600W) are shown in Table 3.2.1.

Table 3.2.1. GPC results of P and RIP at constant water amount with varying microwave energy

	180 W (RIP)	**360 W (RIP)**	**600 W (P)**
$\overline{M}_w$	$1.7x10^4$	$6.1x10^4$	$6.0x10^4$
$\overline{M}_n$	$3.5x10^3$	$1.2x10^4$	$7.7x10^3$
Dispersity (PDI)	4.9	4.9	7.8
DP	14	49	31

Considering the weight average molecular weights of polymers, it can be said that higher molecular weights were obtained with increasing microwave energy. When these results are compared with the polymers synthesized with 1:1 ratio of TBP and $Ca(OH)_2$, higher weight average molecular weights ($\overline{M}_w$) were obtained. Highest molecular weight and DP were obtained at 360 W.

TBP was also studied previously with NaOH, LiOH and KOH under microwave irradiation [38]. $\overline{M}_w$ of polymers are shown in the Table 3.2.2. below:

Table 3.2.2. DLS results of P and RIP [38]

	TBP + NaOH ($\overline{M}_w$)	**TBP + LiOH ($\overline{M}_w$)**
P	$2.9x10^5$ g/mol	$1.1x10^5$ g/mol
RIP	$1.2x10^4$ g/mol	-

When Table 3.2.1. is compared with Table 3.2.2., it is seen that $\overline{M}_w$ of P synthesized from either TBP and NaOH or TBP and LiOH is higher than the ones synthesized from TBP and $Ca(OH)_2$. On the other hand, $\overline{M}_w$ of RIP is the highest for this ratio.

Finally, since the highest weight average molecular weight was obtained with this ratio (at 360 watt), surface morphology of this polymer (RIP) was done by scanning electron microscope (SEM) (Figure 3.2.4a,b and c). In surface morphology of RIP, it is seen that it has sponge like structures which are different from RIP synthesized using TBP and NaOH. (Figure 3.2.4d)

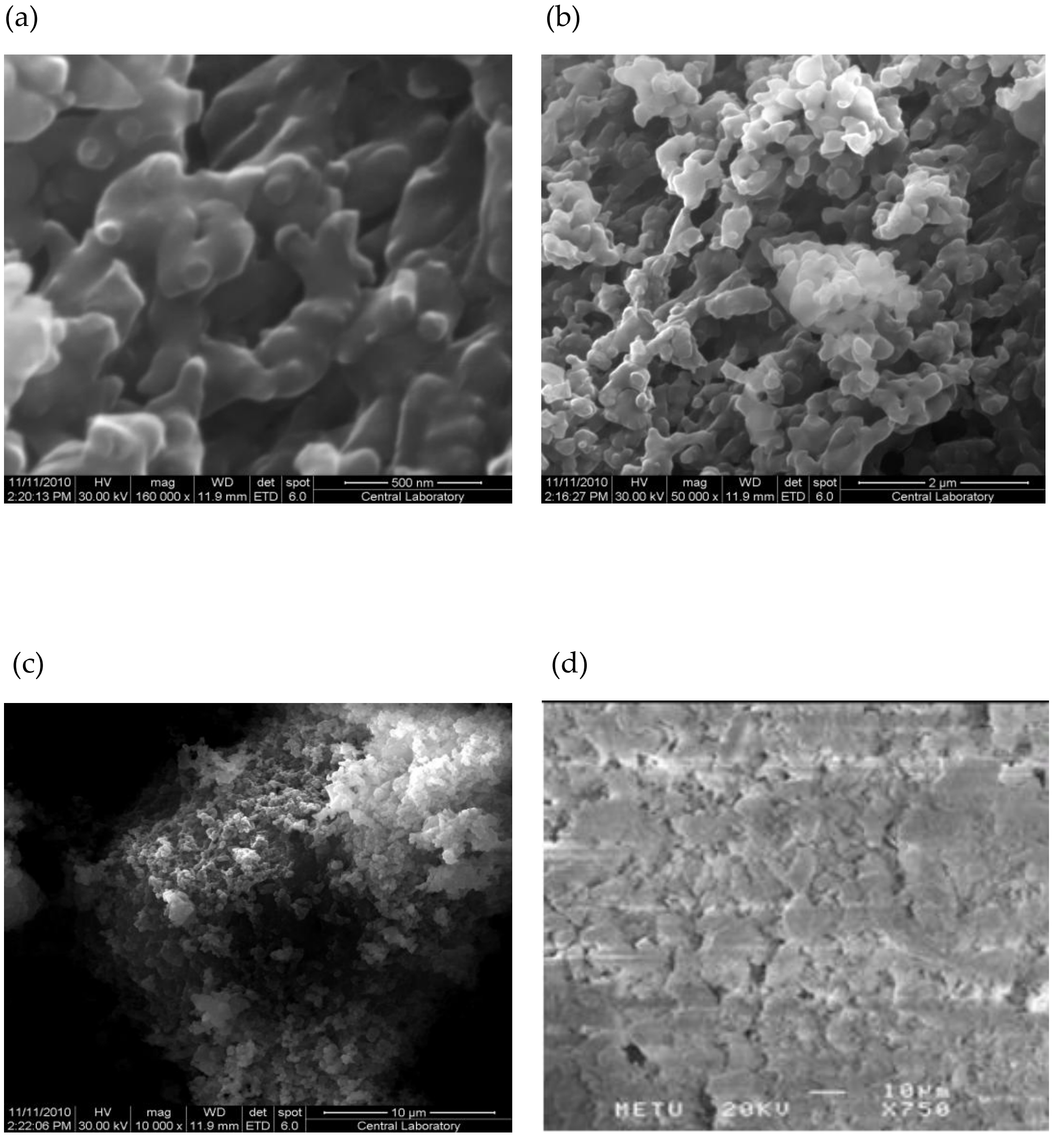

Figure 3.2.4. SEM micrograph of RIP with magnitude of

a)100.000 b) 50.000 c) 10.000

d) [38]

3.3. Synthesis of Polymer with 2:1 Ratio of TBP and $Ca(OH)_2$

In the third experimental part, 0.02 mol TBP and 0.01 mol $Ca(OH)_2$ were reacted for polymerization in microwave oven with different time intervals, different watts and different amounts* of water. Insoluble CLP, toluene soluble P and RIP were synthesized at the end of the experiments. The effects of microwave energy, water amount and time to polymerization are shown in Table 3.3.

Table 3.3. % Conversion and % Wieght Loss Values for Polymers at Different Watts, Times and Water Amounts

90 Watt	**1 ml water** **10 min**	**3 ml water** **10 min**	**5 ml water** **10 min**
% CLP	80.6	88.0	79.2
% RIP	-	2.1	-
% P	-	-	2.5
% WL	19.4	9.9	18.3
180 Watt	**1 ml water** **7 min**	**3 ml water** **7 min**	**5 ml water** **7 min**
% CLP	22.0	74.9	79.1
% RIP	46.0	18.2	3.8
% P	-	-	-
% WL	32.0	6.9	17.1
360 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	21.5	32.0	29.0
% RIP	-	15.3	-
% P	14.3	-	15.1
% WL	64.2	52.7	55.9
600 Watt	**1 ml water** **5 min**	**3 ml water** **5 min**	**5 ml water** **5 min**
% CLP	34.1	34.4	26.5
% RIP	-	-	-
% P	19.7	17.3	19.0
% WL	46.2	48.3	55.5
900 Watt	**1 ml water** **2 min**	**3 ml water** **2 min**	**5 ml water** **2 min**
% CLP	+	38.6	37.5
% RIP	1.1	-	4.6
% P	-	0.3	-
% WL	63.6	61.1	57.9

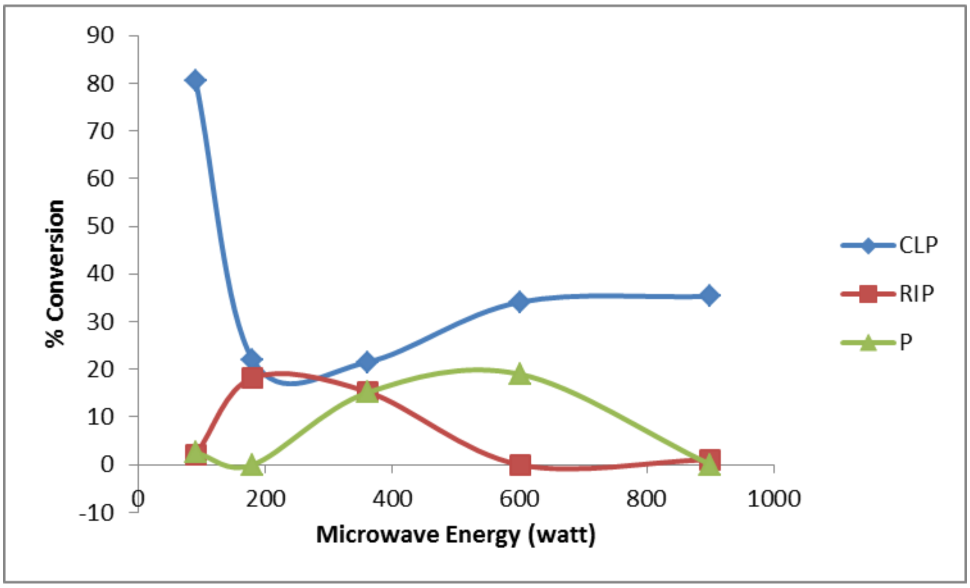

Figure 3.3. Change in % Conversion with Microwave Energy

Figure 3.3. shows the change in % conversion of polymers with microwave energy by keeping water amount constant to show the optimum conditions of P, RIP and CLP.

As seen in Table 3.3., % weight loss is more than the other % weight losses obtained with 1:1 and 1:2 ratio of TBP and $Ca(OH)_2$. % CLP amount is very low when compared to the ones with the other ratios. Maximum % CLP amount is obtained at 90 watt for 10 min. in 3 ml water which is 88%. Then, % CLP amount decreased with increasing microwave energy. % P and % RIP conversion were also decreased when TBP amount was increased. According to Figure 3.3., optimum condition for RIP is at 180 watt for 7 min in 3 ml water. The optimum condition for P is at 600 watt for 5 min. in 5 ml water.

3.3.1. Characterization

ATR-FTIR spectra of P (Figure 3.3.1a) and RIP (Figure 3.3.1b) show that peaks at about 3000 cm^{-1} is related to aromatic C-H stretching, peaks at 1420-1580 cm^{-1} are related to C=C ring stretching, peaks at 1100-1250 cm^{-1} are due to C-O stretching, peaks at 920-1060 cm^{-1} are due to C-O-C stretching and peaks at 850 cm^{-1} are due to out of plane C-H stretching.

In Figure 3.3.1c, ATR-FTIR spectrum of CLP shows similar peaks with P and RIP. One difference is that peak at 1050 cm^{-1} (C-O-C stretching) shifts to 1170 cm^{-1}.

^{1}H-NMR spectrum of P (Figure 3.3.2.) shows that peak at 7.6 ppm is due to the protons of 2,4-dibromo-1,6-phenylene oxide units (1,2 addition) and peak at 7.2 ppm is due to protons of 2,6-dibromo-1,4-phenylene oxide units (1,4 addition). The broader peaks at higher fields indicate both 1,2 and 1,4 addition on the same unit. Similar peaks on ^{1}H-NMR was observed for RIP.

^{13}C-NMR spectrum of P (Figure 3.3.3.) indicates the peaks at 120 ppm are due to C-Br bonds both from 1,2 addition and 1,4 addition of PPO and C=C bonds from 1,4 addition of PPO. Peaks at 126-130 ppm are related to C=C bond due to 1,2 addition of PPO. Peaks at 130-140 ppm are related to C-O bond due to both 1,2 and 1,4 additions (Figure 3.3.3.). It is proved that both 1,2 and 1,4 additons are present on the same monomeric unit as given by both ^{1}H-NMR and ^{13}C-NMR.

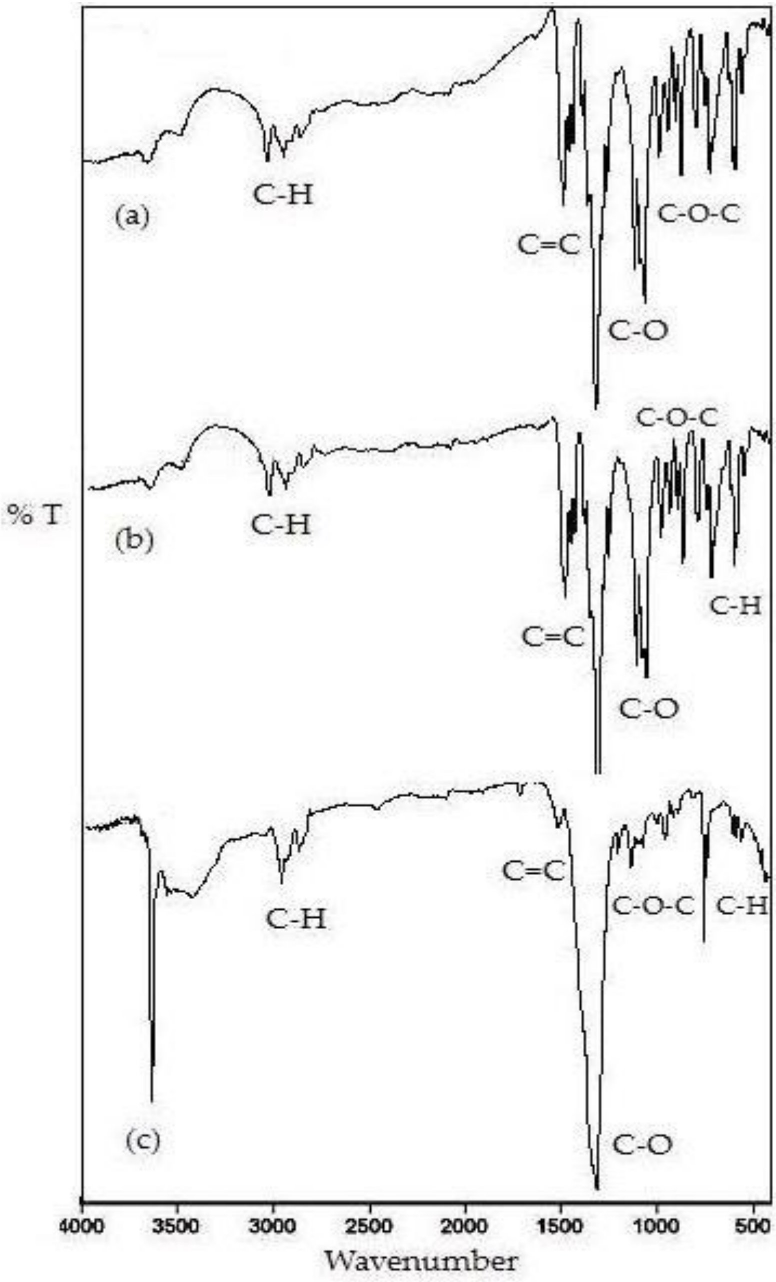

Figure 3.3.1. ATR-FTIR spectrum of a) P, b) RIP and c) CLP

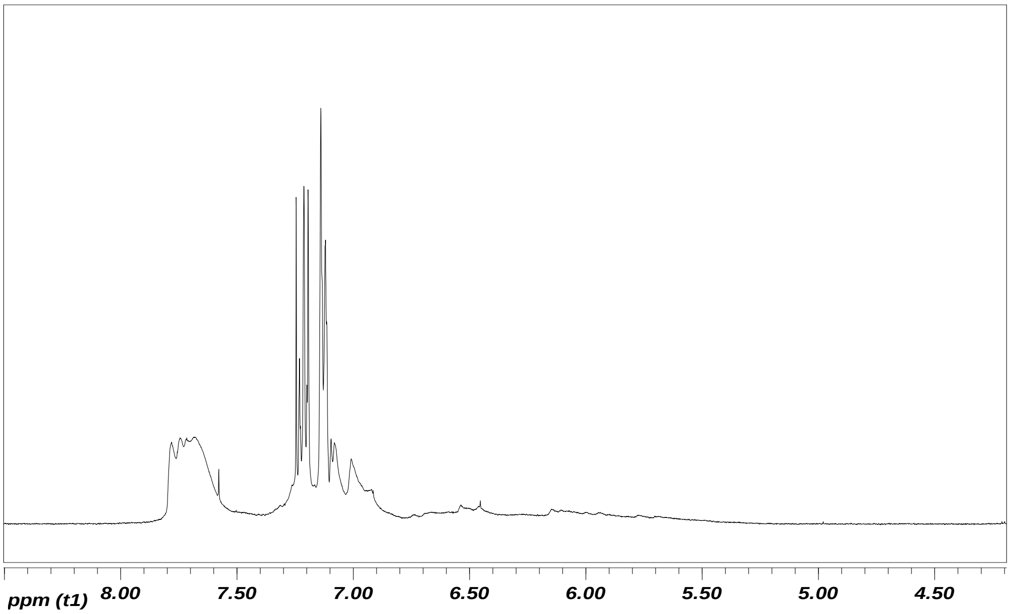

Figure 3.3.2. ^{1}H-NMR spectrum of P

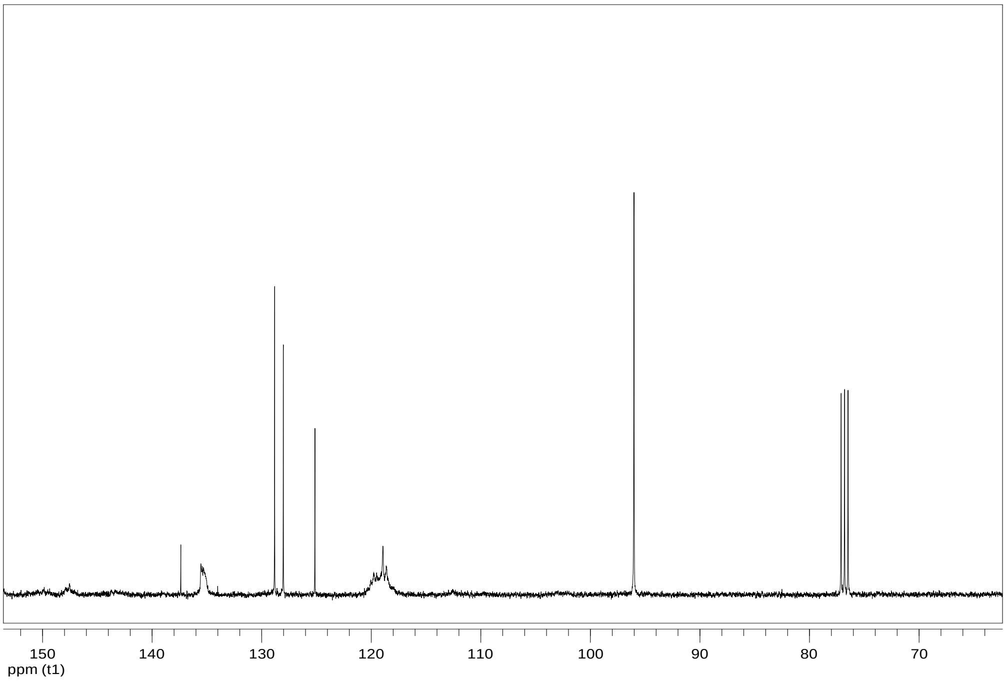

Figure 3.3.3. ^{13}C-NMR spectrum of P

GPC results of polymers (P and RIP) at constant water amount (3ml) with varying microwave energy (180W, 360W, 600W) are shown in Table 3.3.1.

Table 3.3.1. GPC results of P at constant water amount with varying microwave energy

	180 W (RIP)	**360 W (P)**	**600 W (P)**
$\overline{\mathbf{M}}_w$	4.9×10^4	2.3×10^4	2.8×10^4
$\overline{\mathbf{M}}_n$	9.6×10^3	3.5×10^3	7.7×10^3
Dispersity (PDI)	5.1	6.4	3.7
DP	39	14	31

According to Table 3.3.1., different from polymers synthesized with 1:2 ratio of TBP and $Ca(OH)_2$, highest average molecular weight was obtained at 180 watt rather than 360 watt. At 360 watt, $\overline{M}_w$ decreased and then increased again at 600 watt. Except 180 watt, molecular weights of polymers synthesized with this ratio were lower than the molecular weights of polymers synthesized with 1:2 ratio of TBP and $Ca(OH)_2$.

Moreover, weight average molecular weights of polymers synthesized from TBP and NaOH, LiOH or KOH are higher for P than the ones synthesized from 2:1 ratio of TBP and $Ca(OH)_2$. For RIP, $\overline{M}_w$ of polymer (at 180 watt) is higher from the $\overline{M}_w$ of polymer synthesized from TBP and NaOH, LiOH or KOH, lower than the RIP synthesized with 1:2 ratio TBP and $Ca(OH)_2$.

Summary of experimental results are shown in Table 3.3.2.

Table 3.3.2. Summary of Experimental Results

		1mol TBP - 1mol $Ca(OH)_2$	**1 mol TBP - 2 mol $Ca(OH)_2$**	**2 mol TBP - 1 mol $Ca(OH)_2$**	**TBP and LiOH**	**TBP and NaOH**	**TBP and KOH**
Opt. Cond.	**% P**	32.2 900 watt 2 min, 3 ml w	37.5 600 watt 5 min, 1 ml w	19.0 600watt 5 min, 5 ml w	24.5 180watt 2 min, 1ml w	9.2 180watt 10 min, 5 ml w	39.2 350watt 1 min, 5 ml w
	% RIP	35.5 900 watt 2 min, 1 ml w	24.8 360 watt 5 min, 3 ml w	46.0 180 watt 7 min, 1 ml w	-	-	35.0 350watt 3 min, 5 ml w
	% CLP	97.7 90 watt 10 min, 5 ml w	98.2 90 watt 10 min, 5 ml w	88.0 90 watt 10 min, 3 ml w	80.8 900watt 10 min, 5 ml w	20.1 350watt 1 min, 5 ml w	-
$\overline{M}_W$ g/mol	**P**	$3.4x10^4$	$6.0x10^4$ 600 watt	$2.8x10^4$ 600 watt	$1.1x10^5$	$2.9x10^5$ 70 watt	$8.0x10^4$
	RIP	$1.5x10^4$	$1.7x10^4$ 180 watt $6.1x10^4$ 360 watt	$5.0x10^4$ 180 watt $2.3x10^4$ 360 watt	-	$1.2x10^4$	$3.3x10^4$

3.4. Chemical and Microwave Synthesis of Polyaniline

Chemical synthesis of polyaniline was performed in the presence of strong oxidizing agent, $(NH_4)_2S_2O_8$. Aniline and ammonium persulfate (in equal moles) were stirred for 1 minute. By this way, salt form of polyaniline was obtained. When polyaniline salt was neutralized with hydrazine or ammonium hydroxide, polyaniline base was formed. ATR-FTIR results of polyaniline salt and polyaniline base are shown in Figures 3.4.1. and 3.4.2.

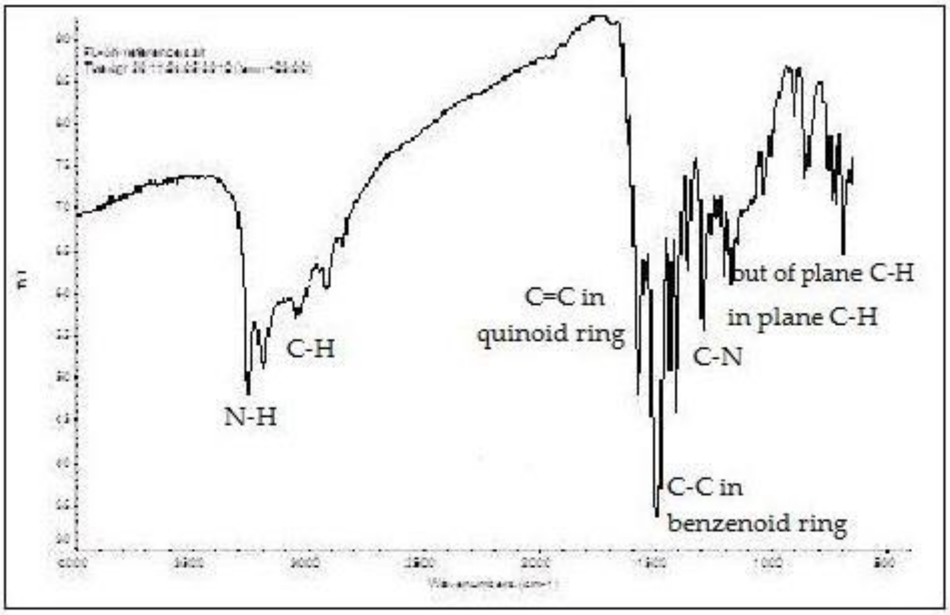

Figure 3.4.1. ATR-FTIR spectrum of Polyaniline salt

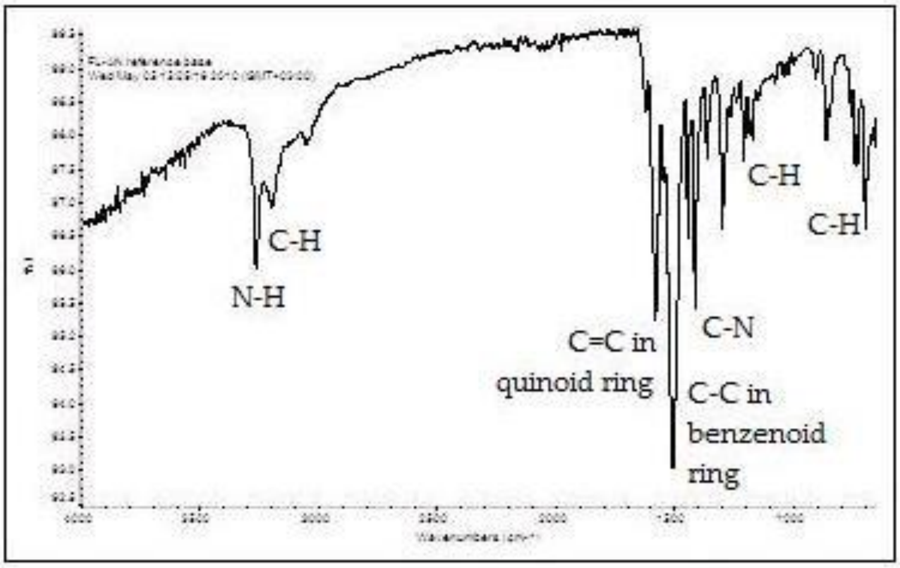

Figure 3.4.2. ATR-FTIR spectrum of Polyaniline base

According to ATR-FTIR spectrum of PANI salt form (Figure 3.4.1.), peak at about 3300 cm^{-1} is due to N-H stretching, peak at 3000 cm^{-1} is due to aromatic C-H stretching, peak at 1600 cm^{-1} is due to C=C stretching in quinoid ring, peak at 1500 cm^{-1} is due to C-C stretching in benzenoid ring, peak at 1250 cm^{-1} is due to C-N stretching, peak at 1150 cm^{-1} is due to in plane C-H bending and peak at 850 cm^{-1} is due to out of plane bending.

According to ATR-FTIR spectrum of PANI base (Figure 3.4.2.), same peaks are seen as in the FTIR spectrum of PANI salt. One difference is that in salt form in plane C-H bending peaks around 1150 cm^{-1} are more intense and broader than the ones in base.

In microwave irradiation, aniline was reacted firstly with KOH at different watts and times in the absence of oxidizing agent. However, polymerization did not take place. One of the reason can be that microwave irradiation is not strong enough to polymerize aniline completely. Other reason can be that, aniline was generally synthesized in acidic medium. When aniline was reacted with KOH, dimer form of aniline was synthesized rather than a polymer. ATR-FTIR spectrum of aniline dimers and aniline is shown in Figure 3.4.3. and 3.4.4. respectively.

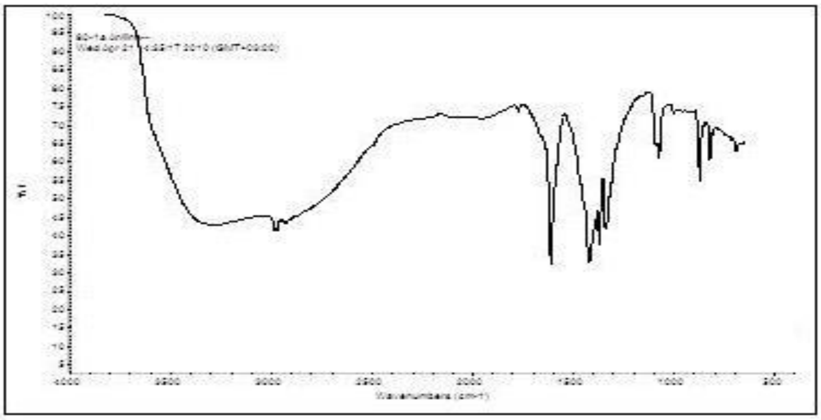

Figure 3.4.3. Aniline dimers synthesized under microwave irradiation

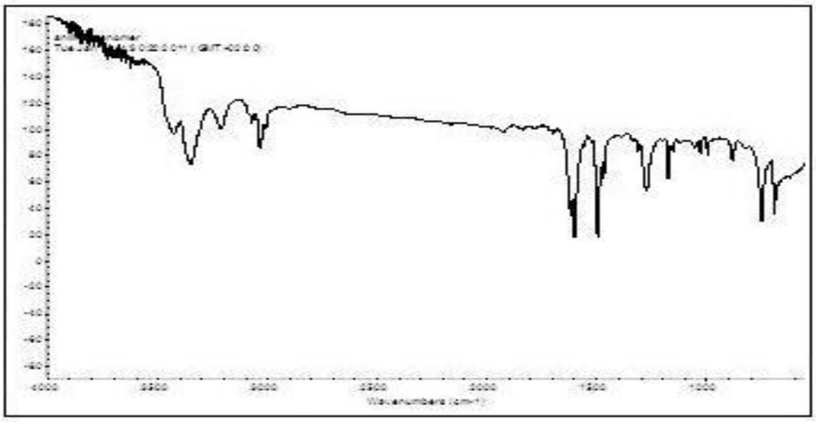

Figure 3.4.4. ATR-FTIR spectrum of aniline

CHAPTER 4

CONCLUSION

In this study the polymerization of TBP with $Ca(OH)_2$ was performed at different ratios. Experimental results were compared with the experiments done previously with TBP and NaOH (LiOH and KOH). Aniline polymerization was also studied chemically and under microwave conditions.

TBP polymerizations were performed at varying microwave energy (90-900 watt), water amounts (1-5 ml) and time intervals ranging from 2 to 10 minutes. At the end of the experiments white coloured polymer (P), radical ion polymer (RIP) and crosslinked polymer (CLP) were synthesized from different TBP and $Ca(OH)_2$ amounts. Effect of TBP and $Ca(OH)_2$ amount were discussed. Polymers were characterized by ATR-FTIR, 1H-NMR, 13C-NMR, TGA/ FTIR, SEM, ESR, GPC, UV-Vis and light scattering.

The highest percent conversion for P was obtained as 37.5 % at 600 watt for 5 min in 1 ml water synthesized with a 1:2 ratio of TBP and $Ca(OH)_2$. However; this yield is lower than the percent conversion of P synthesized from TBP and KOH (39.2 %).

The highest percent conversion for RIP was 46.0 % which was obtained at 180 watt for 7 min in 1 ml water using 2:1 ratio of TBP and $Ca(OH)_2$. This yield is also higher than the % RIP synthesized from TBP and KOH.

Moreover % CLP conversion was the highest at 90 watt for 10 min in 5 ml water with 1:2 ratio of TBP and $Ca(OH)_2$ (98.2 %). This percent conversion is also higher than the one for % RIP with TBP and NaOH (and LiOH).

According to the experimental results, when $Ca(OH)_2$ amount increased, % WL got smaller and % CLP increased. However; when TBP amount increased, % WL increased.

In addition; highest $\overline{M}_w$ for P is $6.0x10^4$ g/mol at 600 watt from TBP and $Ca(OH)_2$. However; using TBP and NaOH, higher $\overline{M}_w$ of P was obtained. For RIP the highest $\overline{M}_w$ is $6.1x10^4$ g/mol and this result is bigger than the $\overline{M}_w$ of P synthesized using TBP and NaOH (and KOH).

Finally, in order to compare the results under microwave conditions; chemical synthesis of polyaniline was carried out. Polyaniline salt and base are synthesized using strong oxidizing agent $(NH_4)_2S_2O_8$ and characterized by ATR-FTIR. When aniline polymerization was studied under microwave condition in both alkali and acidic media, it was seen that only aniline dimers were synthesized rather than a polymer. In conclusion; we can say that aniline could not be polymerized under microwave irradiation without strong oxidizing agent.

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APPENDIX A

FTIR SPECTRA OF EVOLVED VOLATILE COMPONENTS DURING TGA OF P, RIP AND CLP

a)

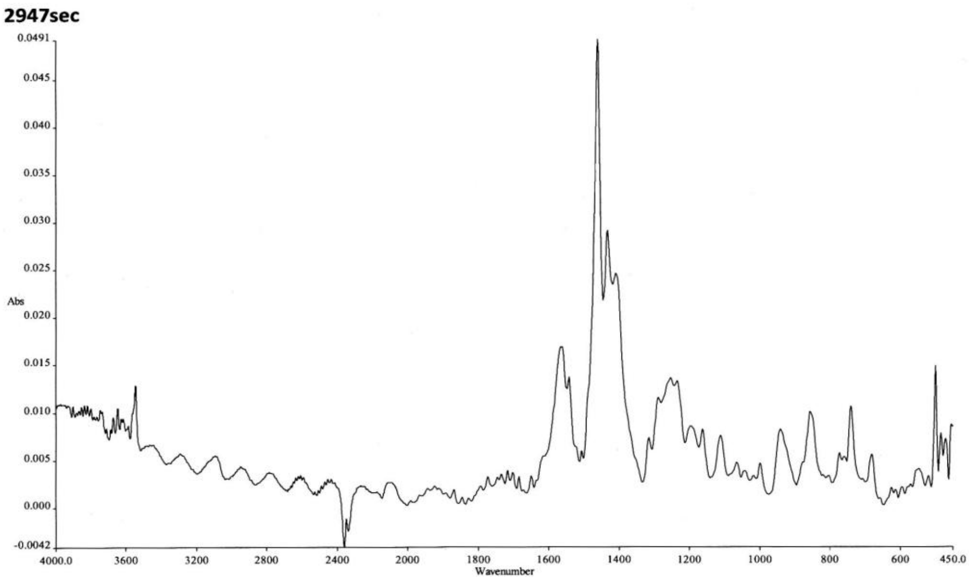

Figure A-1 FTIR spectrum of evolved volatile components during TGA of P b)

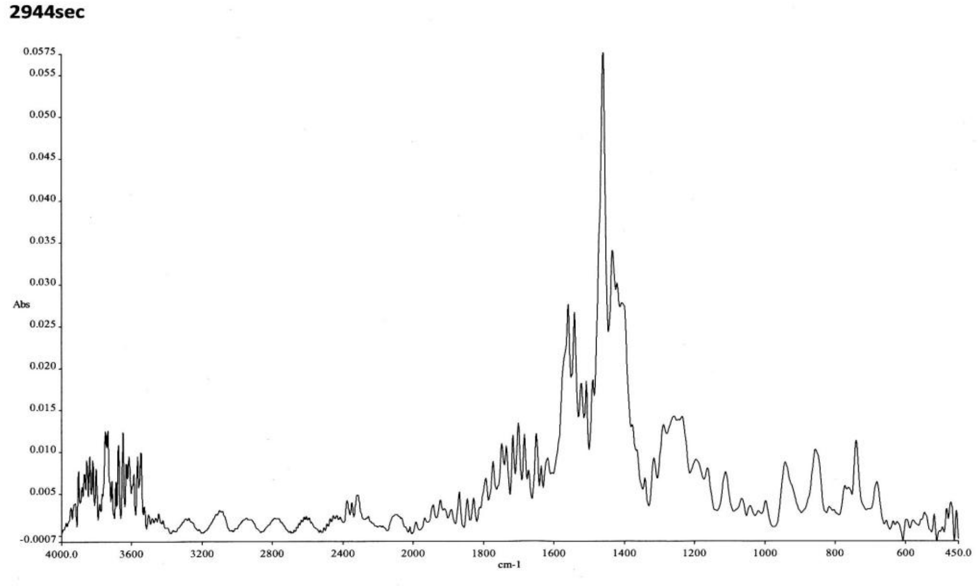

Figure A-2 FTIR spectrum of evolved volatile components during TGA of RIP

c)

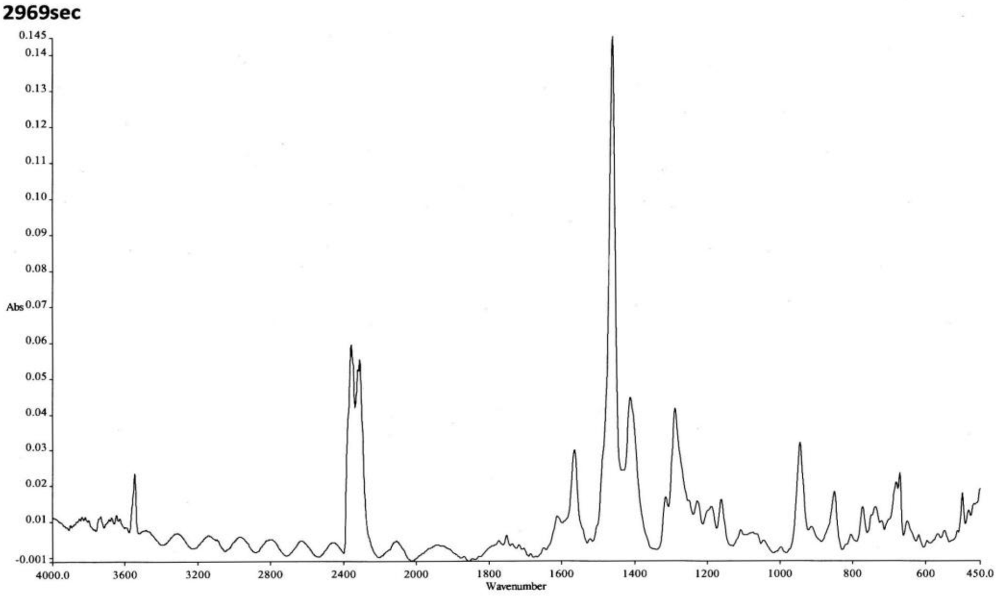

Figure A-3 FTIR spectrum of evolved volatile components during TGA of CLP