

POLYMERIZATION OF 2,4,6 TRICHLOROPHENOL BY
MICROWAVE INITIATION

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POLYMERIZATION OF 2,4,6 TRICHLOROPHENOL BY MICROWAVE
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ABSTRACT

POLYMERIZATION OF 2,4,6 TRICHLOROPHENOL BY MICROWAVE INITIATION

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Polymerization reaction is carried out by the reaction of 2,4,6 trichlorophenol with sodium hydroxide, in the presence of small amount of water by microwave initiation.

Synthesis of polymers were successfully performed under microwave energy. The use of microwave energy was due to advantages of shorter processing time. The main focus of attention was the 90 to 600 watt microwave energy. Polymerizations were performed with different time intervals by keeping the microwave energy and water content constant; or with different energy levels by keeping the time interval and water content constant; or by varying the amount of water by keeping the time and energy level constant.

Beside poly(dichlorophenylene oxide), conducting polymer, ion-radical polymer, crosslinked polymer were also be successfully synthesized and characterized. Characterizations of the products were performed by FTIR, ¹H-NMR, ¹³C-NMR, DSC, TGA and elemental analysis. Molecular weight distribution was measured by PL-GPC 220 Polymer Laboratories Instrument. Conductivity measurements were performed by four probe technique.

Keywords: Microwave, Polydichlorophenylene oxide, Conducting Polymer, Crosslinked Polymer, Ion Radical Polymer

ÖZ

2,4,6-TRIKLOROFENOL'ÜN MİKRODALGA İLE POLİMERLEŞTİRİLMESİ

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Polimerizasyon, 2,4,6 triklorofenol ve sodyum hidroksitin, mikrodalga yardımı ile ve su varlığında reaksiyonu ile gerçekleşir.

Polimerlerin sentezi, mikrodalga enerjisi altında başarı ile gerçekleştirilmiştir. Proses zamanını kısalttığı için mikrodalga kullanılmıştır. 90-600 watt mikrodalga enerjisi aralığında çalışılmıştır. Polimerizasyon reaksiyonları, farklı zaman aralıklarında, mikrodalga enerjisini ve suyu sabit tutarak; ya da farklı enerji seviyelerinde, zaman ve suyu sabit tutarak; ya da su miktarını değiştirip, enerji ve zaman aralığını sabit tutarak gerçekleştirilmiştir.

Poli(diklorofenilen oksit)'in dışında, iletken polimer, iyon radikal polimer, çapraz bağlı polimer sentezlenmiş ve karakterize edilmiştir. Elde edilen ürünlerin karakterizasyonu FTIR, ¹HNMR, ¹³CNMR, TGA, DSC, elemental analiz ve viskometrik ölçümler ile gerçekleştirilmiştir. Molekül ağırlık dağılımı PL-GPC 220

cihazı ile ölçülmüştür. İletkenlik ölçümü, ODTÜ Kimya Bölümü iletkenlik ölçüm cihazı ile gerçekleştirilmiştir.

Anahtar Kelimeler: Mikrodalga, Poli(diklorofenilen oksit), İletken polimer, Çapraz bağlı polimer, İyon radikal polimer,

TO MY PARENTS

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CHAPTER 1

INTRODUCTION

1.1. MICROWAVE FOR POLYMERIZATION

The theory of electromagnetic energy can be illustrated by what happens when a pebble is tossed into a quiet pond. The pebble striking the still surface causes the water to move up and down in the form of ripples, or waves, that radiate in ever-widening circles over the surface of the pond. These waves, which move up and down at right angles to the direction they are traveling, are called transverse waves. Microwave are examples of transverse waves. The disturbance resulting from the pebble landing in the water is transmitted through the water in the form of ripples or waves. The water serves merely as a medium through which the disturbance travels. In this sense, these ripples are more like sound waves, which also need a medium to travel through, normally using the molecules that exist in the air or water. That is why, for example, thundering rocket engines that would deafen the ears under normal circumstances, would be inaudible in the quiet vacuum of space.

On the other hand, electromagnetic forms of energy, such as microwaves, radar waves, radio and TV waves, travel millions of miles through the emptiness of space without the need of any material medium through which to travel. This is because, simply put, electromagnetic waves are, in themselves, stored energy in motion.

A Phenomenal Force

Electromagnetic radiation begins with a phenomenon that occurs when electric current flows through a conductor, such as a copper wire. The motion of the electrons through the wire produces a field of energy that surrounds the wire and floats just off its surface. This floating zone or cloud of energy is actually made up of two different fields of energy, one electric and one magnetic. The electric and

magnetic waves that combine to form an electromagnetic wave travel at right angles to each other and to the direction of motion. If the current flowing through the wire is made to oscillate at a very rapid rate, the floating electromagnetic field will break free and be launched into space.

Then, at the speed of light, the energy will radiate outward in a pulsating pattern, much like the waves in the pond. It is theorized that these waves are made up of tiny packets of radiant energy called photons. Streams of photons, each carrying energy and momentum, travel in waves like an undulating string of cars on a speeding roller coaster. Microwaves used in microwave ovens, similar to microwaves used in radar equipment, and telephone, television and radio communication, are in the *non-ionizing* range of electromagnetic radiation. Non-ionizing radiation is very different from *Ionizing radiation*. Ionizing radiation is extraordinarily high in frequency (millions of trillions of cycles per second). It is, therefore, extremely powerful and penetrating. Even at low levels, ionizing radiation can damage the cells of living tissue. In fact, these dangerous rays, have enough energy and intensity to actually change (ionize) the molecular structure of matter. In sufficient doses, ionizing radiation can even cause genetic mutations. The ionizing range of frequencies includes X-rays, gamma rays, and cosmic rays. Ionizing radiation is the sort of radiation we associate with radioactive substances like uranium, radium, and the fall-out from atomic and thermonuclear explosions.

Non-ionizing radiation is very different. Because of the lower frequencies and reduced energy, it does not have the same damaging and cumulative properties as ionizing radiation. Microwave radiation is non-ionizing, and in sufficient intensity will simply cause the molecules in matter to vibrate, thereby causing friction. [1]

Microwaves are the electromagnetic radiation which can be placed between infrared radiation and radio frequencies with wavelengths of 1 mm to 1 m, which corresponds to the frequencies of 300 GHz to 300 MHz, respectively. The extensive application of microwaves in the field of telecommunication has resulted in only specially assigned frequencies being allowed to be allocated for industrial, scientific or medical applications (e.g., most of the wavelengths between 1 and 25 cm is used

for mobile phones, radar, and radio-line transmissions). Currently, in order to avoid interferences with telecommunication devices, household and industrial microwave ovens (applicators) are operated at either 12.2 cm (2.45 GHz) or 33.3 cm (900 MHz). However, some other frequencies are also available for heating [2]. Most common domestic microwave ovens utilize the frequency of 2.45 GHz, and this may be one reason why almost all commercially available microwave reactors for chemical use operate at the same frequency.

When a piece of material is exposed to microwave irradiation, microwaves can be reflected from its surface (when the surface is conducting as in metals, graphite, etc.), can penetrate the material without absorption (in the case of good insulators), and can be absorbed by the material (lossy dielectrics). Thus, heating in microwave ovens is based upon the ability of some liquids and solids to absorb and to transform electromagnetic energy into heat. Microwave radiation – as every radiation of electromagnetic nature – consists of two components: magnetic and electric fields. The electric field component is responsible for dielectric heating mechanisms since it can cause molecular motion either by migration of ionic species (conduction mechanism) or rotation of dipolar species (dipolar polarization mechanism). In a microwave field, the electric field component oscillates very quickly (at 2.45 GHz the field oscillates 4.9×10^9 times per second), and the strong agitation, provided by cyclic reorientation of molecules, can result in an intense internal heating which can lead to heating rates in excess of 10 °C per second when microwave radiation of a 1 kW-capacity source are used [3].

Microwave heating has gained increasing interest in recent years, and has been used more and more as an activation method for a number of organic synthesis[4]. The use of microwave energy for polymer processing has been receiving increasing attention due to advantages of shorter processing time, improved energy utilization, and the potential for lower processing temperature and improved product uniformity.

The effect of microwave irradiation on chemical reactions is generally evaluated by comparing the time needed to obtain a desired yield of final products with respect to conventional thermal heating. Research in the area of chemical synthesis has shown

some potential advantages in the ability not only to drive chemical reactions but to perform them in reduced time scale. In some cases the products exhibited properties that may not be possible using conventional thermal treatments.[5]

Microwave irradiation has been applied to free-radical polymerization and copolymerization reactions of various unsaturated monomers. In 1983, Teffal and Gourdene investigated the bulk polymerization of 2-hydroxyethyl methacrylate (HEMA) under conventional and microwave conditions[6]. Since HEMA bears ester as well as alcohol functions, it is a polar species capable of interacting and absorbing microwaves. Therefore, the reactions were carried out without any radical initiator, and the liquid monomer polymerized to form a solid material that was insoluble in all usual solvents but swelled in water. Thus, it was demonstrated that the radical polymerization can be achieved by microwave irradiation of neat reagents. In a similar example, Palacios et al. showed that in the case of bulk copolymerization of HEMA with methyl methacrylate (MMA), microwave-assisted polymerizations gave copolymers with molecular weight twice as high and of narrower molecular weight distribution in comparison with copolymers obtained under conventional thermal conditions [7].

Emulsion polymerization of styrene under microwave irradiation in the presence of potassium persulfate (KPS) as an initiator was reported by Palacios and Ververde [8]. The reactions were carried out in glass tubes of 20 ml volume while 15 ml of the reaction mixture with different initiator concentration (0.2–31.1 mmol/l) was added. During the experiments, each tube was placed in a 2-l glass beaker filled with vermiculite. The beakers were irradiated in a multimode microwave with 389 W power in the magnetron, which was turned on and off twice per minute to maintain a constant temperature (50 °C). In order to reach a conversion of styrene of 70%, constant heating in an oil bath for as long as 6 h was required in comparison with only 8.3 min in the microwave oven. More recently, using a bench-scale microwave polymerization reactor, Correa et al. reported that emulsion polymerization of styrene could be carried out more rapidly with significant saving of energy and time when compared to conventional methods [9].

Applying microwave irradiation, Cai et al. demonstrated that *N*-vinylcarbazole (NVC) could be polymerized in bulk in the presence of fullerene-C60 as a charge transfer initiator [10]. Microwave polymerizations were carried out in sealed argon-filled thick-walled Pyrex tubes filled with NVC (from 0.19 to 3.22 g) together with C60 (0.02 g) and placed in a commercially available multimode microwave oven for 10 min. In comparison with polymerization under conventional conditions (water bath, 70 °C), microwave polymerization was found to be advantageous due to decrease in the reaction time and considerable improvement of yield of poly(*N*-vinylcarbazole) (PVK) – 70% as opposed to 8% after 10 min of conventional heating. In fact, during microwave experiments, temperature was neither measured nor evaluated, so that it is hard to make any yield comparison between these two techniques. In spite of different heating methods, the molecular weights and polydispersities of the resultant polymers were similar.

The copolymerization reactions of maleic anhydride with allylthiourea [11] and dibenzyl maleate [12] were studied by Lu et al. The reactions were carried out in the solid state without any initiator in 10-ml vials, which were irradiated in a domestic microwave oven for 20–70 s. In the case of allylthiourea, the conversion of monomers reached ca. 20% after 70 s at 430 W, while yield of the copolymer obtained from dibenzyl maleate was 94% after 32 s of irradiation at 700 W. Under conventional conditions, the copolymer was produced with 89% yield after 2 h at 45 °C [12]. The copolymers were used as a metal complexing agent [11] and suspending agent for the synthesis of superabsorbent oil resins [12].

The microwave copolymerization of dibutyltin maleate (DBTM) and allyl thiourea was investigated, under conditions specified above to produce organo-tin copolymers [13]. Under microwave irradiation, the copolymers could be synthesized without and in the presence of free radical initiator.

Methathesis polymerization of phenylacetylenes under microwave irradiation was achieved by Sundararajan and Dhanalakshmi [14], applying in situ generated (arene)M(CO)₃ complexes. Microwave irradiation was carried out in a domestic microwave oven under oxygen free dry nitrogen atmosphere in a specially designed

long-necked round bottom flask which could withstand elevated pressure. The catalyst/monomer ratio was kept at a 1:50 level. For example, $W(CO)_6$ (0.199 mmol) was taken together with phenylacetylene (5.975 mmol) and toluene (0.5 ml) in a 1,2-dichloroethylene solution and irradiated for 5 min at time intervals of 10 min to cool down the reaction mixture. The reaction time was reduced to 1 h in contrast to refluxing conditions of 24 h. Among the group VIB metal carbonyl, $W(CO)_6$ was found to be the best catalyst precursor, while phenol showed the highest activity among arenes. Under such conditions, poly(phenylacetylene) was obtained in 67–75% yield.

The use of microwave irradiation to polymerize dental materials was reported by Nishii [15], who was able to obtain porosity-free acrylic resin specimens of similar physical and mechanical properties to the water bath cured specimens. Al Doori et al. studied microwave and conventional polymerization of denture base acrylic materials in respect of their molecular weights, conversion of monomer and porosity [16]. For this purpose, four commercially available resins that contained benzoyl peroxide as an initiator were compared while a household microwave oven was applied as a microwave source. It was found that molecular weight values of polymerized materials cured under microwave irradiation and in a water bath were essentially the same.

In a similar study, Usanmaz et al. polymerized commercially available acrylic resins under both conventional (water bath) and microwave conditions (multimode cavity) [17]. In a typical experiment, 100 g of PMMA powder was mixed together with 43 ml of liquid monomer (MMA) to make homogenous dough that was then placed into a mould and polymerized at 70 °C for 30 min. The curing was done in boiling water for 5–35 min or under microwave irradiation for 1–3 min. It was found that viscosity-average molecular weight values were larger for microwave curing and increased with curing time, which is an important advantage of microwave curing in dental applications.

The glass transition temperature of different samples increased with curing periods. However, the values were close to each other for both curing methods. Dynamical

mechanical analysis (DMA) showed that crosslinking density of the samples increased with an increase in cure time but the changes were more noticeable under microwave irradiation compared to conventional thermal curing [17].

The kinetic study of solution imidization under microwave irradiation of polyamic acid prepared from 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) and DDS was performed by Lewis et al. [18]. The microwave equipment consisted of a microwave generator (85 W) and a tunable cavity operating in the TE111 mode, while temperature was monitored using a fiber-optic temperature sensor. The samples were maintained in a Teflon vessel of 1.5 cm diameter hole and 1.5 cm deep. During a typical run, 25 W of microwave power was required to heat the sample to the desired temperature over 80–200 s. It was demonstrated that microwave irradiation increased the rate of solution imidization over that obtained for conventional treatment by a factor of 20–34, depending on the reaction temperature. The apparent activation energy for this imidization, determined from an Arrhenius analysis, was reduced from 105 to 55 kJ/mol when microwave activation was utilized rather than conventional thermal processing.

In the series of papers, synthesis of aliphatic polyamides and polyimides under microwave irradiation was described by Imai et al. [19–20]. The reactions were carried out in a modified domestic microwave oven with a small hole on the top of the oven so that nitrogen was introduced to a 30 ml wide-mouth vial adapted as a reaction vessel. In the case of polyamides synthesis, they were prepared of both *w*-amino acids and nylon salt type monomers while polyimides were obtained from the salt form of monomers composed of aliphatic diamines and pyromellitic acid or its diethyl ester in the presence of a small amount of a polar organic medium.

In conclusion, polymer synthesis as well as processing can greatly benefit from the unique feature offered by modern microwave technology, which was demonstrated in many successful laboratory-scale applications. These can include such technical issues as shorter processing time, increased process yield, and temperature uniformity during polymerization and crosslinking. Although microwave energy is more expensive than electrical energy due to the low conversion efficiency from

electrical energy (50% for 2.45 GHz and 85% for 915 MHz), efficiency of microwave heating is often much higher than conventional heating and more than compensates for the higher energy cost.

1.2. CONDUCTING POLYMERS

Conducting polymers are conjugated polymers, namely organic compounds that have an extended p-orbital system, through which electrons can move from one end of the polymer to the other. The most common are polyaniline (PAni) and polypyrrole (PPY).

For the history of polymer technology one of the most valued properties of synthetic polymers has been their ability to act as excellent electrical insulators, both at high voltages and at high frequencies. In spite of this, there has been interest for many years in the possibility of producing electrically conducting polymers. [21]

Electrical conductivity (σ) results from the existence of charge carriers and the ability of those carriers to move. Thus:

$$\sigma = ne\mu$$

where n is the number of carriers per unit volume, e is the electronic charge and μ is the carrier mobility. Consequently, doped conjugated polymers, “conducting polymers”, are good conductors for two reasons:

1. Doping (through oxidation or reduction) leads to injection of carriers into the π - electron system. Since every monomer is a potential redox site, conjugated polymers can be doped (n-type or p-type) to a relatively high density of charge carriers.
2. The π -bonding leads to π -electron delocalization along the polymer chains, and, thereby, to the possibility of charge carrier mobility, which is extended into three dimensional transport by the interchain electron transfer interactions. In principle the broad π -electron bandwidths can lead to high carrier mobilities.

As a result of the same interchain π -bonding and relatively strong interchain electron transfer interactions, the mechanical properties of conjugated polymers are potentially superior to those of saturated polymers such as polyolefins. Moreover, because of these two features, it may be possible to exceptional mechanical properties with aligned conjugated polymers at lower chain lengths than required for their saturated counterparts. [22]

The intractable properties of conducting polymers don't allow much manipulation of the morphology, so that most studies are restricted to effects of different nascent morphologies on properties.

The mechanical properties of conducting polymers can be compared with those of other crystalline and glassy polymers. For polyacetylene and polypyrrole, the strength and elongation to break are quite respectable, suggesting that the material is a high polymer and not a low molecular weight or heavily crosslinked resin. In contrast, the properties of polyphenylene are significantly worse. The mechanical properties of all conducting polymers, would be expected to depend on the dopant content and on plasticization by residual solvent, but there seem to have been no systematic studies of these effects.

The availability of the electronic states, arising from the conjugated π electron system and capable of facile oxidation and reduction, is the key to the doping behaviour and electrochemistry of conducting polymers but it is also responsible for much of their environmental instability. For any conjugated structure there are two critical properties which it is possible to calculate, from a consideration of the configuration of the π -orbital system, the band gap and the ionization potential. The ionization potential is important for the ability -of oxidizing agents (dopants) to remove electrons from the π -orbitals and to the stability of polymer to oxidation in air. The band gap will determine the number of electronic defects in the undoped polymer and its optical spectrum. Some of these defects will be neutral, such as solitons (unpaired spins) in polyacetylene, other defects will be charged and so can act as current carriers. The conductivity of the undoped polymer will be depend on the number of charged defects and their mobility.

1.2.1. Applications of Conducting Polymers

When it comes to the applications, until about 30 years ago all carbon based polymers were rigidly regarded as insulators. The notion that plastics could be made to conduct electricity would have been considered to be absurd. Indeed, plastics have been extensively utilized by the electronics industry for this very property. They are used as inactive packaging and insulating material. This very narrow perspective is rapidly changing as a new class of polymers known as intrinsically conductive polymers or electroactive polymers are being discovered. Although this class of polymer is in its infancy, much like the plastic industry was between the 1930's and 50's, the potential uses of these polymers are quite significant.[23]

Intrinsically conducting polymers (ICPs) represent a special class of weak materials with electronic and ionic conductivity. Chemical and physical properties are dependent on their redox state. [24] The understanding of the redox behavior of conducting polymers is essential for a successful application of these so-called synthetic metals as functional coatings. The redox process involves the exchange of ions and solvent molecules. This so called doping/dedoping process involves changes of the mechanical and the electronic structure of the polymer. [25]

These properties allow a wide application as functional coatings. The application of ICPs in functional coatings requires special properties such as fast response (e.g. in ms), stability for 10³ cycles for batteries and 10⁶ switches for displays, and a constant potential of discharge for batteries. Moreover, the stability against corrosion, overoxidation and delamination has to be guaranteed. Chemical modification of the monomer allows wide variations of properties, but economic requirements limit the price of the monomer and, thereby, the thickness or quality of the coating. [24]

The first conducting plastics were discovered by accident at the Plastics Research Laboratory of BASF in Germany. They were attempting the oxidative coupling of aromatic compounds. When they made polyphenylene and polythiophene they found

that they showed electrical conductivities of up to 0.1 s cm^{-1} . Since then other conducting polymers have been discovered.

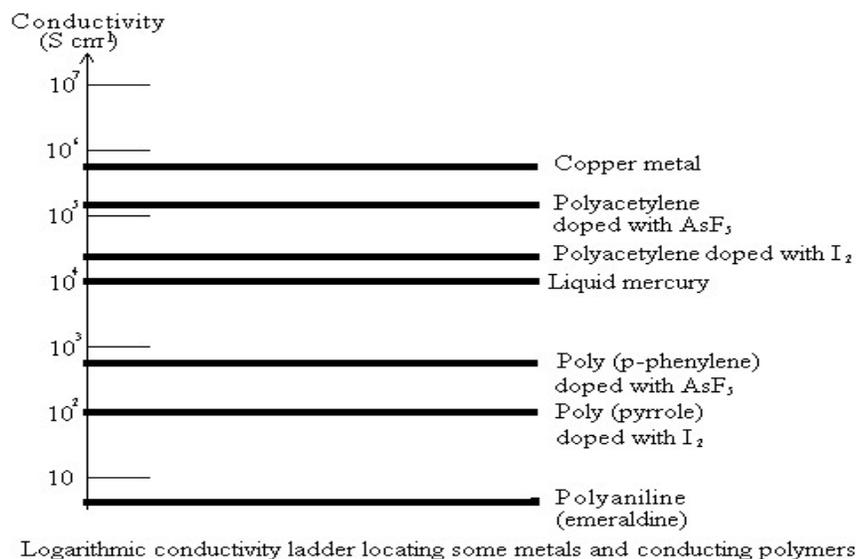


Figure 1.1 Logarithmic conductivity ladder locating some metals and conducting polymers

There are two main groups of applications for these polymers. The first group utilizes their conductivity as its main property. The second group utilizes their electroactivity. The extended π -systems of conjugated polymer are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. Since these reactions are often reversible, it is possible to systematically control the electrical and optical properties with a great deal of precision. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are shown below:

Group 1

Conducting adhesives
Electromagnetic shielding
Printed circuit boards

Artificial nerves
Antistatic clothing
Piezoceramics
Active electronics (diodes, transistors)
Aircraft structures

Group 2

Molecular electronics
Electrical displays
Rechargeable batteries and solid electrolytes
Drug release systems
Optical computers
Ion exchange membranes
Electromechanical actuators
'Smart' structures
Switches

By coating an insulator with a very thin layer of conducting polymer, it is possible to prevent the buildup of static electricity. This is particularly important where such a discharge is undesirable. Such a discharge can be dangerous in an environment with flammable gasses and liquids and also in the explosives industry. In the computer industry the sudden discharge of static electricity can damage microcircuits. This has become particularly acute in recent years with the development of modern integrated circuits. To increase speed and reduce power consumption, junctions and connecting lines are finer and closer together. The resulting integrated circuits are more sensitive and can be easily damaged by static discharge at a very low voltage. By modifying the thermoplastic used by adding a conducting plastic into the resin results in a plastic that can be used for the protection against electrostatic discharge.[27]

Many electrical appliances use printed circuit boards. These are copper coated epoxy-resins. The copper is selectively etched to produce conducting lines used to connect various devices. These devices are placed in holes cut into the resin. In order to get a good connection the holes need to be lined with a conductor. Copper has been used but the coating method, electroless copper plating, has several problems. It is an expensive multistage process, the copper plating is not very selective and the adhesion is generally poor. This process is being replaced by the polymerisation of a conducting plastic. If the board is etched with potassium

permanganate solution a thin layer of manganese dioxide is produced only on the surface of the resin. This will then initiate polymerisation of a suitable monomer to produce a layer of conducting polymer. This is much cheaper, easy and quick to do, is very selective and has good adhesion. [28]

Weight is at a premium for aircraft and spacecraft. The use of polymers with a density of about 1 g cm^{-3} rather than 10 g cm^{-3} for metals is attractive. Moreover, the power ratio of the internal combustion engine is about 676.6 watts per kilogramme. This compares to 33.8 watts per kilogramme for a battery-electric motor combination. A drop in magnitude of weight could give similar ratios to the internal combustion engine. Modern planes are often made with light weight composites. This makes them vulnerable to damage from lightning bolts. By coating aircraft with a conducting polymer the electricity can be directed away from the vulnerable internals of the aircraft.[29]

Depending on the conducting polymer chosen, the doped and undoped states can be either colourless or intensely coloured. However, the colour of the doped state is greatly redshifted from that of the undoped state. The colour of this state can be altered by using dopant ions that absorb in visible light. Because conducting polymers are intensely coloured, only a very thin layer is required for devices with a high contrast and large viewing angle. Unlike liquid crystal displays, the image formed by redox of a conducting polymer can have a high stability even in the absence of an applied field. The switching time achieved with such systems has been as low as 100 ms but a time of about 2 ms is more common. The cycle lifetime is generally about 10 cycles. Experiments are being done to try to increase cycle lifetime to above 10 cycles.

The chemical properties of conducting polymers make them very useful for use in sensors. This utilizes the ability of such materials to change their electrical properties during reaction with various redox agents (dopants) or via their instability to moisture and heat. An example of this is the development of gas sensors. It has been shown that polypyrrole behaves as a quasi 'p' type material. Its resistance increases in the presence of a reducing gas such as ammonia, and decreases in the

presence of an oxidizing gas such as nitrogen dioxide. The gases cause a change in the near surface charge carrier (here electron holes) density by reacting with surface adsorbed oxygen ions.[30] Another type of sensor developed is a biosensor. This utilizes the ability of triiodide to oxidize polyacetylene as a means to measure glucose concentration. Glucose is oxidized with oxygen with the help of glucose oxidase. This produces hydrogen peroxide which oxidizes iodide ions to form triiodide ions. Hence, conductivity is proportional to the peroxide concentration which is proportional to the glucose concentration.[31]

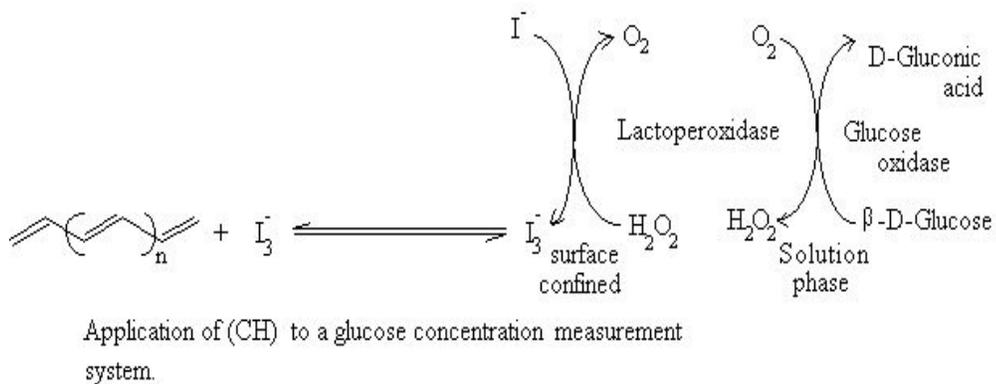


Figure 1.2 Application of (CH) to glucose concentration measurement system

Probably the most publicized and promising of the current applications are light weight rechargeable batteries. Some prototype cells are comparable to, or better than nickel-cadmium cells now on the market. The polymer battery, such as a polypyrrole- lithium cell operates by the oxidation and reduction of the polymer backbone. During charging the polymer oxidizes anions in the electrolyte enter the porous polymer to balance the charge created simultaneously, lithium ions in electrolyte are electrodeposited at the lithium surface. During discharging electrons are removed from the lithium, causing lithium ions to reenter the electrolyte and to pass through the load and into the oxidized polymer. The positive sites on the

polymer are reduced, releasing the charge-balancing anions back to the electrolyte. This process can be repeated about as often as a typical secondary battery cell.[32]

Conducting polymers can be used to directly convert electrical energy into mechanical energy. This utilizes large changes in size undergone during the doping and dedoping of many conducting polymers. This can be as large as 10%. Electrochemical actuators can function by using changes in a dimension of a conducting polymer, changes in the relative dimensions of a conducting polymer and a counter electrode and changes in total volume of a conducting polymer electrode, electrolyte and counter electrode. The method of doping and dedoping is very similar as that used in rechargeable batteries discussed above. What is required are the anodic strip and the cathodic strip changing size at different rates during charging and discharging. The applications of this include microtweezers, microvalves, micropositioners for microscopic optical elements, and actuators for micromechanical sorting (such as the sorting of biological cells).

One of the most futuristic applications for conducting polymers are 'smart' structures. These are items which alter themselves to make themselves better. An example is a golf club which adapt in real time to a persons tendency to slice or undercut their shots. A more realizable application is vibration control. Smart skis have recently been developed which do not vibrate during skiing. This is achieved by using the force of the vibration to apply a force oPsite to the vibration. Other applications of smart structures include active suspension systems on cars, trucks and train; traffic control in tunnels and on roads and bridges; damage assessment on boats; automatic damping of buildings and programmable floors for robotics and AGV's.

Much research will be needed before many of the above applications will become a reality. The stability and processibility both need to be substantially improved if they are to be used in the market place. The cost of such polymers must also be substantially lowered. However, one must consider that, although conventional polymers were synthesized and studied in laboratories around the world, they did not become widespread until years of research and development had been done. In a

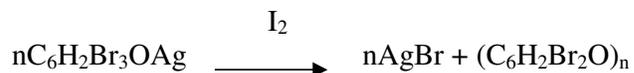
way, conducting polymers are at the same stage of development as their insulating brothers were some 50 years ago. Regardless of the practical application that are eventually developed for them, they will certainly challenge researchers in the years to come with new and unexpected phenomena. Only time will tell whether the impact of these novel plastics will be as large as their insulating relatives. [24]

1.3. POLY (PHENYLENE ETHER)

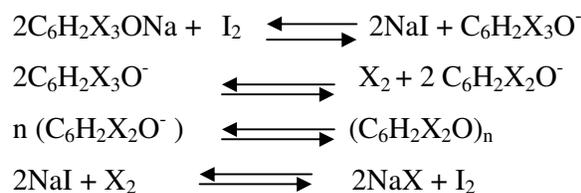
Poly (phenylene ether) alloys have developed into important engineering thermoplastics in the short period of time since the discovery of the oxidative coupling of phenols. The largest commercial usage of poly (phenylene ether) is in Noryl (General Electric Resins, which are the alloys of poly (2,6-dimethyl-1,4-phenylene ether) and polystyrene. The trademark of the General Electric Co. for poly (2,6-dimethyl-1,4-phenylene ether) is P. Since poly(2,6-dimethyl-1,4-phenylene ether) and polystyrene are thermodynamically compatible over the complete composition range, a family of Noryl resins can be produced that offers a combination of physical properties and processibility. [33]

History of Polyphenylene Oxide Synthesis

Hunter was the first to prepare a polyphenylene oxide by ethyl iodide induced decomposition of anhydrous silver 2, 4, 6-tribromo phenoxide in 1916. The polymer is isolated as a white, amorphous powder with a softening point above 300 °C. The molecular weight was estimated to be about 6,000-12,000. Hunter reported in a series of papers the polymerization of other trihalophenols and established that iodine was displaced more readily than bromine and the latter more rapidly than chlorine. The *p*-halogen reacted more readily than the *o*-chlorine group and only halogen with a free ionizable phenolic group could be displaced.[34]



Then, Hunter and his colleagues worked on the polymerization of mixed halophenols and they reported that iodine was displaced more readily than bromine and the latter more rapidly than chlorine and para halogen reacted more rapidly than ortho group.[35] The action of the iodine on polymerization was also investigated by Hunter et.al. They proposed the following equations to clear up the effect of iodine.



Where X: halogen

In 1932, Hunter and Dahlen reported that only the halogen in the hydroxyl bearing nucleus could be displaced in the catalytic decomposition of metallic salts of halogenated phenols. [36]

Price studied the polymerization of 4-bromo-2,6-dimethylphenol with several oxidizing agents such as ferricyanide in PbO_2 , I_2 , O_2 , and light in 1959. The soluble polymer had molecular weights in the range 2,000-10,000. Sterically hindered halogenated phenols (4-bromo-2,6-di-tert-butylphenol, bromodureneol, and pentabromophenol) failed to polymerize under the same conditions. A radical mechanism was suggested for this reaction, and was later confirmed.

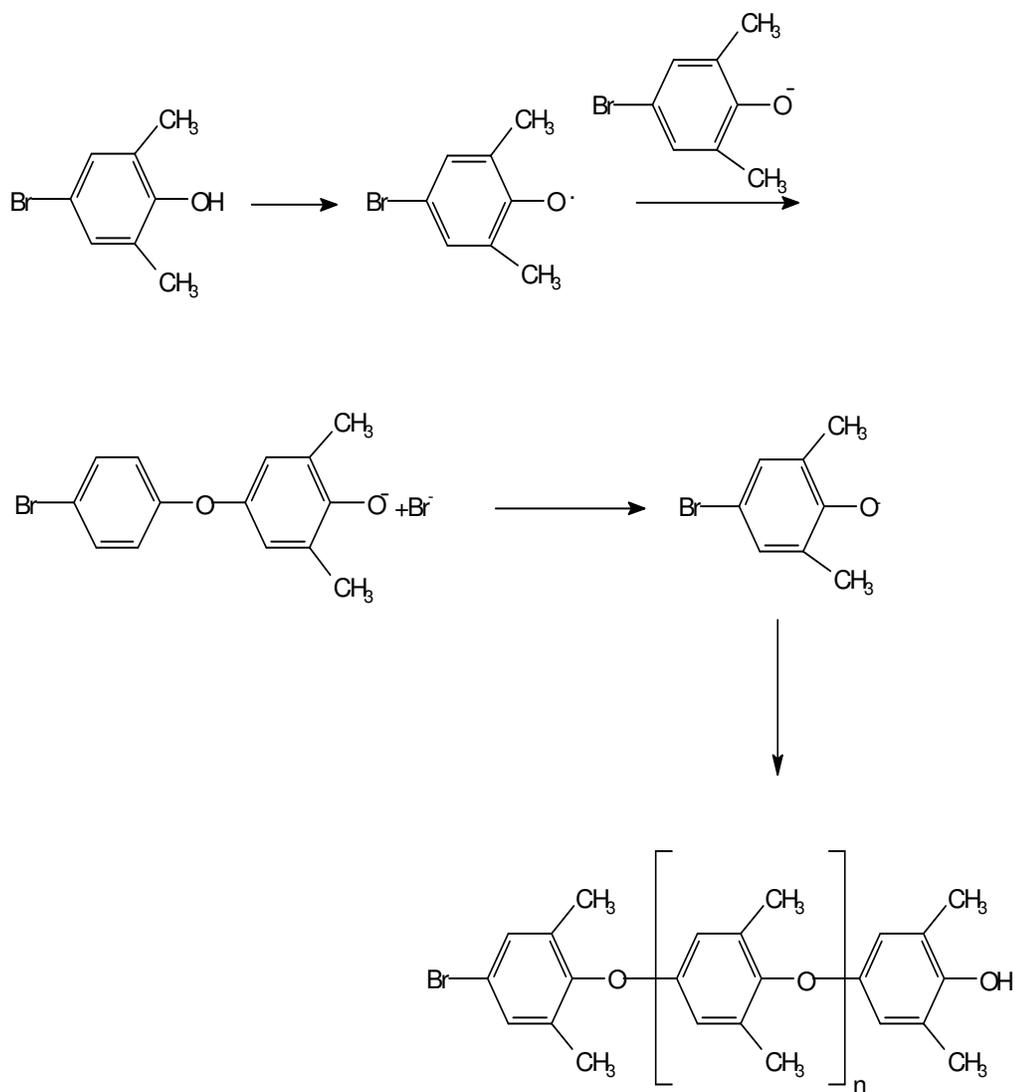


Figure 1.3. Mechanism for the polymerization of 4-bromo-2,6-dimethylphenol

Polyphenylene oxides were also reported to be prepared by the pyrolysis of diazoxides and by the pyrolysis of phenol mercuriacetates. Price suggested that a similar radical process can also be used to explain the reaction shown below.

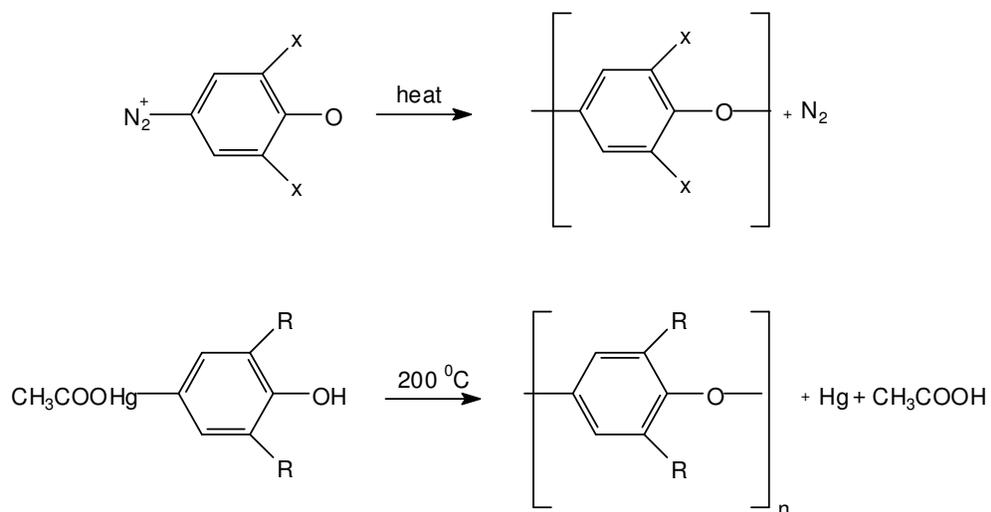


Figure 1.4. Preparation of Polyphenylene oxides by the pyrolysis of diazoxides and by the pyrolysis of phenol mercuriacetates.

Hay and coworkers were the first to report that oxidative coupling of 2, 6-disubstituted 1, 4-phenylene ethers (for R=CH₃) in 1959. When the substituents are bulky, such as R= tert-butyl, then only carbon-carbon coupling occurs to give diphenoquinones as the sole product.[37]

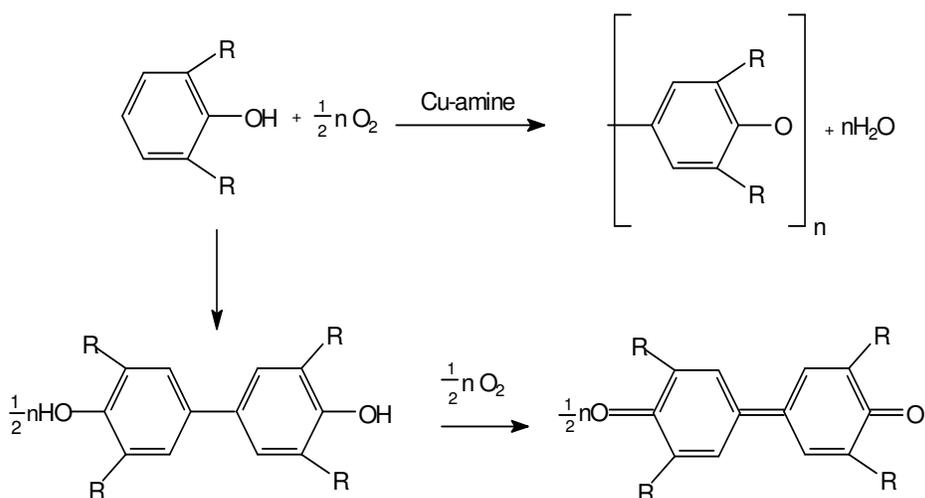


Figure 1.5. Oxidative coupling of 2, 6-disubstituted 1, 4-phenylene ethers

Hay reported that the oxidative polymerization of 2, 6-diphenyl phenol could be effected with either oxygen-amine copper salts, lead dioxide or silver oxide.

Blanchard et.al carried out the synthesis of poly(chlorophenylene ether)s from the decomposition of bis (2,4,6-trichlorophenolate)bis(pyridine)copper(II) complexes in 1962.[38]

Harrod studied the thermal decomposition of copper complexes containing a variety of amine ligands. The suggested general chemical reaction is shown below:

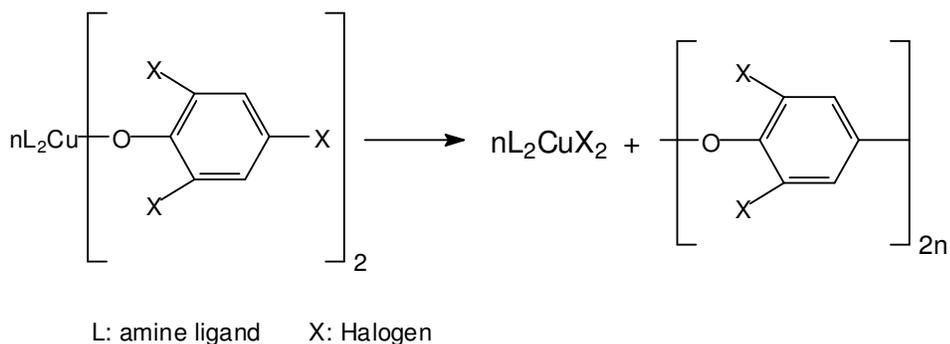


Figure 1.6. Thermal decomposition of copper complexes containing a variety of amine ligands.

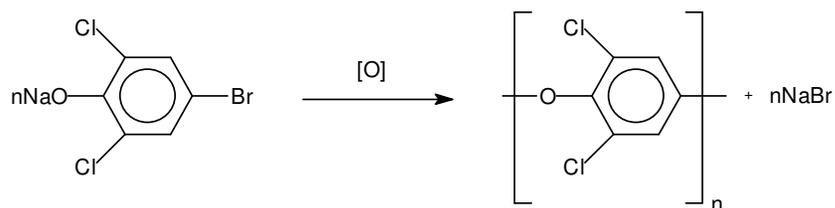
Harrod et.al. reported that the molecular weights (Mn) of poly(phenyleneoxide)s produced by thermal decomposition of bis (2,4,6-trichlorophenoxy) bis(pyridine) copper (II) complex were found to increase with increasing concentration of complex, decreasing concentration of free liquid trichlorophenol, changing solvent from cumene to toluene, to benzene and changing the amine ligand from N,N,N', N'- tetramethyl ethylenediamine to pyridine. Decomposition temperature had little effect on Mn.

Since 1980's Kısakürek et.al made progress in synthesis and characterization of poly(dihalophenylene oxide)s by decomposition of the isolated transition metal complex of different type of phenols with various amine ligands. Electroinitiation in solution, thermal decomposition in solid state or in solution were studied. It was found that besides the decomposition method, type of amine ligand and the type of halogen substituted on the phenol ring were found to be effective on the structure, molecular weight and the %conversion of the polymer. The lowest molecular weight polymers are obtained in electroinitiated polymerization and the highest with thermal decomposition in solution where the solid state polymerization is close to electroinitiation with slightly higher values. [36]

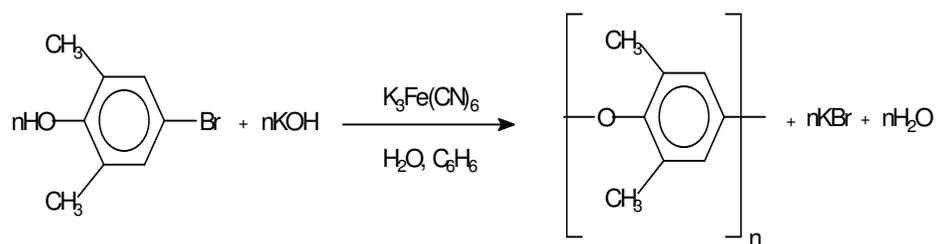
Pulat et.al carried out investigations on poly(dihalophenylene oxide)s formation by using different trihalophenols (THP) and changing polymerization methods at various temperatures. They have found that the polymerization yield was higher in the electro-initiation rather than the thermal decomposition method. As the temperature increased; the yield significantly increased and reached a maximum value, than decreased till zero near 250 °C.[39]

POLYPHENYLENE OXIDE POLYMERIZATION

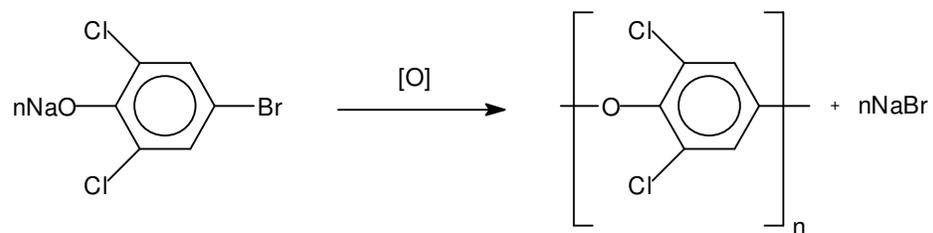
- Oxidative coupling of 2,6-disubstituted phenols.



- Free radical initiated displacement process.



- From metal complex of 2,4,6-trihalophenols.



MECHANISM FOR THE POLYMERIZATION REACTION

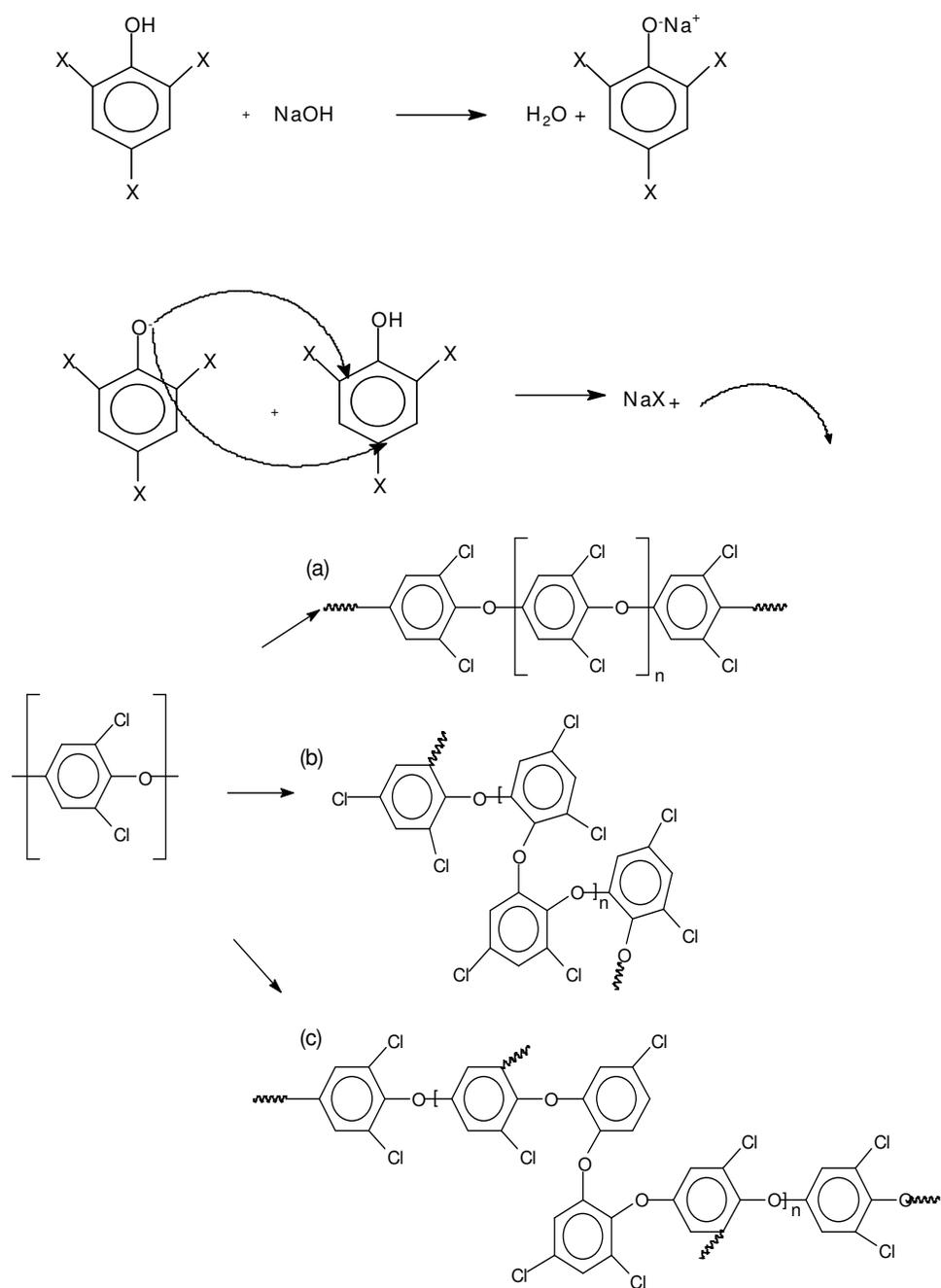


Figure 1.7. Possible Structures of poly(dichlorophenylene oxide)

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

1.4. THEORIES OF CROSSLINKING

The most severe mechanism for decreasing molecular freedom in chemical crosslinking – linking the polymer chains together through covalent or ionic bonds to form a network. Occasionally the term *curing* is used to denote crosslinking. There are a number of ways crosslinking can be brought about, but basically they fall into two categories: (1) crosslinking during polymerization by use of polyfunctional instead of difunctional monomers, and (2) crosslinking in a separate processing step after the linear (or branched) polymer is formed.

When polymer chemists use the term crosslinking, they usually mean covalent chemical crosslinking. Covalent crosslinking has certain disadvantages, however. Once crosslinked, a polymer cannot be dissolved or molded. [40]

The mechanism of cross-linking by radiation is either free radical or ionic. Cross-linking by interaction with high energy (ionizing) radiation sources occurs through both mechanisms.[41]

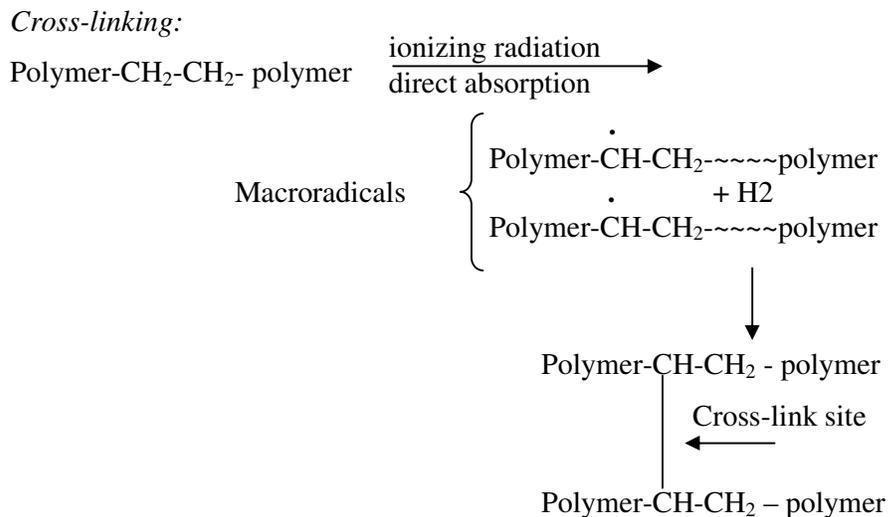


Figure 1.8. Mechanism of Crosslinking

Crosslinking reactions are those that lead to the formation of insoluble and infusible polymers in which chains are joined together to form a three-dimensional network structure. A simple crosslinking reaction is exemplified by polymer chains with several functional groups designated A that are capable of reacting among themselves to form chemical bonds A-A. If these polymer chains are exposed to conditions such that the functional groups do react, then all the chains in the reaction vessel will be tied to each other through A-A bonds.

In principle, the polymer molecules in the reaction vessel will have formed one giant molecule.

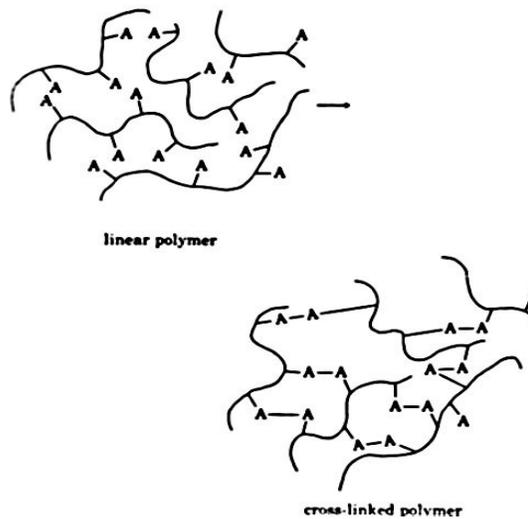


Figure 1.9. Cross-linked Structure

An example of cross-linking is the vulcanization process, which makes rubber useful in applications where mechanical strength is important. Other cross-linked polymers are widely used in paints, printing inks, adhesives, sealants, encapsulates and electrical and electronic components.

In the example above, the macromolecules were self reacting, but this is not necessary for network formation. Crosslinking can be carried about through the use

of a cross-linking agent, a molecule that has two or more groups, capable of reacting with the functional groups on the polymer chain. Cross-linked polymers can also be prepared by the polymerization of monomers with an average functionality greater than two. [42]

1.5. AIM OF THE STUDY

- To synthesize poly(dichlorophenylene oxide), conducting polymer, radical ion polymer and crosslinked polymer at various energy levels, in various time intervals and in various amounts of water
- To study the effect of time, water and microwave energy level on polymerization

CHAPTER 2

EXPERIMENTAL

2.1 CHEMICALS

2.1.1 2,4,6- Trichloro Phenol (TCP)

Analytical grade 2,4,6-Trichlorophenol was provided from Merck and was used without further purification.

2.1.2 Sodium Hydroxide (NaOH)

NaOH produced by Merck, was used in the polymerization.

2.1.3 Toluene

Toluene was provided from Merck and was used as a solvent for the polymer.

2.1.4 Ethyl Alcohol

Ethyl alcohol was commercially available technical grade and fractionally distilled under atmospheric pressure at 76 °C. It was non solvent for the polymers and used as precipitating reagent.

2.1.5 Hydrochloric Acid

It was provided from Merck and used in the precipitation of the synthesized polymers to dissolve the by product salts formed during polymerization.

2.1.6 Deuterated Chloroform (CDCl₃)

CDCl₃ was provided from Merck and was used as a solvent to obtain NMR spectra of the polymers.

2.1.7 Potassium Bromide (KBr)

Spectroscopic grade KBr was provided from Merck and was used to take FTIR spectra of complexes and polymers which were dispersed in KBr discs.

2.2. Apparatus and Instruments

2.2.1 Microwave Oven

Domestic Microwave oven works at 2450 MHz and has a period of 10 seconds. It has several time intervals (1-60 min) and microwave energies (90-900 watt) and it was used for polymerization.

2.2.2 Differential Scanning Calorimeter (DSC)

DSC thermogram was recorded on Shimadzu Differential Scanning Calorimeter in order to obtain thermal behaviour of the polymer and conducting polymer in the first run of the the DSC analysis both of the samples were heated to 150 °C from room temperature with a heating rate of 20 °C/ min than cooled to 50 °C with a cooling rate of 10 °C/ min to reduce the effect of contamination. At the second run, polymers were heated to 300 °C by the rate of 10 °C/ min. Treatment of the samples was performed under nitrogen atmosphere.

2.2.3 Thermal Gravimetric Analysis

Weight losses of the polymer and the conducting black powder due to the increasing temperature were determined by Perkin Elmer Pyris 1 TGA & Spectrum 1 FT-IR Spectrometer. Both of the samples are heated from 30 °C to 750 °C with a heating rate of 10 °C/min under nitrogen atmosphere.

2.2.4 Fourier-Transform Infrared Spectrophotometer (FTIR)

IR Spectrum of the Polydichlorophenylene oxide as KBr pellet was recorded on Shimadzu Fourier Transform Infrared Spectrometer IR Prestige-21/FTIR-8400S.

2.2.5 NMR Spectrophotometer

¹H-NMR and ¹³C-NMR spectrum was recorded on Mercury-300 NMR spectrometer.

2.2.6 Elemental Analysis (CHO) Analyzer

Carbon-Hydrogen analysis of samples were carried out with Leco 932 CHNSO elemental analyzer.

2.2.7 Conductivity Measurement

Conductivity was measured by four probe technique.

2.2.8 Mw Distribution Measurement

Molecular weight distribution was measured by PL-GPC 220 Polymer Laboratories.

2.2.9 Light Scattering

Molecular weight, radius of gyration and virial coefficient of **polymers** were determined by using multiangle laser scattering spectrometer. The ALV/CG-3

Goniometer system is designed to perform dynamic and static light scattering simultaneously.

2.2.10 ESR Analysis

ESR spectrum of the products was recorded by Bruker Xepr ELEXSY-580 spectrometer in quartz cell at room temperature.

2.2.11 Scanning electron microscope (SEM) analysis

Analysis of the surface morphologies of films were done by using JEOL JSM-6400 scanning electron microscope.

2.3 Procedure

Sodium hydroxide, trichlorophenol and water were used as starting material for the polymerization.

2.3.1 Synthesis of Poly(dichlorophenylene oxide), Conducting Polymer, Ion Radical Polymer, Crosslinked Polymer

2,4,6 trichlorophenol and sodium hydroxide were mixed by grinding and wetted by various amounts (0.5 ml- 50 ml) of distilled water. This mixture is put into a glass vessel and irradiated in a microwave oven for several time intervals (1-20 min) and microwave energies (90-900 watt).

At the end of the reaction at each time intervals, the mixture is poured into a 100 ml of toluene and stirred to dissolve. Insoluble part is a conducting polymer at some time intervals and at some microwave energy levels. The color of the conducting polymer is black and removed by filtration. Soluble part is poured into 400-500 ml ethanol containing small amount of water. A white precipitate is obtained and that is polyphenylene oxide.

At some time intervals and at some microwave energy levels, insoluble part in toluene is a white in color and called as crosslinked polymer. Beside this, at some time intervals and some microwave energies, a yellowish brown precipitate occurs that is called ion radical polymer.

2.3.2 Characterisation of the Poly(dichlorophenylene oxide)

Poly(dichlorophenylene oxide) was characterized by FTIR,¹HNMR,¹³CNMR, Elemental analysis, DSC, TGA, ESR.

2.3.3 Characterisation of the Conducting Polymer

Conducting Polymer was characterized by FTIR, Elemental analysis, DSC, TGA,ESR. Conductivity of the conducting polymer was measured.

2.3.4 Characterisation of the Radical Ion Polymer

Radical Ion Polymer was characterized by FTIR, ¹H NMR,¹³C NMR, DSC, TGA, ESR.

2.3.5 Characterisation of the Crosslinked Polymer

Crosslinked Polymer was characterized by FTIR, ¹H NMR,¹³C NMR, DSC, TGA,ESR.

CHAPTER 3

RESULTS AND DISCUSSION

The aim of this study was to polymerize 2,4,6-trichlorophenol by microwave initiation and to synthesize poly(dichlorophenylene oxide), conducting polymer, radical ion polymer and crosslinked polymer. In this section, these products are characterised and the optimum conditions for the synthesis of each product will be discussed. Effects of time, amount of water and microwave energy level on polymerization will also be discussed.

3.1 Synthesis of Polydichlorophenylene oxide (P), Conducting polymer (CP), Radical ion polymer (RIP) and Crosslinked polymer (CP)

Polymerizations were performed in different time intervals by keeping the microwave energy and water content constant; or with different energy levels by keeping the time interval and water content constant; or by varying the amount of water by keeping the time and energy level constant.

Percentage yield values of each product were calculated by using the following equation:

$$\text{Yield (\%)} = \frac{\text{Weight of Product}}{\text{Initial weight of monomer (TCP)}} \times 100$$

Percent Weight Loss was calculated by a similar equation:

$$\text{Weight Loss (\%)} = \frac{W_{\text{TCP+NaOH}} - \text{Weight of Product}}{\text{Initial Weight of monomer(TCP)} + \text{Weight of NaOH}} \times 100$$

The effect of polymerization time (2-9 min) and energy (90-600 Watt) on the yield for the P, CP, and WL in 0.5 cm³ were investigated. (Table 3.1.a)

Table 3.1.a Conversion & Weight Loss Table

	90 watt (2 min)	90 watt (3 min)	90 watt (4 min)	90 watt (5 min)	90 watt (6 min)	90 watt (7 min)	90 watt (9 min)
% WL	13.4	15.2	-	39.5	62.5	59.5	90.9
%P	2.0	0.7	-	1.6	4.8	3.2	5.3
%CP	84.6	84.1	-	58.9	32.7	37.3	13.8
	180 watt (2 min)	180 watt (3 min)	180 watt (4 min)	180 watt (5 min)	180 watt (6 min)	180 watt (7 min)	180 watt (8 min)
% WL	43.4	35.8	34.8	41.6	67.9	58.4	-
%P	2.5	12.3	11.1	9.9	3.4	1.9	-
%CP	54.1	51.9	54.1	48.5	28.7	39.7	-
	360 watt (2 min)	360 watt (3 min)	360 watt (4 min)	360 watt (5 min)	360 watt (6 min)	360 watt (7 min)	360 watt (10 min)
% WL	63.2	40.7	-	-	71.1	72.2	82
%P	1.8	4.8	-	-	4.0	1.3	0.9
%CP	35.0	54.5	-	-	24.9	26.5	17.1
	600 watt (1 min)	600 watt (1,5 min)	600 watt (2 min)	600 watt (3 min)	600 watt (4 min)	600 watt (5 min)	600 watt (6 min)
% WL	82.1	-	-	-	-	-	-
%P	0.5	-	-	-	-	-	-
%CP	17.4	-	-	-	-	-	-

According to *Conversion & Weight Loss Table (Table 3.1.a)*, following graphs can be drawn to show the trend with time and microwave energy.

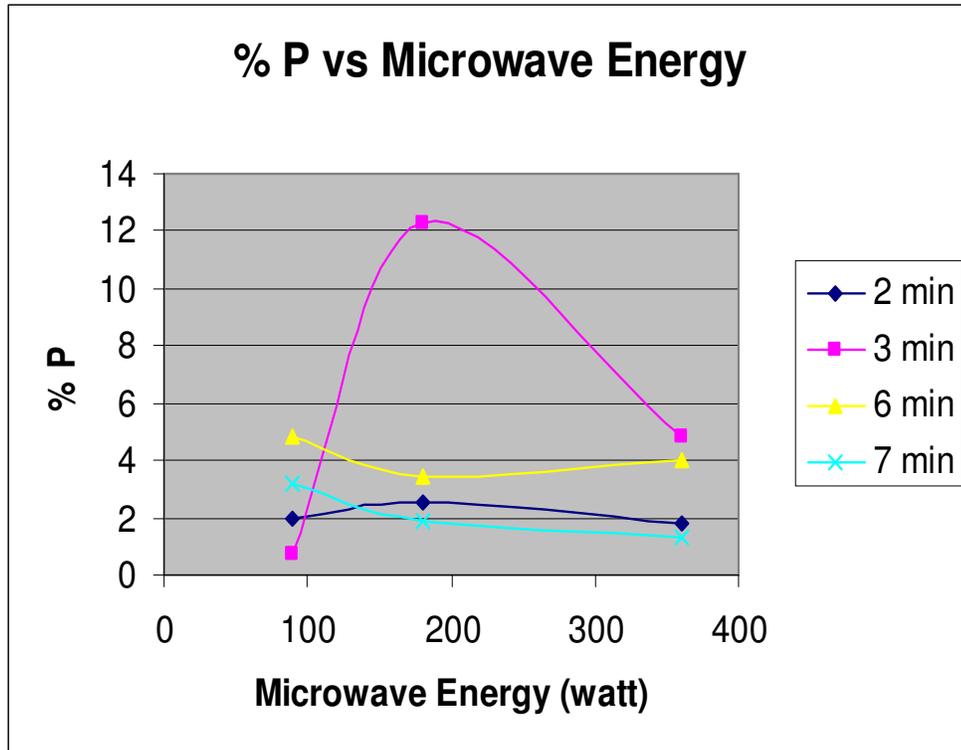


Figure 3.1 %P vs MWE Graph

In figure 3.1, at the end of 2 min, as the microwave energy is increased, % conversion to P is also increased slightly from 0.2% at 90 watt to a value of 2.5% at 180 watt, followed by a slight decrease to 1.8% at 360 watt. As the microwave energy increased, % conversion to P is also increased from 0.7% at 90 watt to a maximum value of 12.3% at 180 watt, followed by a decrease to 4.8% at 360 watt (3 min). Microwave energy decreased from 4.8% at 90 watt to a value of 3.4% at 180 watt and slightly increased to 4.0% at 360 watt (6 min). As the microwave energy increased, % conversion to P is decreased slightly from 3.2% at 90 watt to a value of

1.3% at 360 watt (7 min). Generally slight change in %P observed except at 3 min with 180 watt energy which is the optimum condition for conversion to P.

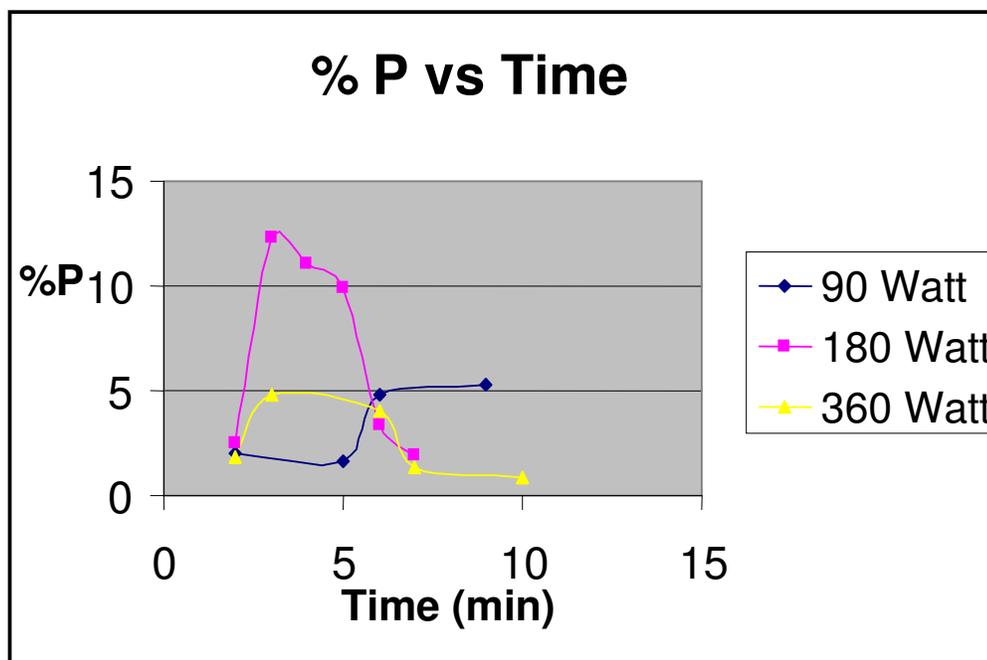


Figure 3.2 %P vs Time Graph

In figure 3.2, at 90 Watt, as the time increased, % conversion to P is also increased from 2% at the end of 2 min to a value of 5.3% at the end of 9 min. At 180 watt, as the time increased, % conversion to P is also increased from 2.5% (2 min) to a maximum value of 12.3% (3 min), followed by a decrease to 1.9% (7 min). At 360 watt, as the time increased, % conversion to P is increased from 1.8% (2 min) to a value of 4.8% (3 min) and slightly decreased to 0.9% (10 min). Maximum percent conversion to P is achieved at the end of 3 min having a value of 12.3% at 180 watt.

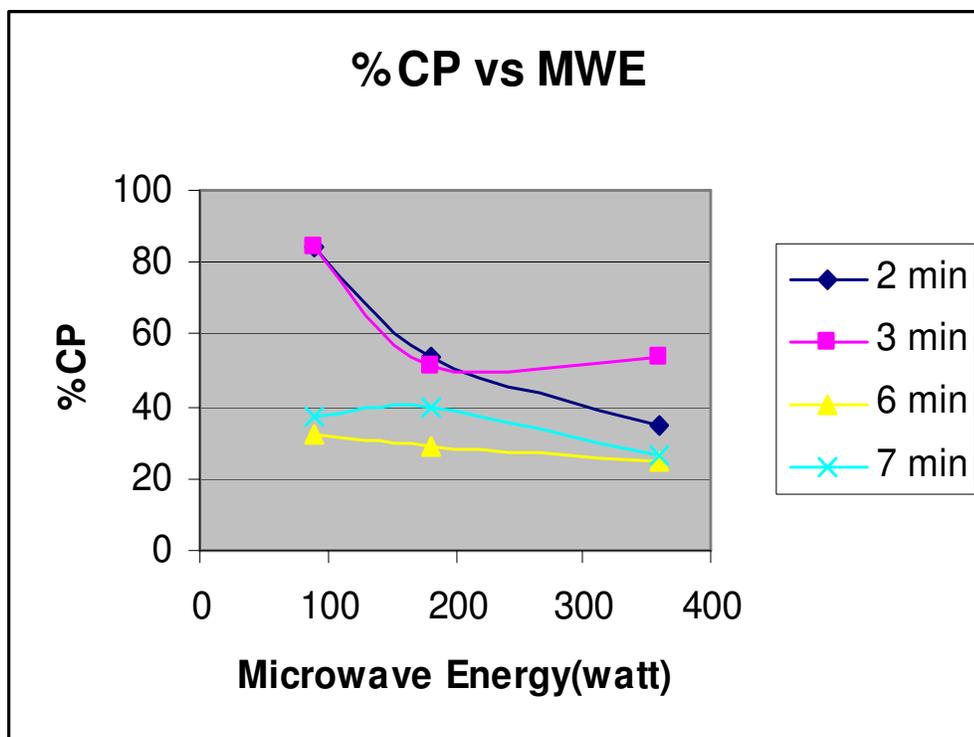


Figure 3.3. %CP vs MWE Graph

In figure 3.3, at the end of 2 min, as the microwave energy increased, the maximum 84.6% yield value of CP at 90 watt, is decreased to 35.0% at 360 watt. As the microwave energy increased, the yield value of CP is 84.1% at 90 watt is decreased to value of 51.9% at 180 watt, followed by a slight increase to 54.5% at 360 watt (3 min). As the microwave energy increased, % conversion to CP is decreased slightly from the value 32.7% at 90 watt to 24.9 % at 360 watt (6 min). As the microwave energy is increased, % conversion to CP is increased slightly from 37.302% at 90 watt to a value of 39.639% at 180 watt and decreased to a value of 26.5% at 360 watt (7 min).

Generally %CP tends to decrease with increasing microwave energy at various time intervals. Maximum percent conversion to conducting polymer is achieved at 90 Watt and at the end of 2 min.

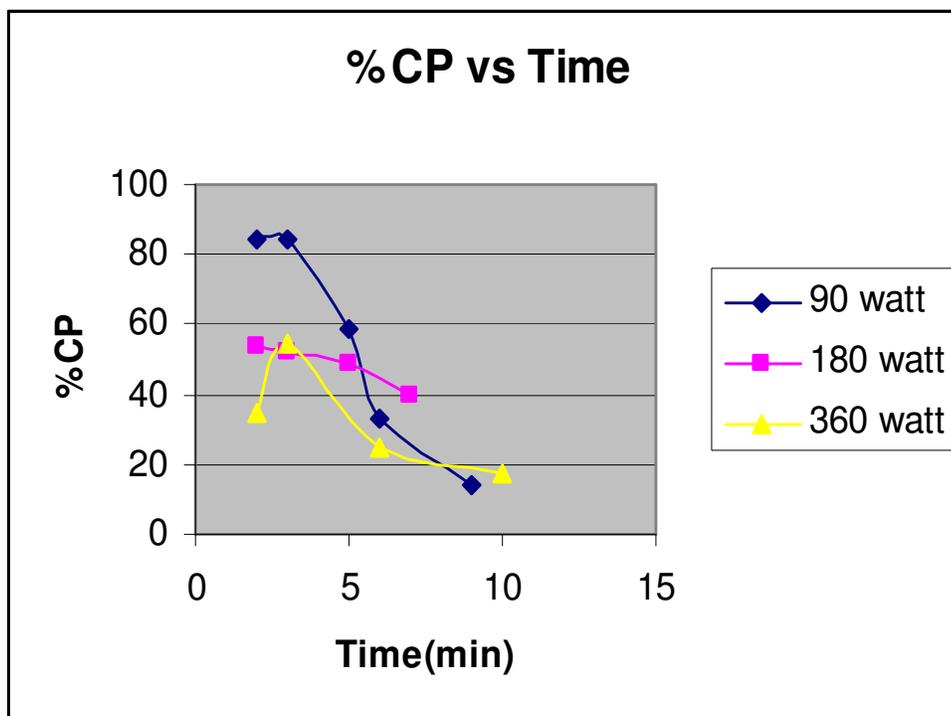


Figure 3.4. %CP vs Time Graph

In figure 3.4, at 90 Watt, as the time increased, the maximum 84.6% yield value of CP at the end of 2 min, is decreased to a value of 13.8% at the end of 9 min. At 180 watt, it is observed that, as the time increased, % conversion to CP is decreased from the value of 54.067% (2 min) to a value of 39.369% (7 min). At 360 watt, as the time increased, % conversion to CP is decreased from the value of 35.005% (2 min) to a value of 17.1% (9 min).

Generally %CP tends to decrease with increasing time. Optimum condition for the conversion to the conducting polymer is obtained at 90 Watt at the end of 2 min.

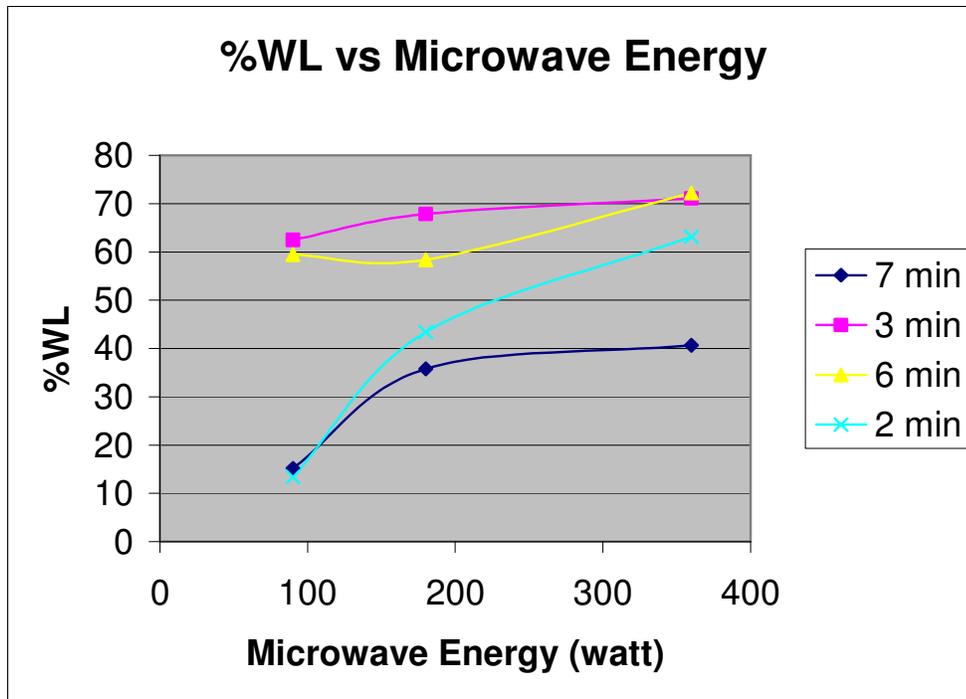


Figure 3.5. Weight Loss vs MWE Graph

In figure 3.5, at the end of 2 min, as the microwave energy increased from 90 watt to 360 watt, %weight loss is increased from 13.9% to 61.1%. As the microwave energy increased from 90 watt to 360 watt, %weight loss is also increased from 14.2% to 40.0% (3 min). As the microwave energy increased from 90 watt to 360 watt, %weight loss is also increased from 58.1% to 71.1% (6 min). %weight loss is decreased slightly from 59.5% at 90 watt to 56.4% at 180 watt, followed by slight increase to 72.1% at 360 watt (7 min).

Generally as the microwave energy increases, weight loss tends to increase in various time intervals.

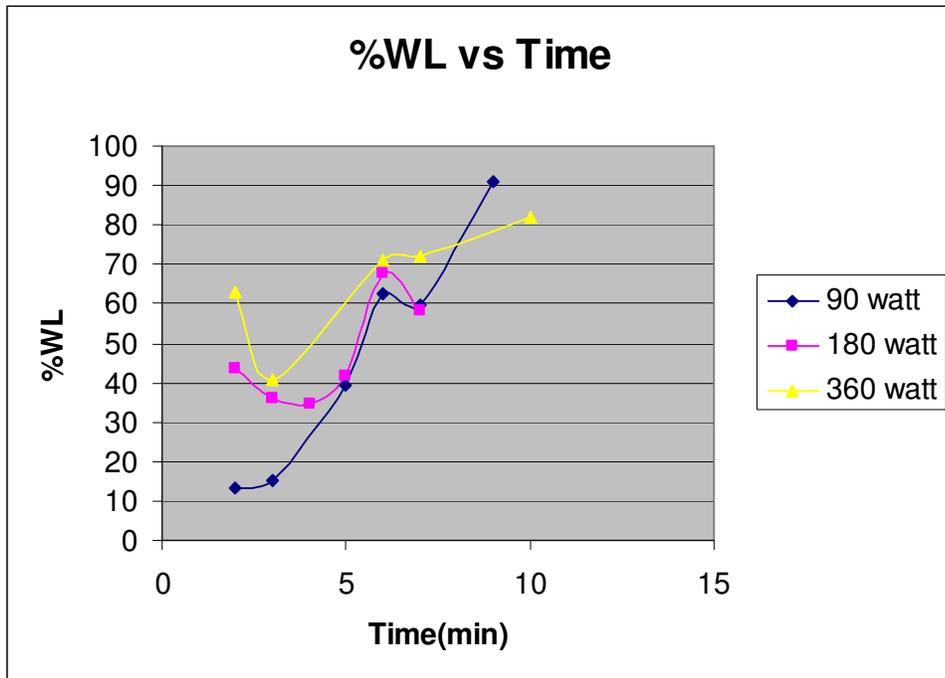


Figure 3.6. Weight Loss vs Time Graph

In figure 3.6, at 90 Watt, as the time increased, weight loss is increased from 13.9% at the end of 2 min to 79.9% at the end of 9 min. At 180 watt, as the time increased, weight loss is decreased slightly from 41.9% (2 min) to 33.8% (4 min) followed by an increase to 56.4 % (7 min). At 360 watt, as the time increased, weight loss decreased from 61.1% (2 min) to 40.0% (3 min) followed by sharp increase to 71.1% (6 min).

As time increases, %Weight Loss generally tends to increase.

By changing the amount of water between 1 cm³ and 20 cm³, simultaneous synthesis of radical ion polymer and crosslinked polymer beside polydichlorophenylene oxide and conducting polymer could be achieved.

Table 3.1.b MWE & Amount of water & Product

MWE & Amount of water	Time	Colour	Product
90watt 0.5 cm ³ water	2 min	Black + White	CP+P
90watt 0.5 cm ³ water	3 min	Black + White	CP+P
90watt 0.5 cm ³ water	5 min	Black + White	CP+P
90watt 0.5 cm ³ water	7 min	Black + White	CP+P
90watt 0.5 cm ³ water	9 min	Black + White	CP+P
90watt 1 cm ³ water	4 min	White + Black	CLP+CP
90watt 1 cm ³ water	7 min	White + Black	CLP+CP
90watt 1 cm ³ water	8 min	White + Black	CLP+CP
90watt 1 cm ³ water	11 min	Black + White+ Yellow	CP+ CLP+RIP
90watt 5 cm ³ water	4 min	Yellow + White	RIP+ CLP
90watt 5 cm ³ water	5 min	Yellow + White	RIP+CLP
90watt 6 cm ³ water	17 min	Yellow + White	RIP+CLP
90watt 7 cm ³ water	20 min	White	CLP
90watt 10 cm ³ water	32 min	White	CLP

Table 3.1.b MWE & Amount of water & Product (continued)

MWE & Amount of water	Time	Colour	Product
180watt 0.5cm ³ water	2 min	Black + White	CP+P
180watt 0.5 cm ³ water	3 min	Black + White	CP+P
180watt 0.5cm ³ water	4 min	Black + White	CP+P
180watt 0.5 cm ³ water	5 min	Black + White	CP+P
180watt 0.5 cm ³ water	6 min	Black + White	CP+P
180watt 0.5 cm ³ water	7 min	Black + White	CP+P
180watt 1 cm ³ water	1 min	White + Black	CLP+CP
180watt 1 cm ³ water	2 min	White + Black	CLP+CP
180watt 1 cm ³ water	3 min	Black + White	CP+P
180watt 1 cm ³ water	5 min	Black + White	CP+P
180watt 5 cm ³ water	5 min	Black + White	CP+P
180watt 5 cm ³ water	7 min	Yellow + Black	RIP+CP
180watt 5 cm ³ water	8 min	Yellow + Black	RIP+CP
180watt 6 cm ³ water	6 min	Yellow +White+ Black	RIP+CLP+CP
180watt 7 cm ³ water	6 min	Yellow +White	RIP+CLP
180watt 7 cm ³ water	7 min	Yellow +White+ Black	RIP+CLP+P+CP
180watt 8 cm ³ water	6 min	Yellow +White	CP+CLP
180watt 10 cm ³ water	18 min	White	CLP
360watt 0.5 cm ³ water	2 min	Black + White	CP+P

Table 3.1.b MWE & Amount of water & Product (continued)

MWE & Amount of water	Time	Colour	Product
360watt 0.5 cm ³ water	3 min	Black + White	CP+P
360watt 0.5 cm ³ water	6 min	Black + White	CP+P
360watt 0.5 cm ³ water	7 min	Black + White	CP+P
360watt 0.5 cm ³ water	10 min	Black + White	CP+P
360watt 1 cm ³ water	1 min	White + Black	CLP+CP
360watt 1 cm ³ water	2.5 min	Black + White	CP+P
360watt 10 cm ³ water	1 min	White +Yellow	CLP+RIP
360watt 10 cm ³ water	2 min	White	CLP
360watt 10cm ³ water	3 min	White+Black	CLP+P+CP
360watt 10 cm ³ water	5 min	Black+White	CP+P
600watt 0.5cm ³ water	1 min	Black+White	CP+P
600watt 1 cm ³ water	0.5 min	Black+White	CP+CLP
600watt 1 cm ³ water	1 min	Black+White	CP+P
600watt 1 cm ³ water	1.5 min	Black+White	CP+P
600watt 5 cm ³ water	1 min	White	CLP
600watt 5 cm ³ water	1.5 min	Black+White	CP+CLP
600watt 5 cm ³ water	2 min	Black+White	CP+CLP
600watt 5 cm ³ water	2.5 min	Black+White	CP+CLP
600watt 5 cm ³ water	3 min	Black+White+Yellow	CP+CLP+RIP

Table 3.1.b MWE & Amount of water & Product (continued)

MWE & Amount of water	Time	Colour	Product
600watt 10cm ³ water	1.5 min	White	CLP
600watt 10cm ³ water	2 min	Black+White	CP+CLP
600watt 10cm ³ water	2.5 min	Black+White	CP+CLP
600watt 10cm ³ water	3 min	Black+White	CP+CLP
600watt 15cm ³ water	2.5 min	White	CLP
600watt 20 cm ³ water	2.5 min	White	CLP

The results of the study indicated that:

1. Poly(dichlorophenylene oxide) can be synthesized either with lower amount of water and in shorter time intervals or with higher amount of water and in longer time intervals at microwave energy levels of 90-600 watt.
2. Conducting polymers can be synthesized either with lower amount of water or in longer time intervals with higher amount of water, at microwave energy levels of 90-600 watt.
3. Crosslinked polymers can be synthesized in longer time intervals (4min-32 min) with 1-10 cm³ of water at 90 watt and 180 watt whereas, it can be synthesized in shorter time intervals (1min-3min) with 1-10 cm³ of water at 360 and 600 watt. By increasing the microwave energy, pure CLP can be achieved in shorter time intervals (1.5 min).
4. Radical ion polymer can be synthesized with higher amount of water (1-10 cm³) at microwave energy levels of 90-600 watt instead of poly(dichlorophenylene oxide). By increasing the microwave energy, RIP can be achieved in shorter time intervals (1-3 min).

3.2 CHARACTERIZATION

3.2.1 CHARACTERIZATION OF POLYDICHLOROPHENYLENE OXIDE

FTIR Spectrum Poly(dichlorophenylene oxide) (P) formation was followed by the peaks around $950\text{-}1030\text{ cm}^{-1}$ that represents the etheric bond formation during polymerization. FTIR spectrum of polymer exhibits the characteristic absorptions at 850 cm^{-1} (out of plane C-H bending), $955\text{-}1040\text{ cm}^{-1}$ (C-O-C stretching), $1140\text{-}1210\text{ cm}^{-1}$ (C-O stretching), $1440\text{-}1580\text{ cm}^{-1}$ (C=C stretching), 3079 cm^{-1} C-H stretching of the benzene ring. The peak around 3500 cm^{-1} shows phenolic end group. The spectrum was presented as *Figure 3.7*.

$^1\text{H-NMR}$ Spectrum The peak at 6.8 ppm is due to the protons of 2,6 dichloro 1,4 phenylene oxide units (1,4 catenation) and the peak at lower field at 7.3 ppm is due to the protons of 2,4 dichloro 1,6 phenylene oxide units (1,2 catenation). As can be from the spectrum 1,2 has higher intensity. The broad peak at higher fields (6.5-5.8 ppm) indicates branching. The spectrum was presented as *Figure 3.8*.

$^{13}\text{C-NMR}$ Spectrum The binary relations between the observed and the calculated data for the poly(dichloro phenylene oxide) are shown in figure 3.9. According to the observed and calculated ^{13}C NMR spectra of poly(dichlorophenylene oxide), it is possible to say poly(dichloro phenylene oxide) mainly has 1-2 structure which is confirmed by ^1H NMR. The spectrum is presented as figure 3.10 and the data are given in figure 3.9.

TGA-FTIR Thermogram TGA thermogram of the poly(dichloro phenylene oxide), is presented as figure 3.11. Figure 3.12 shows FTIR spectra of evolved volatile components at each mass loss. The generation of CO_2 and H_2O were observed over the whole range. In the beginning stage of degradation, the characteristic peaks at 3500 cm^{-1} of an phenolic end group (trap phenol) and the peaks at 3600 cm^{-1} of water (trap water) were observed. The peak at 3050 cm^{-1} , is due to the aromatic C-H stretching. The peaks due to C=C ring stretching, $1440\text{-}1580\text{ cm}^{-1}$, as well as C-O stretching of phenoxy group, $1140\text{-}1210\text{ cm}^{-1}$, are observed. The peaks at $955\text{-}1040$

cm⁻¹ correspond to C-O-C stretching and the peak at 730-760 cm⁻¹ is due to the C-Cl stretching. According to the FTIR spectra of the volatile gas at different times and the TGA thermogram, there isn't a drastic change in weight loss. Weight loss increases steadily until 700 °C and 100% of sample was lost at 700 °C.

DSC Thermogram The DSC thermogram of poly(dichloro phenylene oxide) has a glass transition temperature (T_g) at 121.30, indicating high rigidity. (Figure 3.13)

Elemental analysis Elemental analysis results for C and H atoms of the poly(dichlorophenylene)oxide, conducting polymer and radical ion polymer are correlated with the calculated values in table Table3.2.1.a.

Table3.2.1.a Elemental Analysis of P, CP, RIP

	% Calc.	C Found	% Calc.	H Found
P	44.72	45.84	1.24	1.11
CP	76.1	76.7	1.34	1.41
RIP	45.12	45.47	1.31	1.59

Light Scattering Molecular weight, radius of gyration, and virial coefficient of P and RIP were determined at 37 °C by using multiangle laser scattering spectrometer. The weight average molecular weight (M_w) of the P was determined as 8.052 × 10⁵ by the light scattering. The radius of gyration and the second virial coefficient for P determined as 1.310 × 10¹ nm and 1.061 × 10⁻⁷ mol dm³/g².

ESR The ESR spectrum of poly(dichlorophenylene oxide) revealed a singlet with the g value of 2.001 which is very close to the g value of free electron. (Figure 3.14)

Scanning electron microscope (SEM) analysis Analysis of the surface morphologies of P indicated fine granular surface structure. (Figure 3.15)

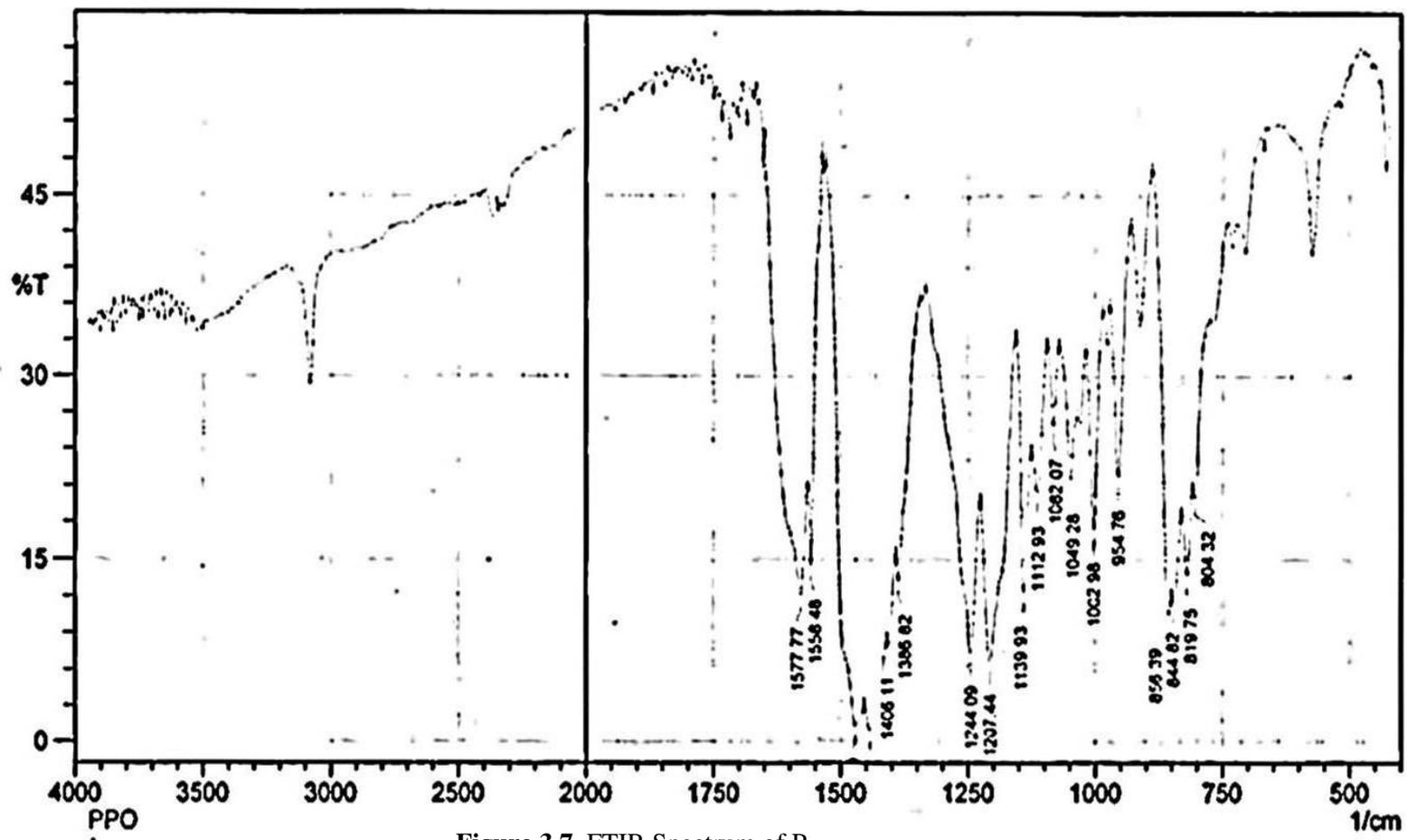


Figure 3.7. FTIR Spectrum of P.

```

STANDARD 1H OBSERVE
exp10 s2pu1
SAMPLE
date Mar 15 2005 temp SPECIAL not used
solvent CDCl3 gain not used
file ACQUISITION exp spin not used
sw 4798.5 pvsd 15.400
at 1.938 aifa 20.000
np 19374 FLAGS n
fb 2400 in n
bs 16 in n
dl 1.000 ds y
nl 64 hs y
ct 64 hs PROCESSING nn
tn H1 fn not used
tfrs 299.928 sp DISPLAY -184.3
tofs 255.9 wd 3663.6
tpwr 56 rf1 633.2
pw DECOUPLER fp 89.9
dn C13 fp -45.7
dof 0 PLOT 250
dms C SC 605
dprf 0 vs
dmf 200 tn cdc ph 2

```

INDEX	FREQUENCY	PPM	HEI
1	2196.270	7.323	
2	2160.246	7.203	1
3	2133.887	7.115	
4	2081.170	6.939	
5	2047.489	6.827	
6	2012.637	6.710	
7	1936.490	6.457	
8	1923.310	6.419	
9	1881.722	6.274	
10	1796.495	5.990	
11	1767.709	5.961	
12	1752.271	5.842	
13	1726.498	5.756	
14	684.156	2.281	
15	454.835	1.517	
16	353.207	1.178	
17	230.200	0.768	
18	0.000	0.000	

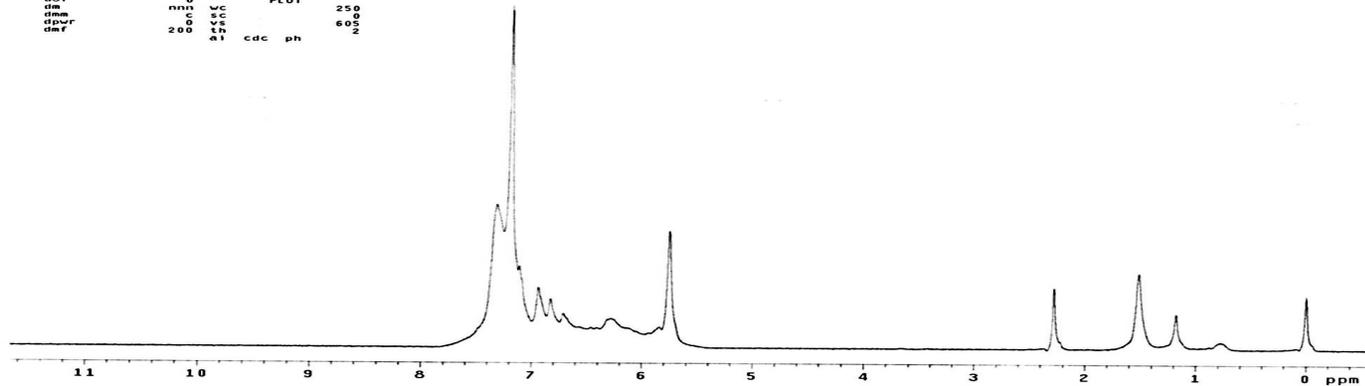


Figure 3.8. ¹H-NMR Spectrum of P

^{13}C -NMR Shift Data of the Polymer

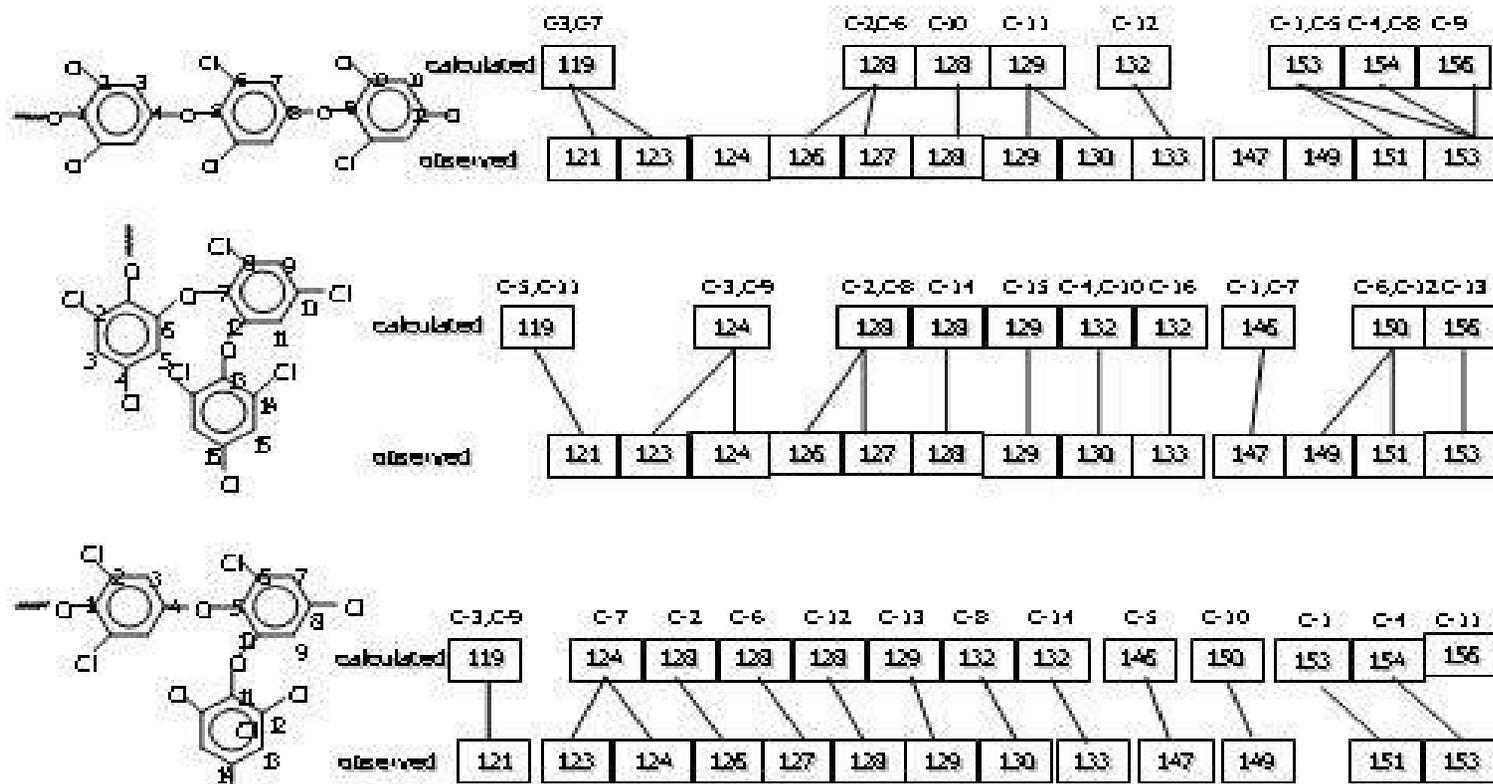


Figure 3.9. ^{13}C -NMR Shift Data of P

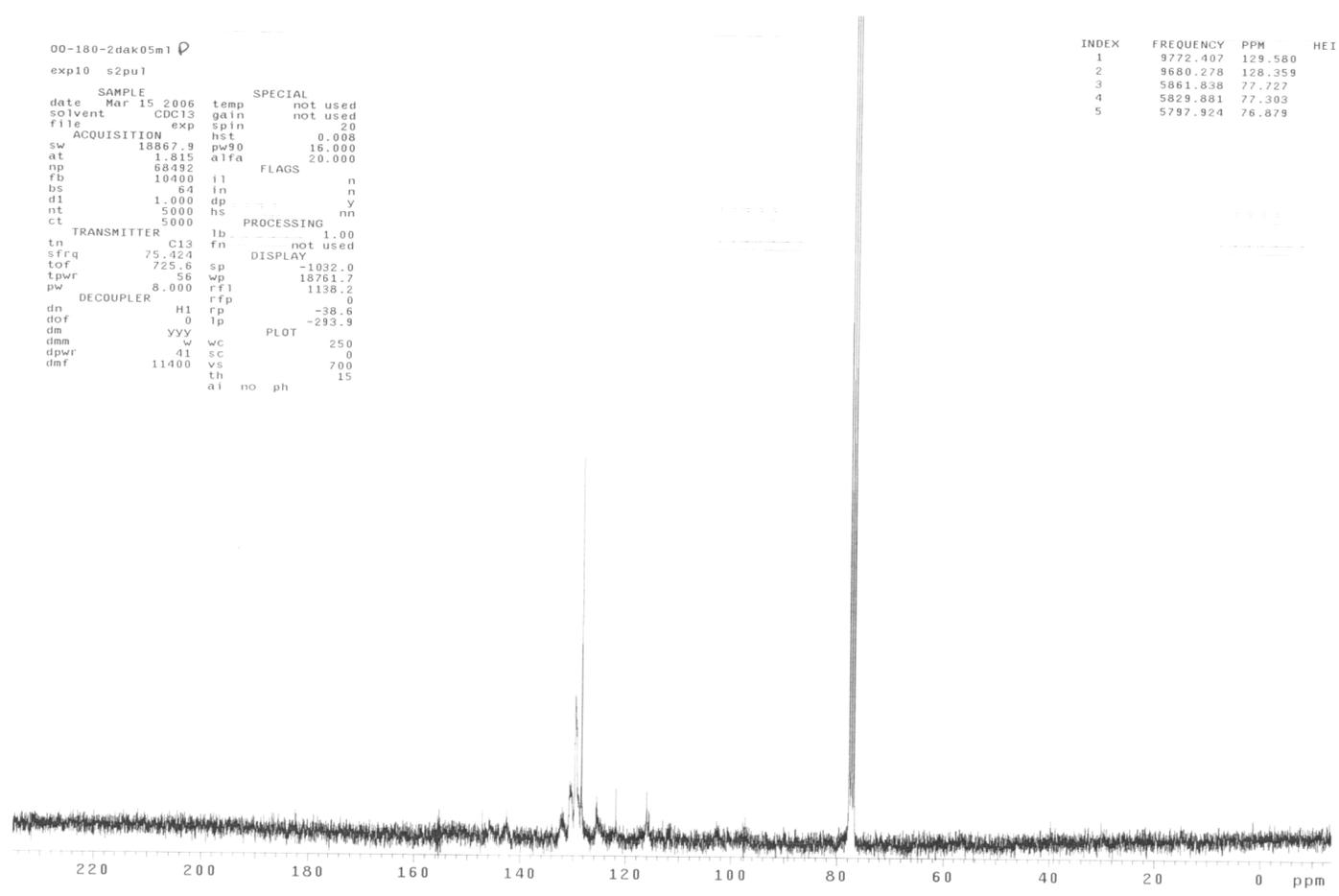


Figure 3.10. ¹³C-NMR Spectrum of P

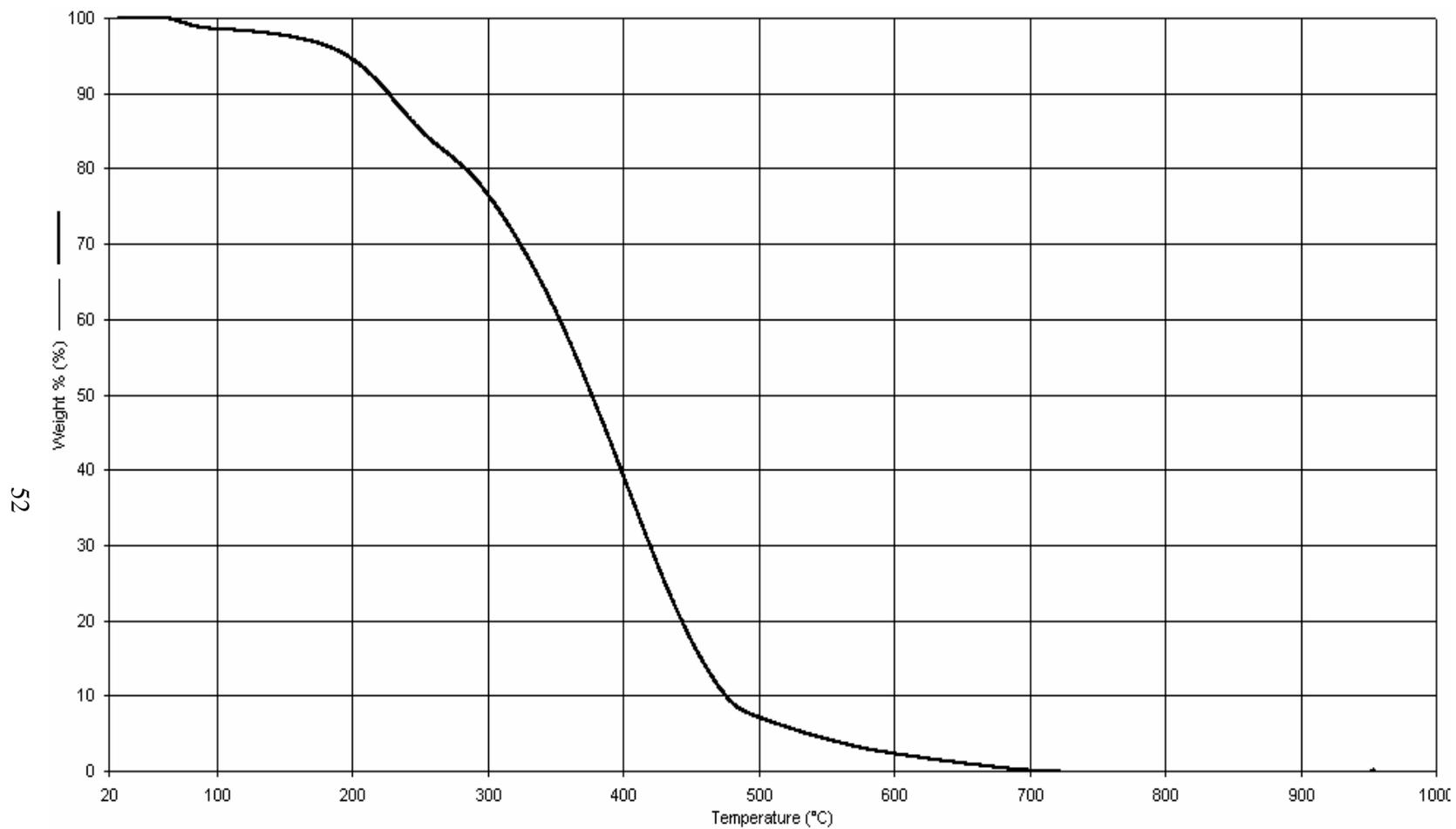
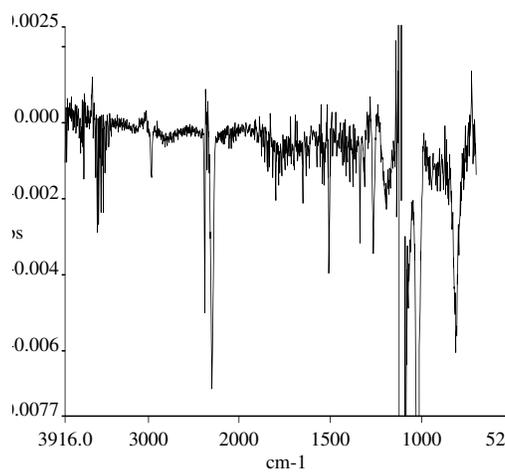
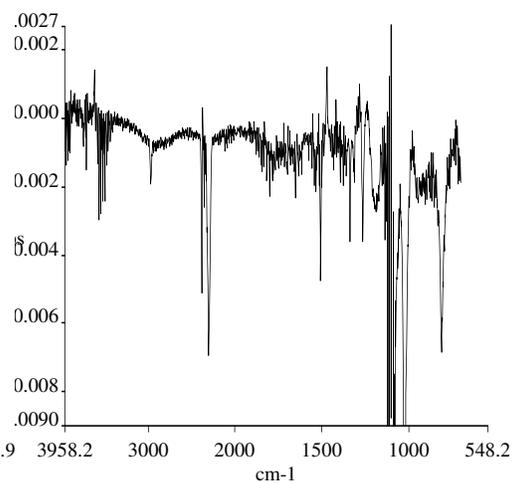


Figure 3.11. TGA thermogram of P

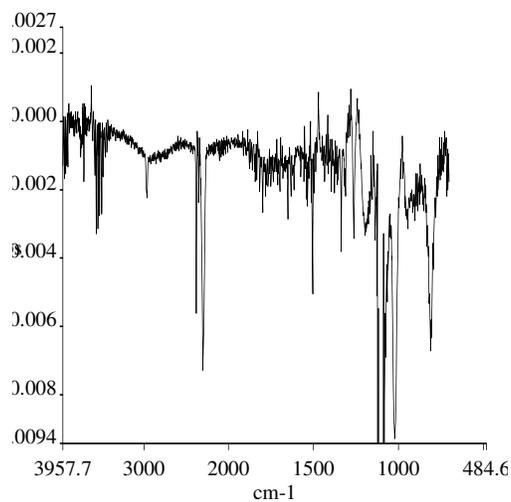
385.1 Secs



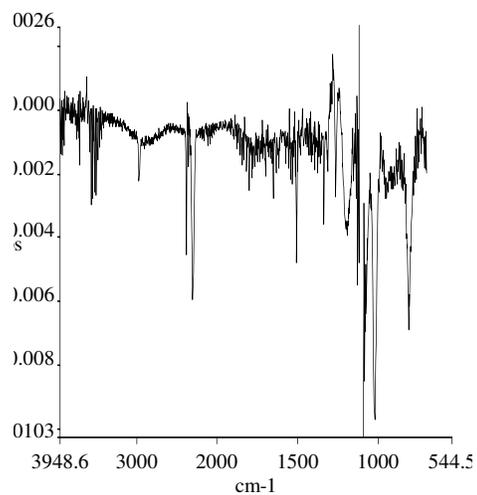
1299.8 Secs



2348.1 Secs



3601.9 Secs



4804.4 Secs

5400.5 Secs

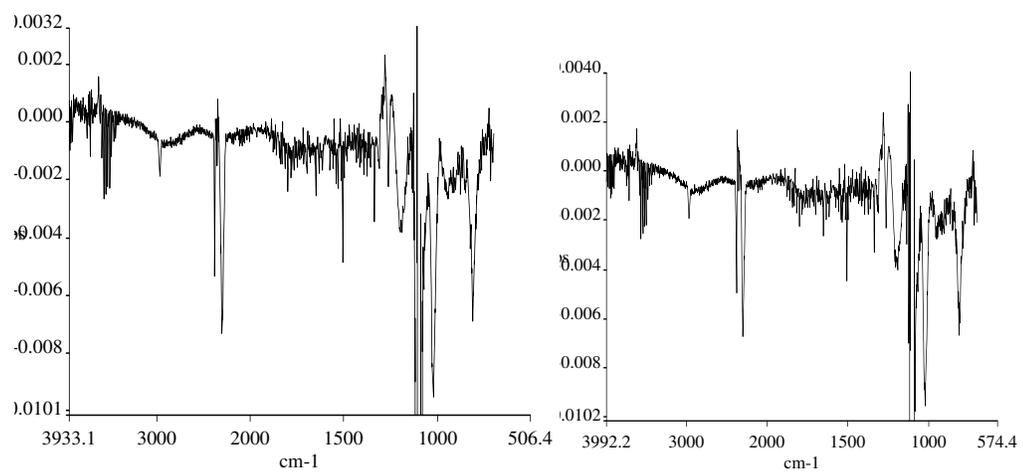


Figure 3.12 TGA-FTIR spectrums of P.

Sample: PPO
Size: 7.9000 mg
Method: 10°C/MIN (25°C to 350°C)
Comment: RUN*2 (AT N2 ATM.)

DSC

File: OZDENOKYAY.13
Operator: SEVIM ULUPINAR
Run Date: 13-Dec-06 14:12

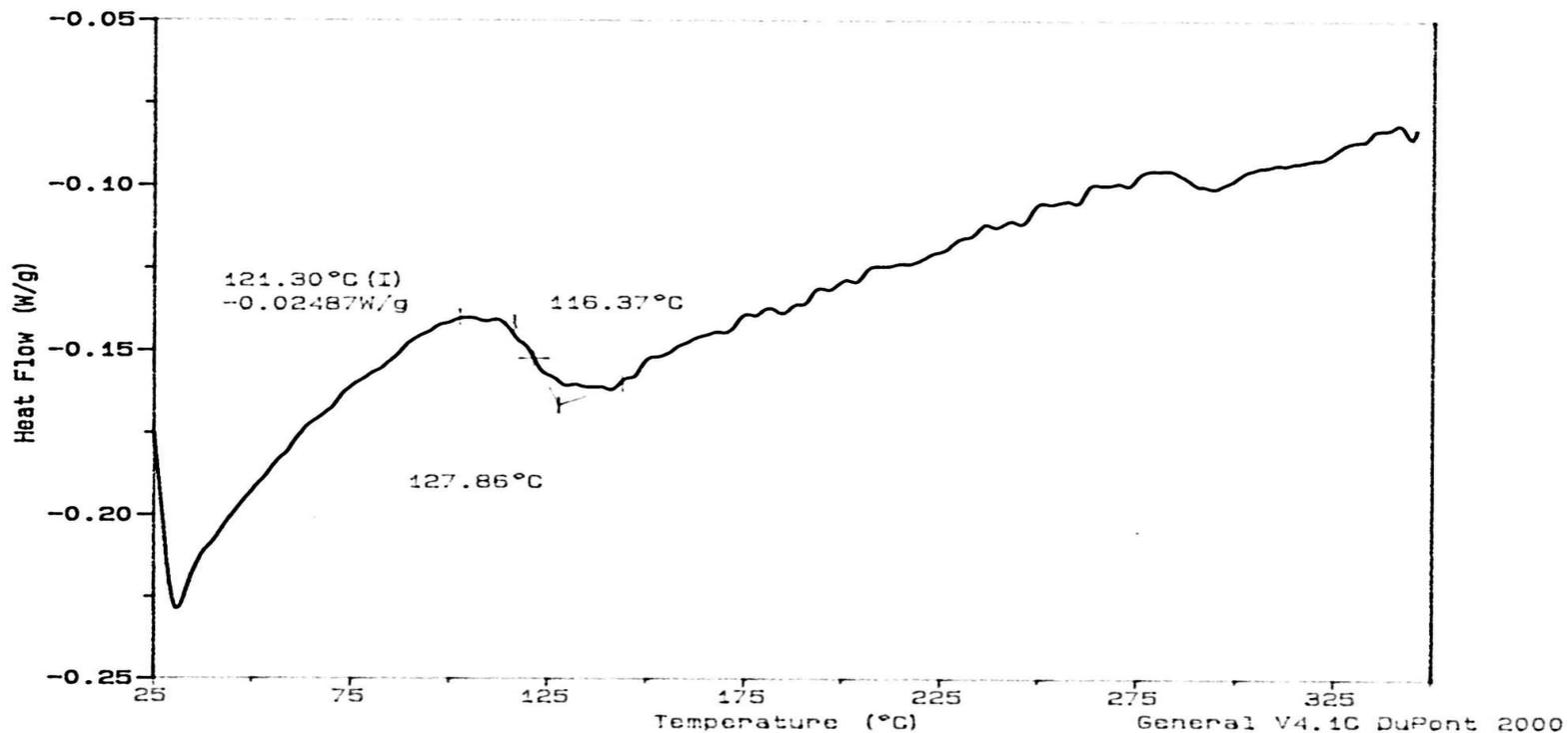


Figure 3.13 DSC thermogram of P.

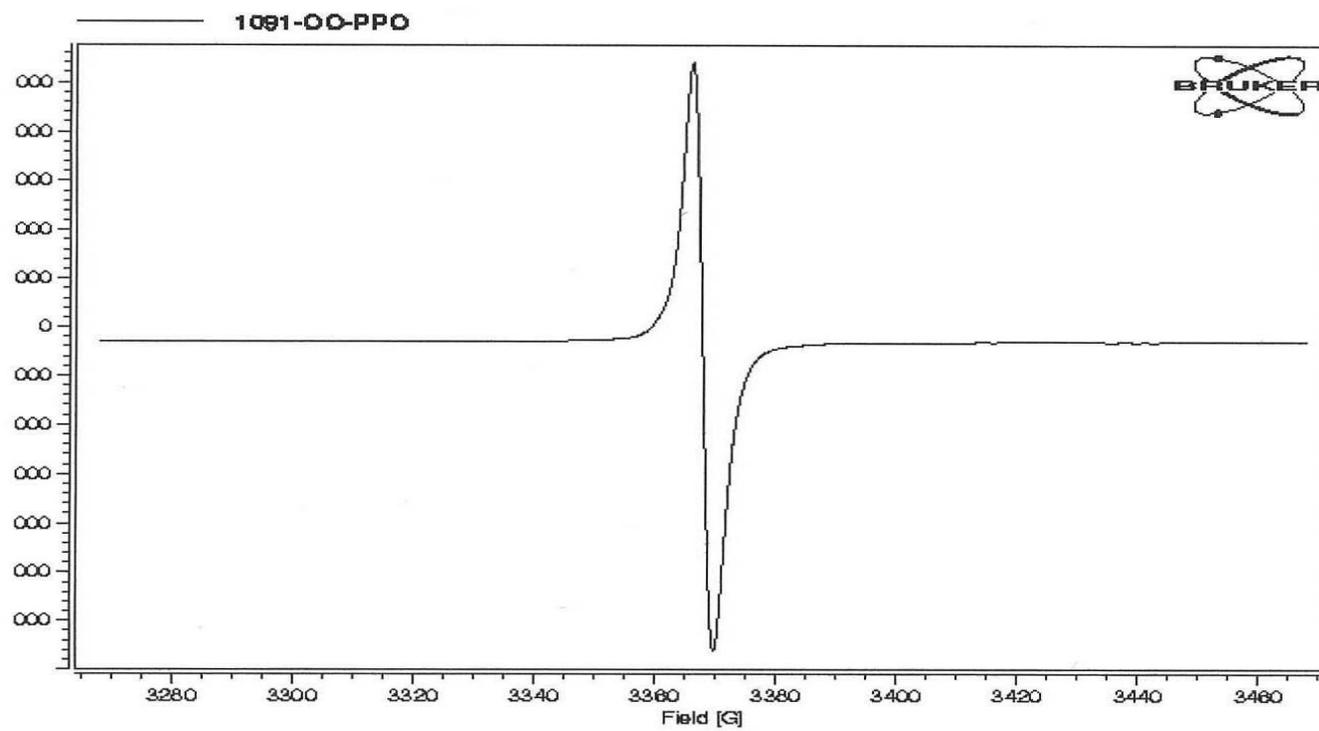


Figure 3.14 ESR spectrum of P

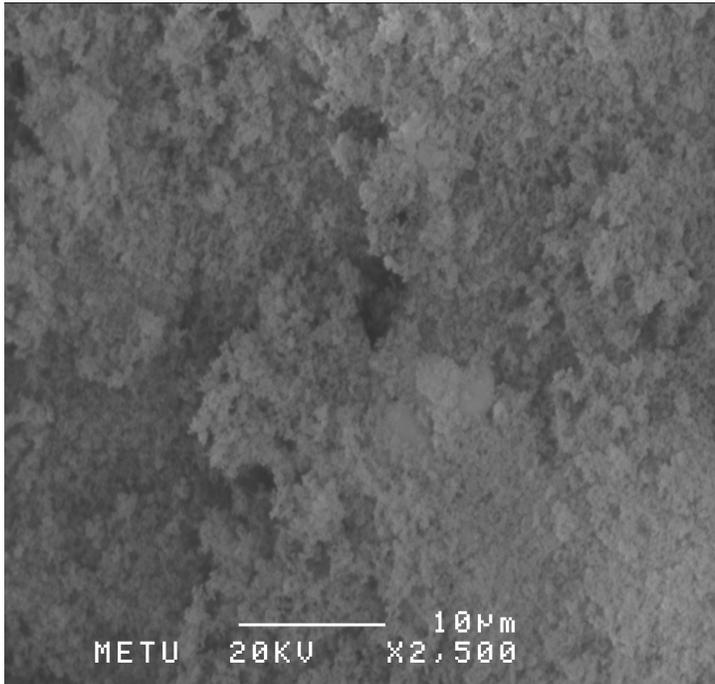


Figure 3.15. SEM micrograph of P

3.2.2 CHARACTERISATION OF RADICAL ION POLYMER

FTIR Spectrum RIP exhibits the characteristic absorptions at $726-770\text{ cm}^{-1}$ is due to the C-Cl stretching, 850 cm^{-1} (out of plane C-H bending), $955-1040\text{ cm}^{-1}$ (C-O-C stretching), $1140-1210\text{ cm}^{-1}$ (C-O stretching), 1440 and 1580 cm^{-1} (C=C ring stretching), 3079 cm^{-1} (aromatic C-H stretching) and 3500 cm^{-1} (the phenolic end group). FTIR spectrum of RIP is very similar to P.

The spectrum was presented as *figure 3.16*.

$^1\text{H-NMR}$ Spectrum The peak at 6.8 ppm is due to the protons of 2,6 dichloro 1,4 phenylene oxide units (1,4 catenation) and the peak at lower field at 7.3 ppm is due to the protons of 2,4 dichloro 1,6 phenylene oxide units (1,2 catenation). $^1\text{H-NMR}$ spectrum of RIP is very similar to the $^1\text{H-NMR}$ spectrum of P. The spectrum was presented as *figure 3.17*.

$^{13}\text{C-NMR}$ Spectrum It is very similar to the $^{13}\text{C-NMR}$ spectrum of P. It mainly has 1-2 structure which is confirmed by $^1\text{H NMR}$. The spectrum is presented as *figure 3.18*.

DSC Thermogram According to the DSC thermogram of RIP, glass transition temperature (T_g) is not observed for RIP. (*figure 3. 19*)

TGA-FTIR Thermogram TGA thermogram of RIP, is presented as *figure 3.20*. TGA-FTIR spectrums are presented as *figure 3.21*. The generation of CO_2 were observed over the whole range. Characteristic peaks at 3500 cm^{-1} of an phenolic end group (trap phenol) and the peaks at 3600 cm^{-1} of water (trap water) were not observed. Therefore degradation starts beyond $100\text{ }^\circ\text{C}$. The peak at 3050 cm^{-1} , is due to the aromatic C-H stretching. The peaks at $1440-1600\text{ cm}^{-1}$ due to C=C ring stretching is observed. The peaks at 1400 cm^{-1} represents C-H deformation. C-O stretching of phenoxy group, $1140-1210\text{ cm}^{-1}$, are observed. The peaks at $955-1040\text{ cm}^{-1}$ correspond to C-O-C stretching, peaks at 830 cm^{-1} are due to aromatic C-H stretching and the peaks at $726-770\text{ cm}^{-1}$ is due to the C-Cl stretching. According to

TGA thermogram and the FTIR spectra of the volatile gas at different times, there is not a drastic change in weight loss. Weight loss increases steadily until 700 °C and 100% of sample was lost when the temperature reaches 700 °C.

Light Scattering The weight average molecular weight (M_w) of the RIP was determined as 5.138×10^5 by the light scattering. The radius of gyration and the second virial coefficient for P determined as 2.045×10^2 nm and 2.153×10^{-6} mol dm^3/g^2 .

ESR ESR spectrum of RIP revealed the signals with g values 1.9168 and 1.9645 which were different from g values of free electron. ESR spectra of most 2,6 disubstituted phenoxy radicals show hyperfine ortho coupling connected with the ring at the end of the polymer.[43]The ESR spectrum is presented as *figure 3.22*.

Scanning electron microscope (SEM) analysis Analysis of the surface morphologies of RIP indicated coarse surface structure. (*figure 3.23*)

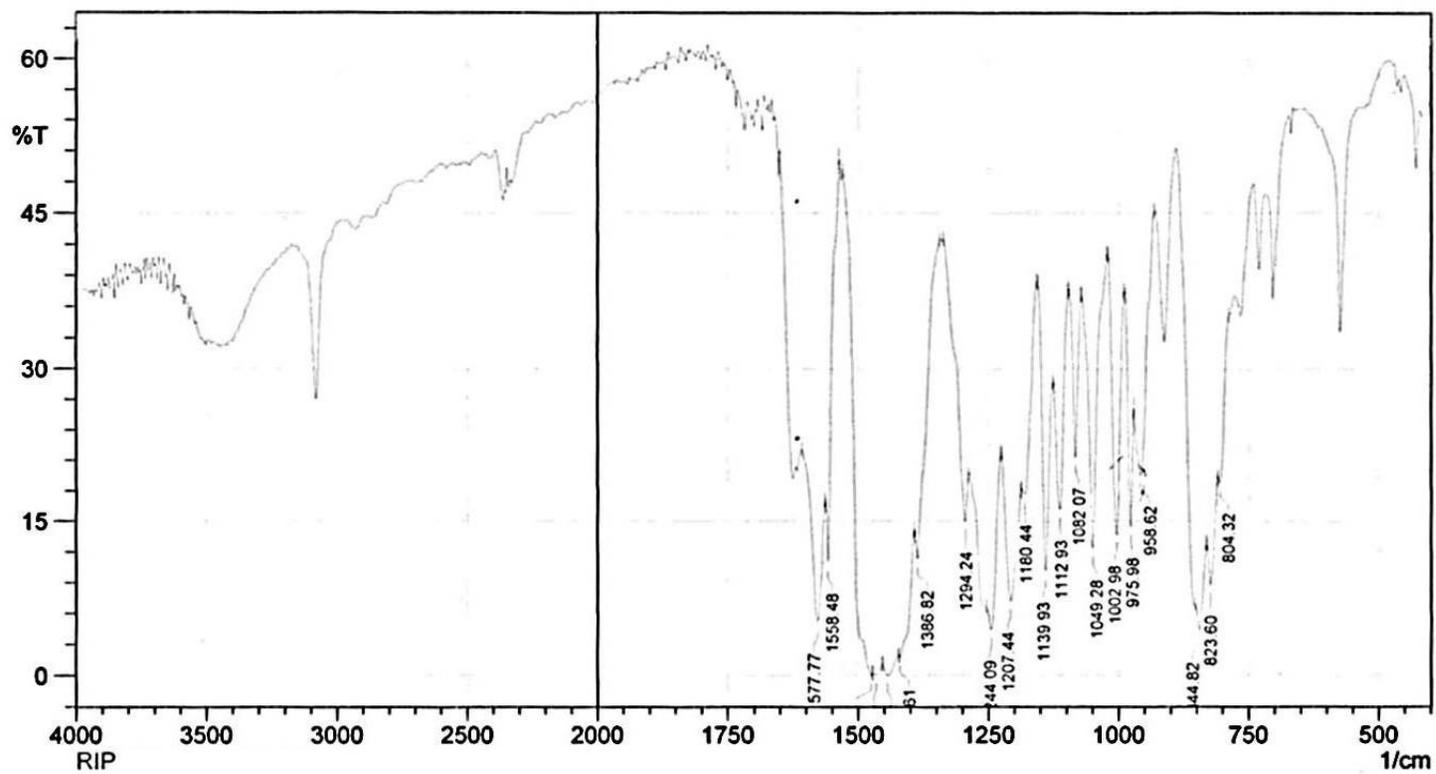


Figure 3.16. FTIR spectrum of RIP.

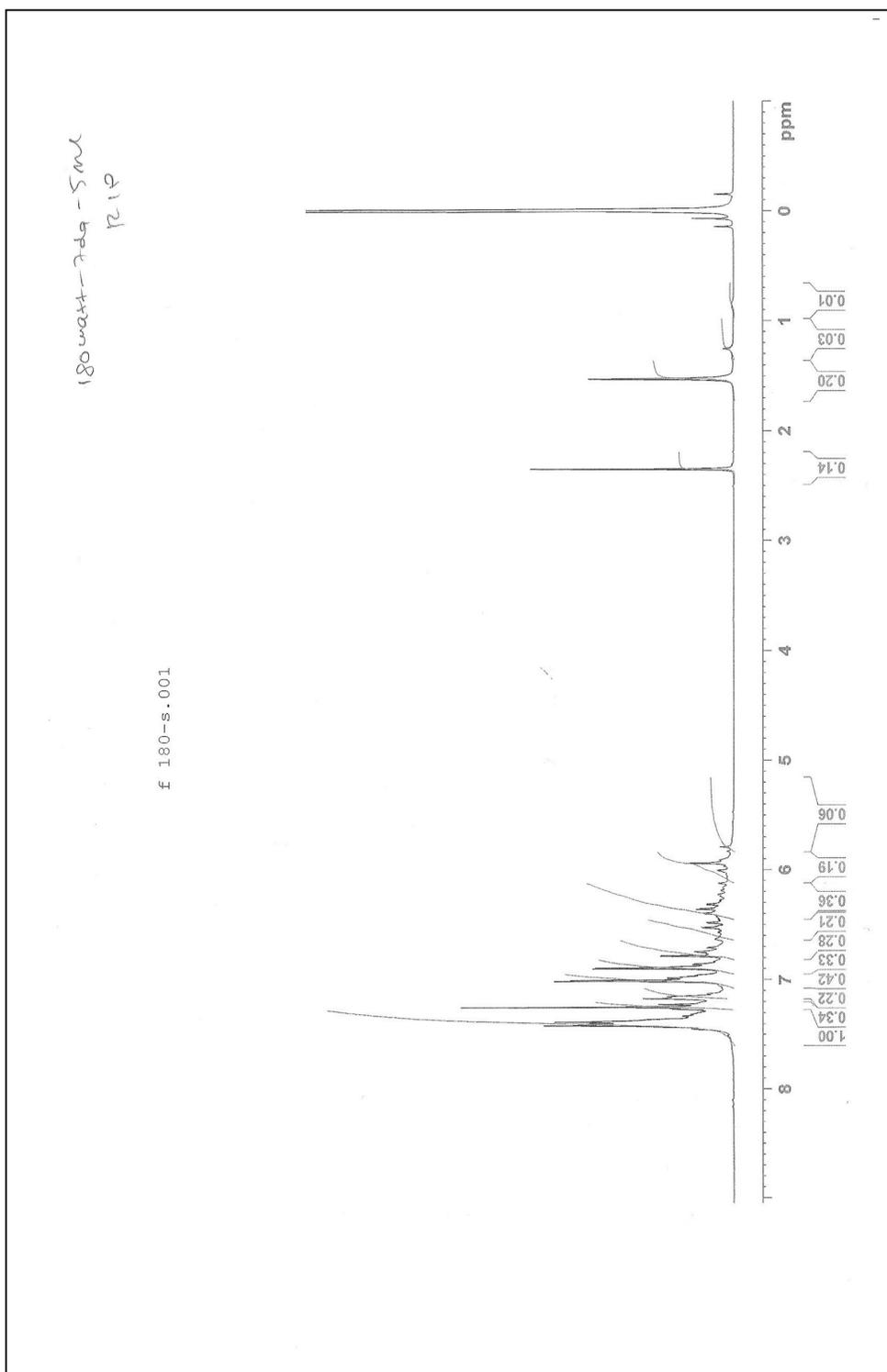


Figure 3.17. ¹H-NMR spectrum of RIP

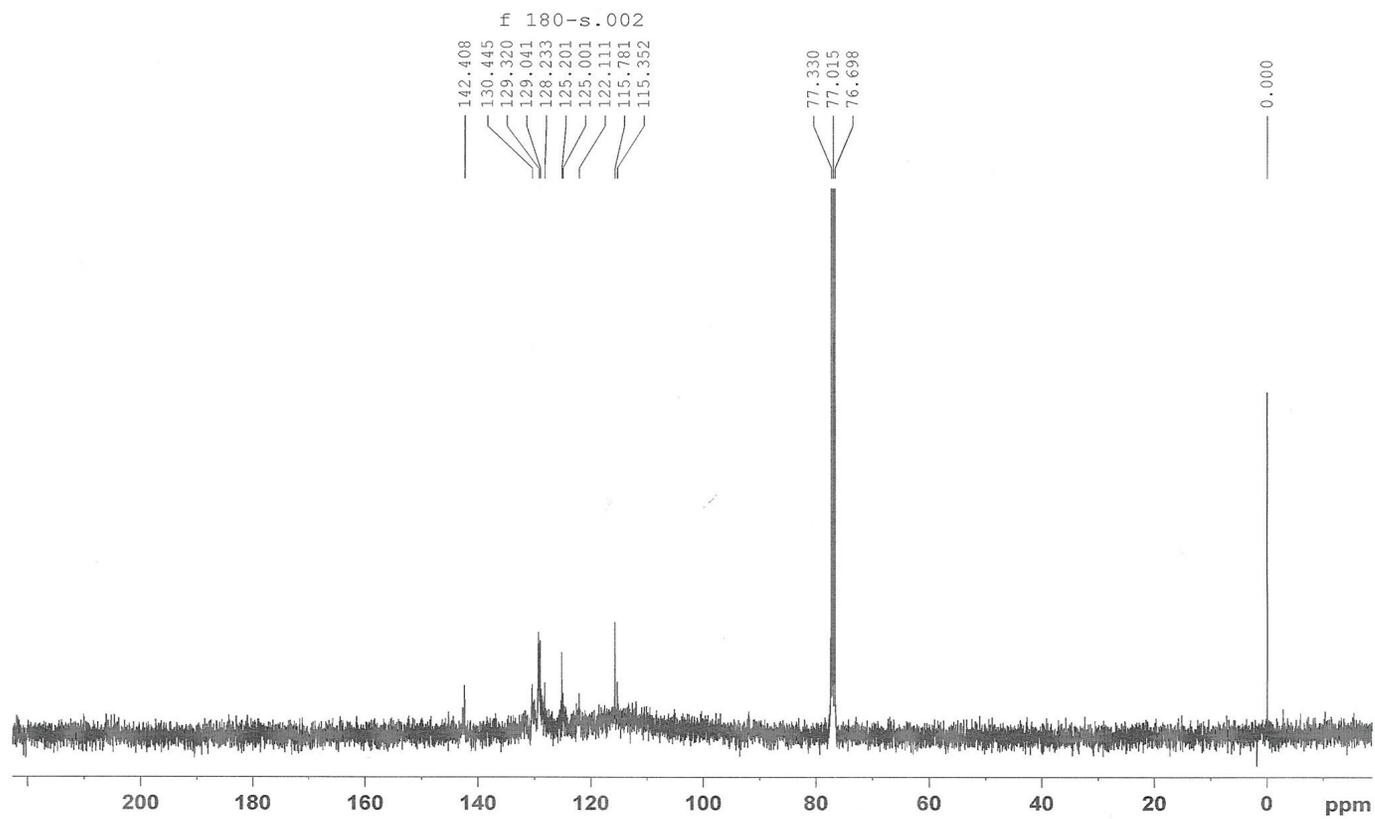


Figure 3.18. ^{13}C -NMR spectrum of RIP

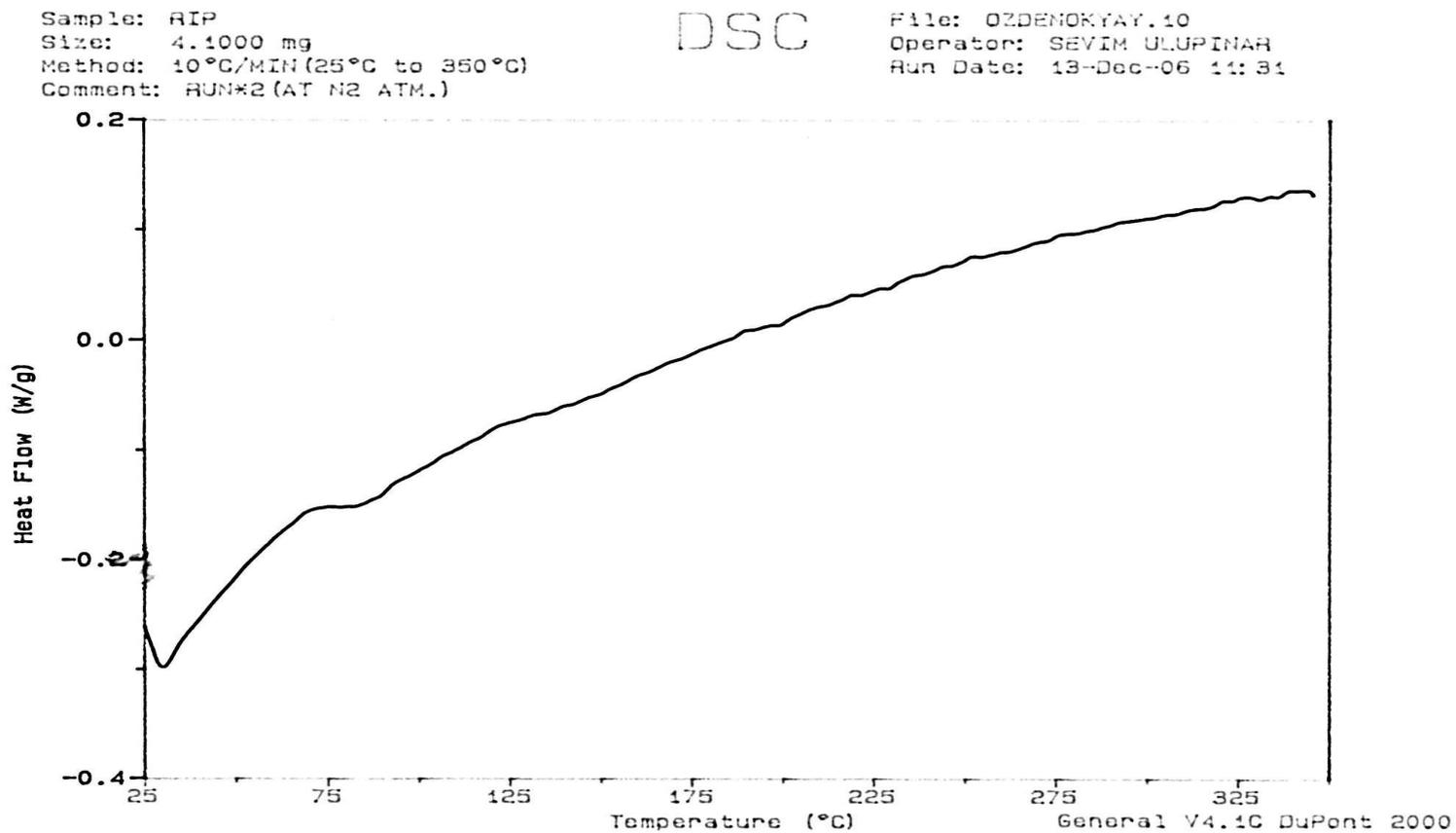


Figure 3.19. DSC thermogram of RIP

1. Numune: RIP

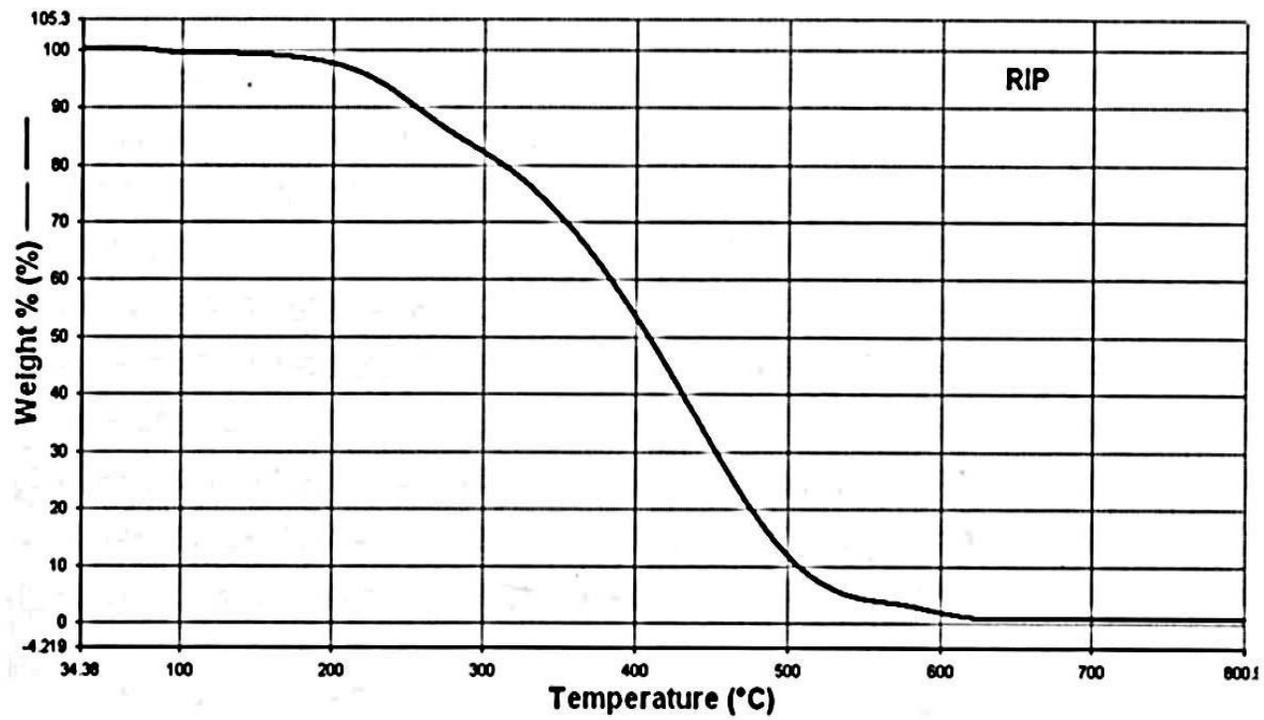
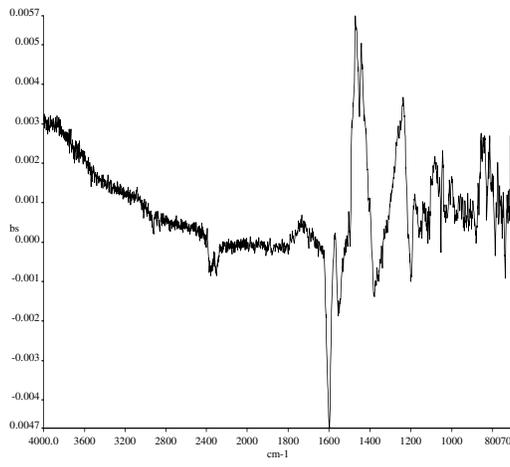
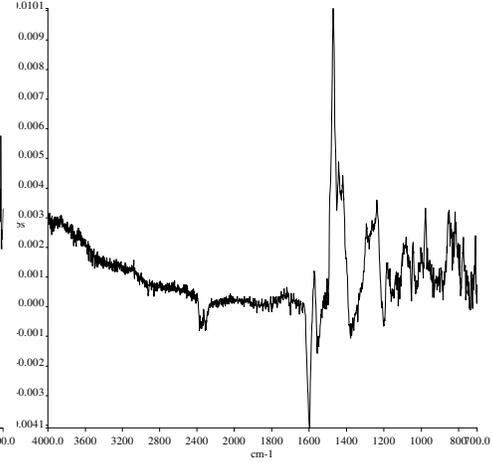


Figure 3.20. TGA thermogram of RIP

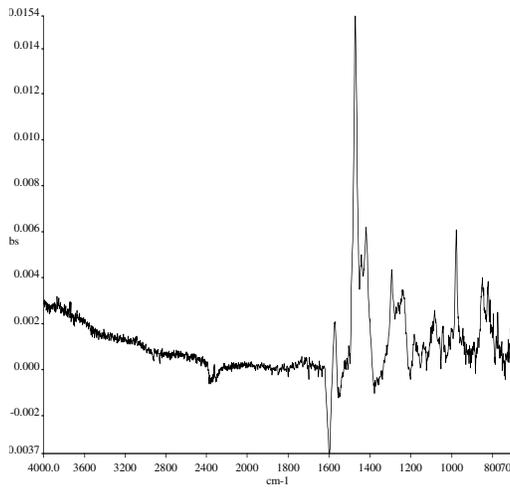
26.1 sec



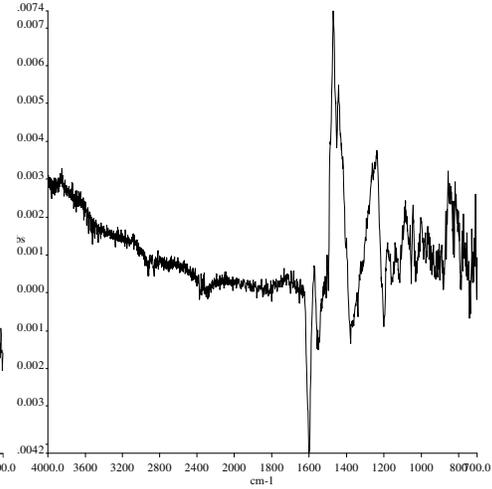
1146.3 sec



1434.0 sec



2215,2 sec



2554.4 sec

3407.4 sec

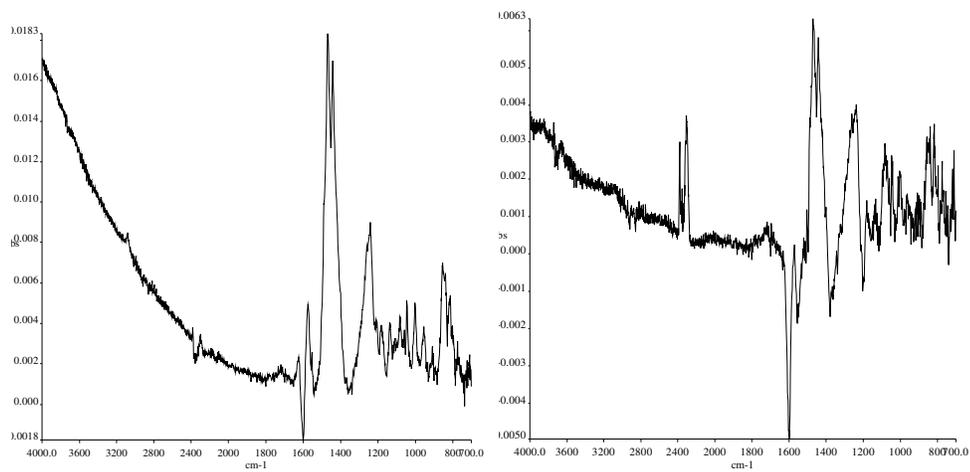


Figure 3.21. TGA-FTIR spectrums of RIP

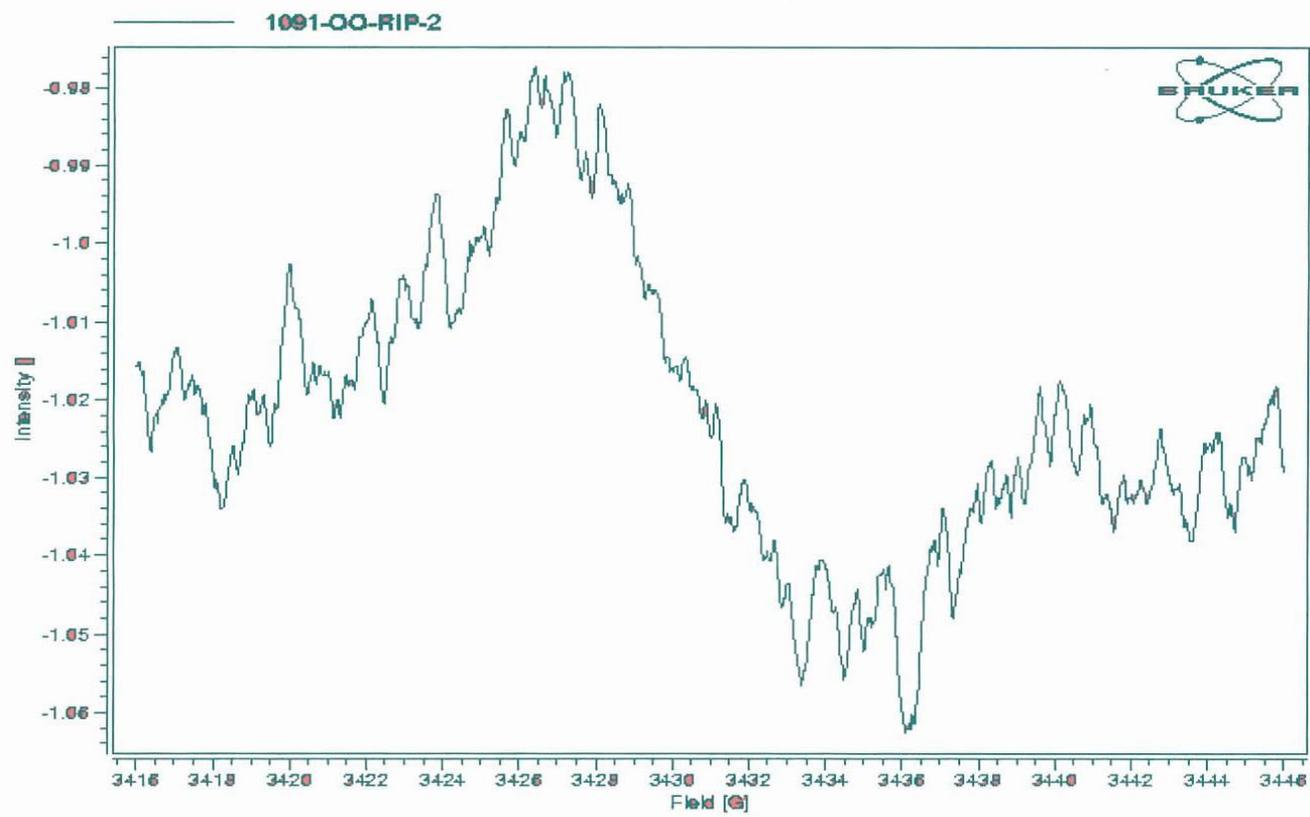


Figure 3.22. ESR spectrum of RIP

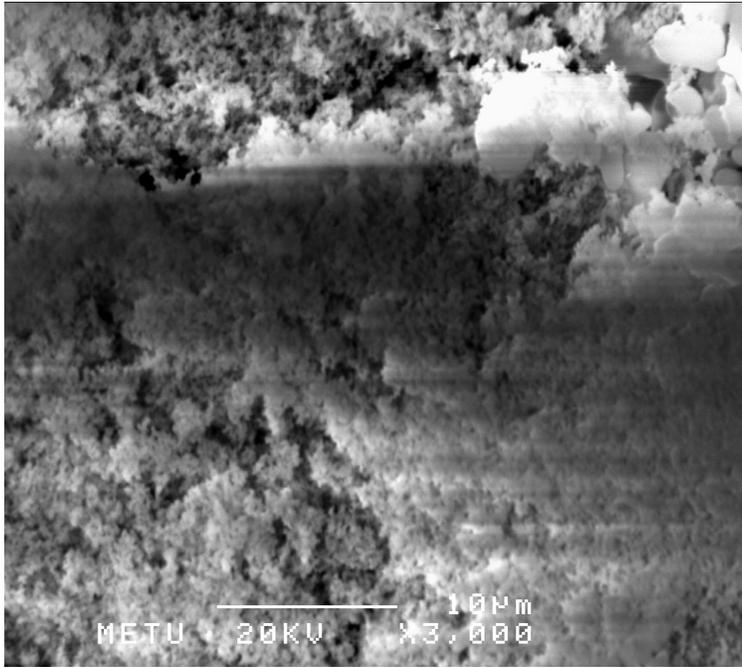


Figure 3.23. SEM micrograph of RIP

3.2.3 CHARACTERISATION OF CONDUCTING POLYMER

FTIR Spectrum The peaks at around 726 and 770 cm^{-1} are corresponding to peaks of halogen substituted benzene ring. The peak at 820 cm^{-1} refers to the trisubstituted benzene ring. The peaks at 1100, 1180 and 1280 cm^{-1} are attributed to C-O stretching. Peaks around 1460 and 1600 cm^{-1} are due to the C=C stretching of both benzenoid and quinoid structures. The peak at 1710 cm^{-1} represents C=O stretching. The broad peak around 3050 cm^{-1} is caused by C-H stretching. The spectrum was presented as *figure 3.24*.

$^1\text{H-NMR}$ and ^{13}C NMR Spectrum Conducting Polymer has no solubility in acetonitrile, benzene, CDCl_3 , DMSO, Deuterated Acetone and can not be characterised by ^1H NMR and ^{13}C NMR.

Conductivity Measurement Conductivity was measured by four probe technique. As microwave energy increases, conductivity of the conducting polymer increases.

Table3.2.2.a Microwave Energy vs Conductivity

Microwave Energy	Conductivity
90 Watt	0.0002 S / cm^2
180 Watt	0.011 S / cm^2
360 Watt	0.0513 S / cm^2

TGA Thermogram TGA thermogram of the conducting polymer, is presented as *figure 3.25*. TGA-FTIR spectrums are presented as *figure 3.26*. The generation of CO_2 and H_2O were observed over the whole range. In the beginning stage of degradation, the characteristic peaks at 3500 cm^{-1} of an phenolic end group (trap phenol) and the peaks at 3600 cm^{-1} of water (trap water) were observed. The peaks

around 3050 cm^{-1} , is due to the aromatic C-H stretching and the peaks around 1710 cm^{-1} are due to C=O stretching. The peaks due to C=C ring stretching, $1460\text{-}1600\text{ cm}^{-1}$, as well as C-O stretching of phenoxy group, $1110\text{-}1280\text{ cm}^{-1}$, are observed. The peak at $726\text{-}770\text{ cm}^{-1}$ is due to the C-Cl stretching. According to the the TGA thermogram and FTIR spectra of the volatile gas at different times, there isn't a drastic change in weight loss. Weight loss increases steadily until $400\text{ }^{\circ}\text{C}$ and some trap phenol and water removed. Almost 35% of sample is lost when the temperature reaches $750\text{ }^{\circ}\text{C}$.

In the TGA thermogram of P and RIP, when the temperature reaches $700\text{ }^{\circ}\text{C}$, 100% of sample is lost. However in case of CP, at $750\text{ }^{\circ}\text{C}$, still having residues indicating higher thermal stability.

DSC Thermogram According to the DSC thermogram of conducting polymer, glass transition temperature (T_g) is not observed for CP. (*figure 3.27*)

Scanning electron microscope (SEM) analysis Analysis of the surface morphologies of CP indicated sponge-like structure. (*figure 3.28*)

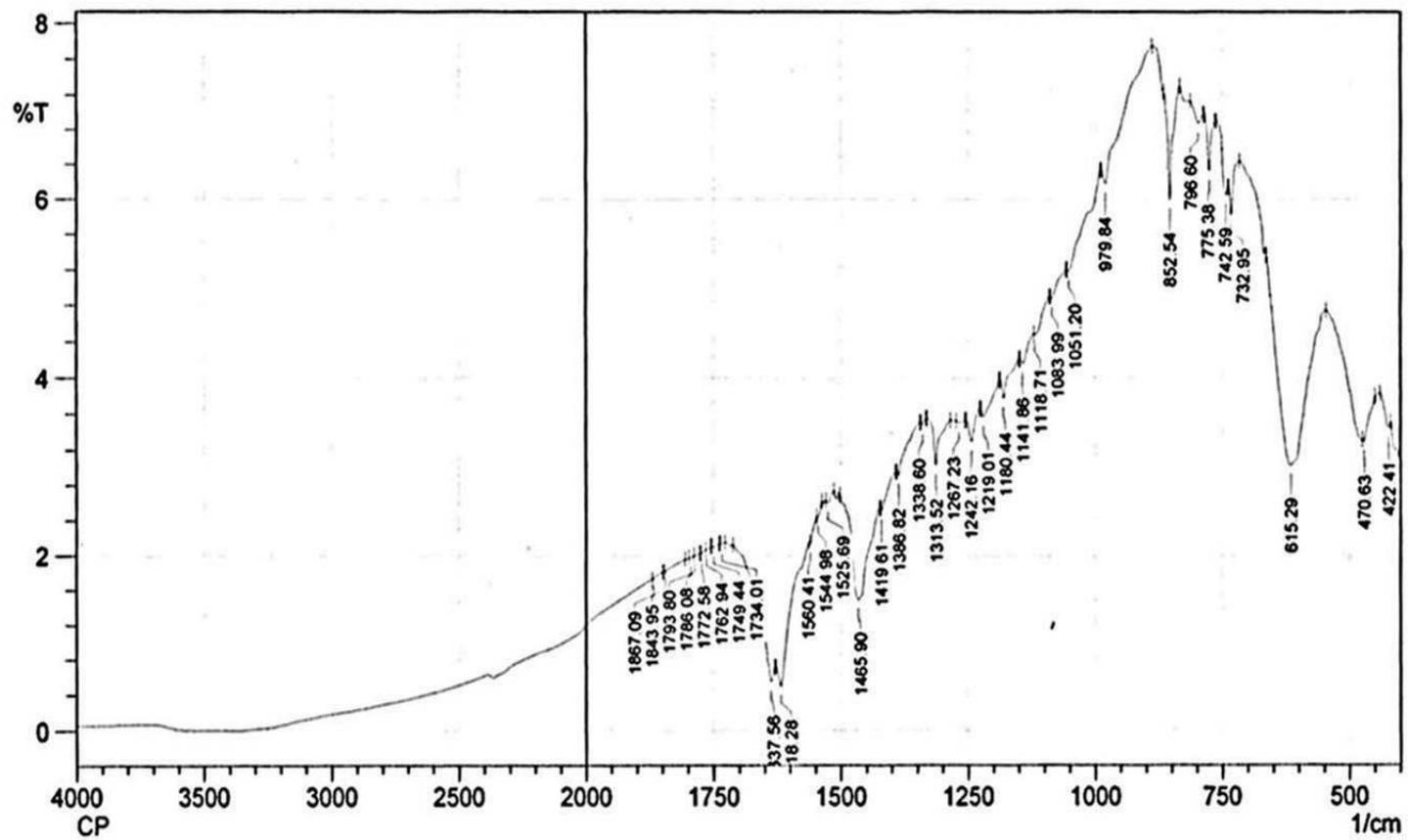


Figure 3.24. FTIR Spectrum of CP.

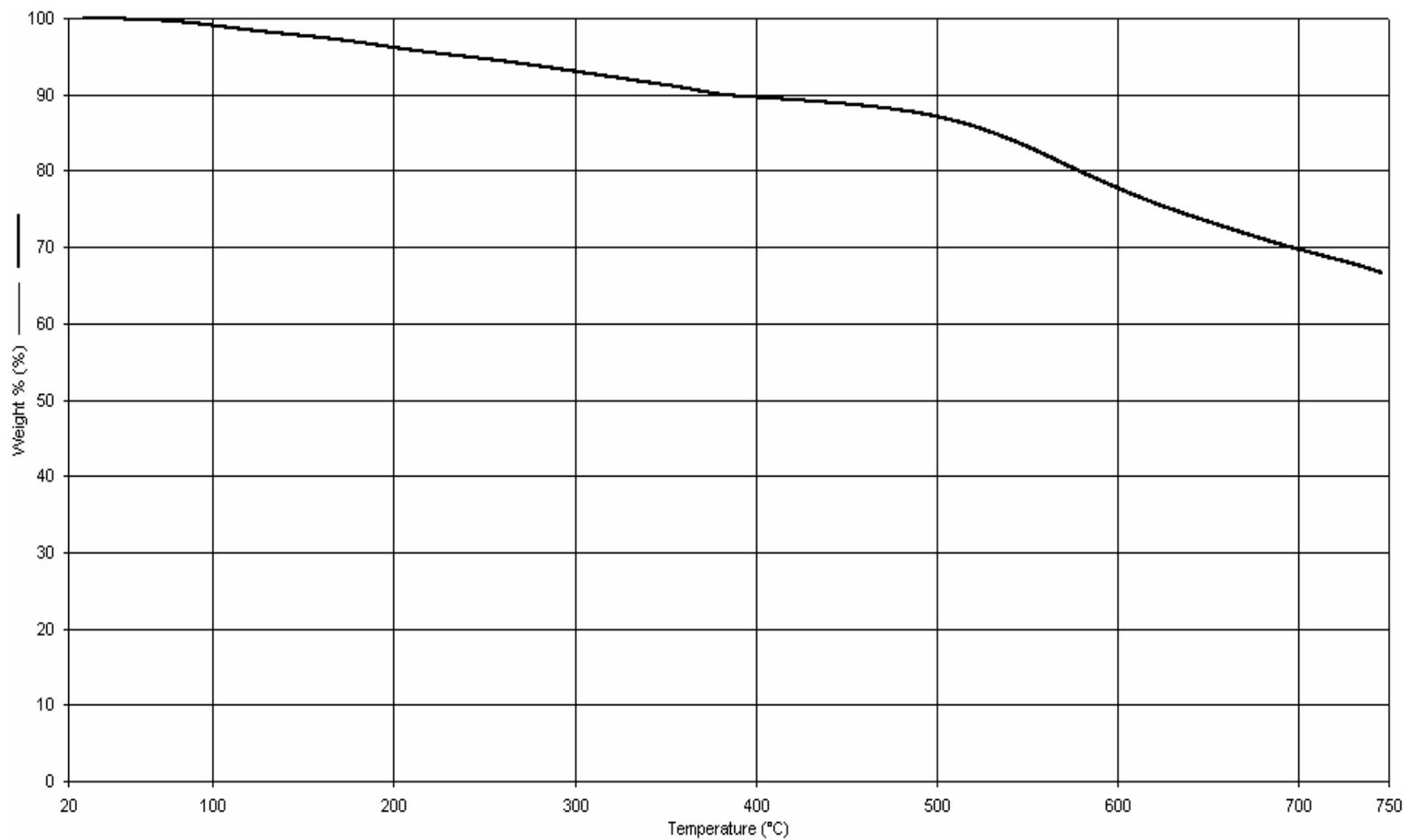
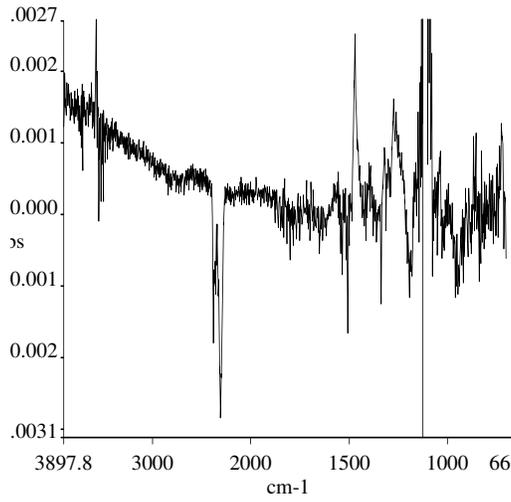
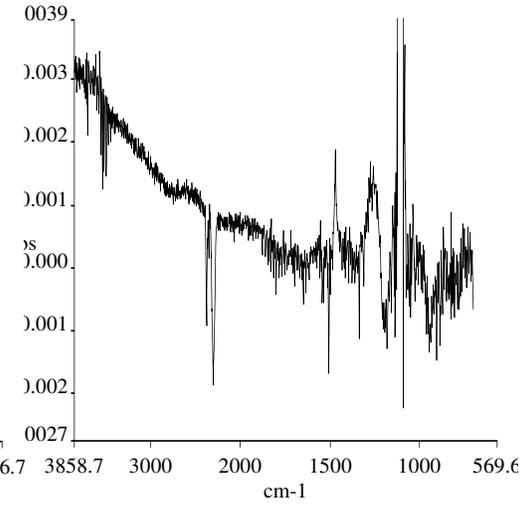


Figure 3.25. TGA thermogram of CP.

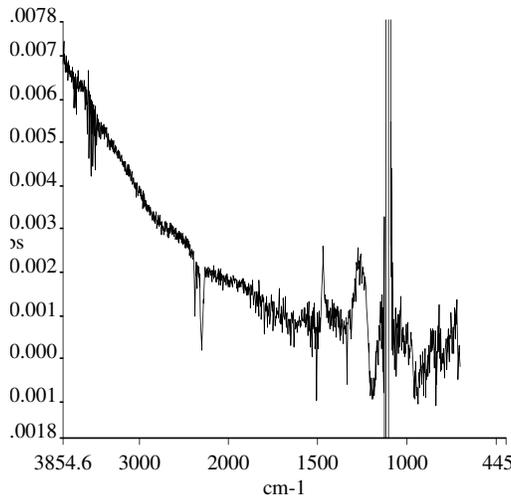
568.2 Secs



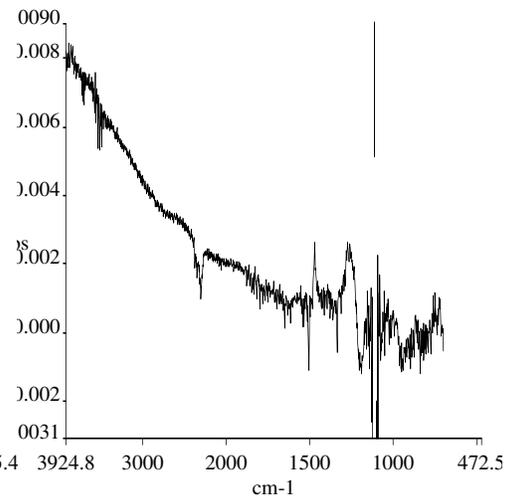
1092.3 Secs



1924.7 Secs



2161.1 Secs



3363.6Secs

3898.0 Secs

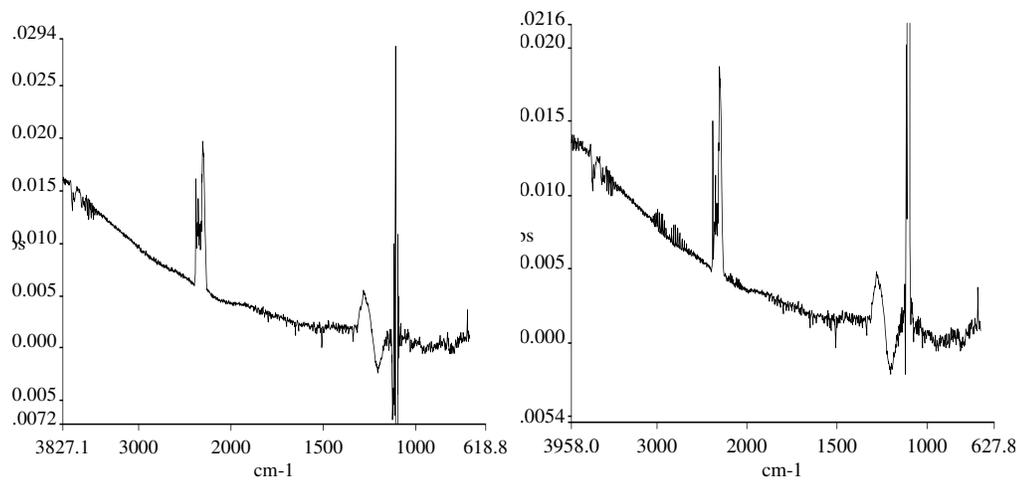


Figure 3.26. TGA-FTIR spectrums of CP.

Sample: CP
Size: 9.6000 mg
Method: 10°C/MIN (25°C to 350°C)
Comment: RUN*2 (AT N2 ATM.)

DSC

File: OZDENOKYAY.16
Operator: SEVIM ULUPINAR
Run Date: 13-Dec-06 16:19

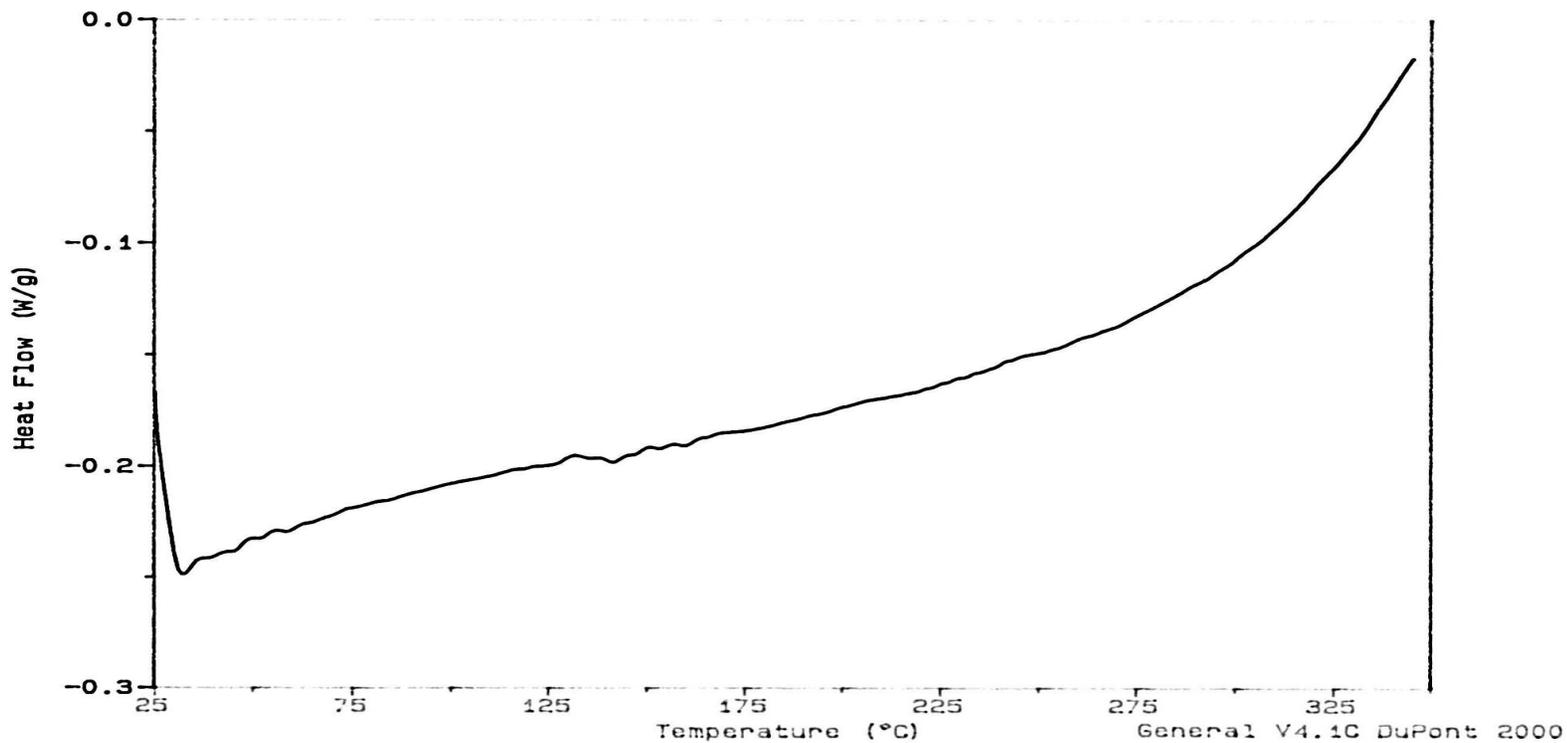


Figure 3.27. DSC t of CP.

75

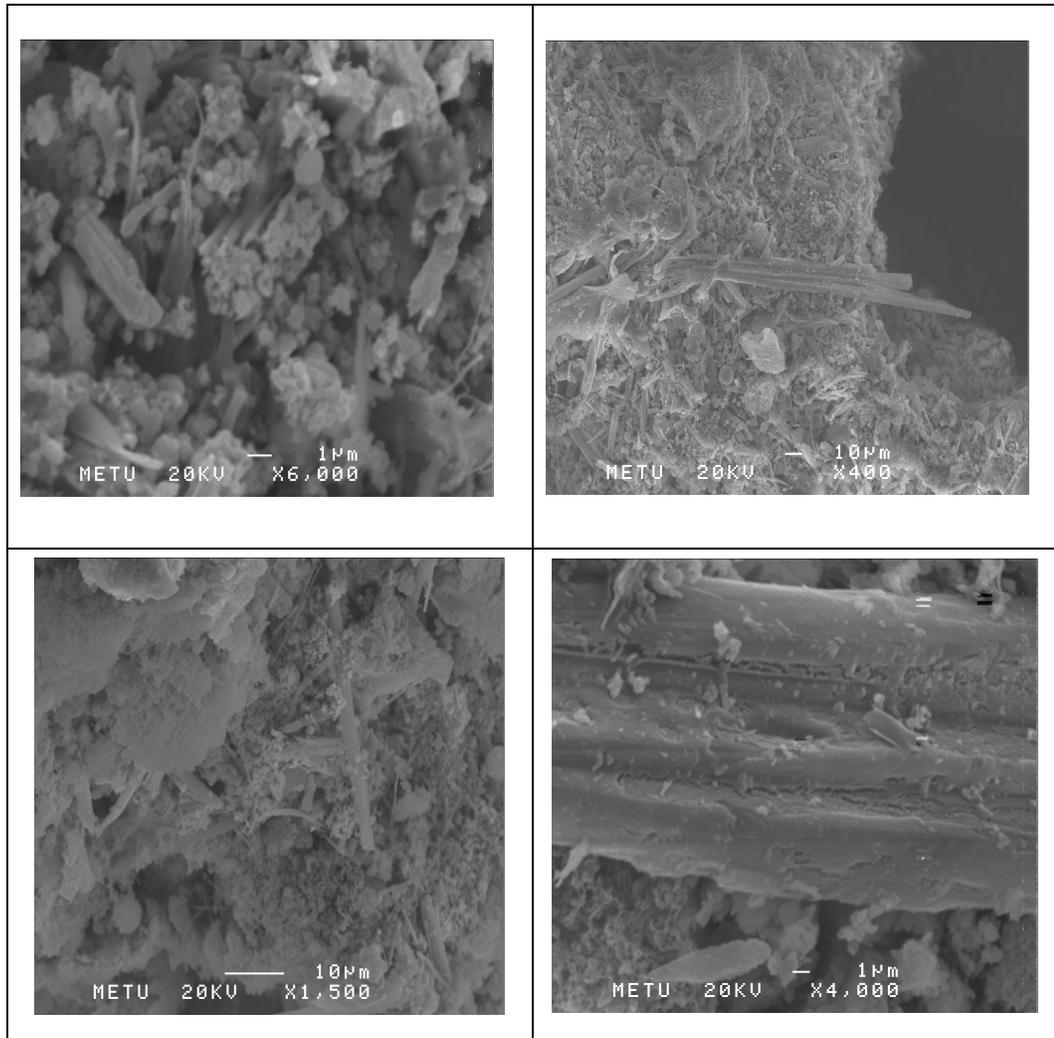


Figure 3.28. SEM micrographs of CP

3.2.4 CHARACTERISATION OF CROSSLINKED POLYMER

FTIR Spectrum FTIR spectrum of CLP was similar to P, except 955-1040 cm^{-1} (C-O-C stretching) was shifted to 1050-1200 cm^{-1} . The spectrum was presented as *figure 3.29*.

$^1\text{H-NMR}$ and $^{13}\text{C NMR}$ Spectrum Crosslinked polymer has no solubility in acetonitrile, benzene, CDCl_3 , DMSO, Deuterated Acetone and can not be characterised by $^1\text{H NMR}$ and $^{13}\text{C NMR}$.

TGA-FTIR Thermogram TGA thermogram of the crosslinked polymer is presented as *figure 3.30*. *Figure 3.31* shows FTIR spectra of evolved volatile components at each mass loss. The generation of CO_2 and H_2O were observed over the whole range. In the beginning stage of degradation, the characteristic peaks at 3500 cm^{-1} of an phenolic end group (trap phenol) and the peaks at 3600 cm^{-1} of water (trap water) were observed.

The peak at 3050 cm^{-1} , is due to the aromatic C-H stretching. The peaks due to C=C ring stretching, 1440-1580 cm^{-1} , as well as C-O stretching of phenoxy group, 1140-1210 cm^{-1} , are observed. The peaks at 1050-1200 cm^{-1} correspond to C-O-C stretching and the peak at 730-760 cm^{-1} is due to the C-Cl stretching. According to the FTIR spectra of the volatile gas at different times, weight loss increases steadily until 120 $^{\circ}\text{C}$ and trap water and phenol evolve in the initial mass loss region. Between 120 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$ there isn't any significant change of the peaks, this suggests not significant change in weight loss. But at 400 $^{\circ}\text{C}$, the intensity of 1440-1580 cm^{-1} (C=C ring stretching) significantly increases and beyond 400 $^{\circ}\text{C}$, intensity of peaks correspond to C-O-C stretching and the peaks due to the aromatic C-H stretching increases. This suggests that ring opening followed by the cleavage of crosslinking site occurs. Weight loss increases till 800 $^{\circ}\text{C}$, and still having residues at this temperature indicating higher thermal stability.

DSC Thermogram According to the DSC thermogram of crosslinked polymer, glass transition temperature (T_g) is not observed. (*Figure 3. 32*)

ESR ESR spectrum of CLP revealed the signals with g values 2.0032 which was very close to g values of free electron. Superhyperfine splittings could be assigned due to the neighbouring H-atoms in the molecular structure. The ESR spectrum is presented as *figure 3.33*.

Scanning electron microscope (SEM) analysis Analysis of the surface morphologies of CLP indicated dendrite structure. (*Figure 3. 34*)

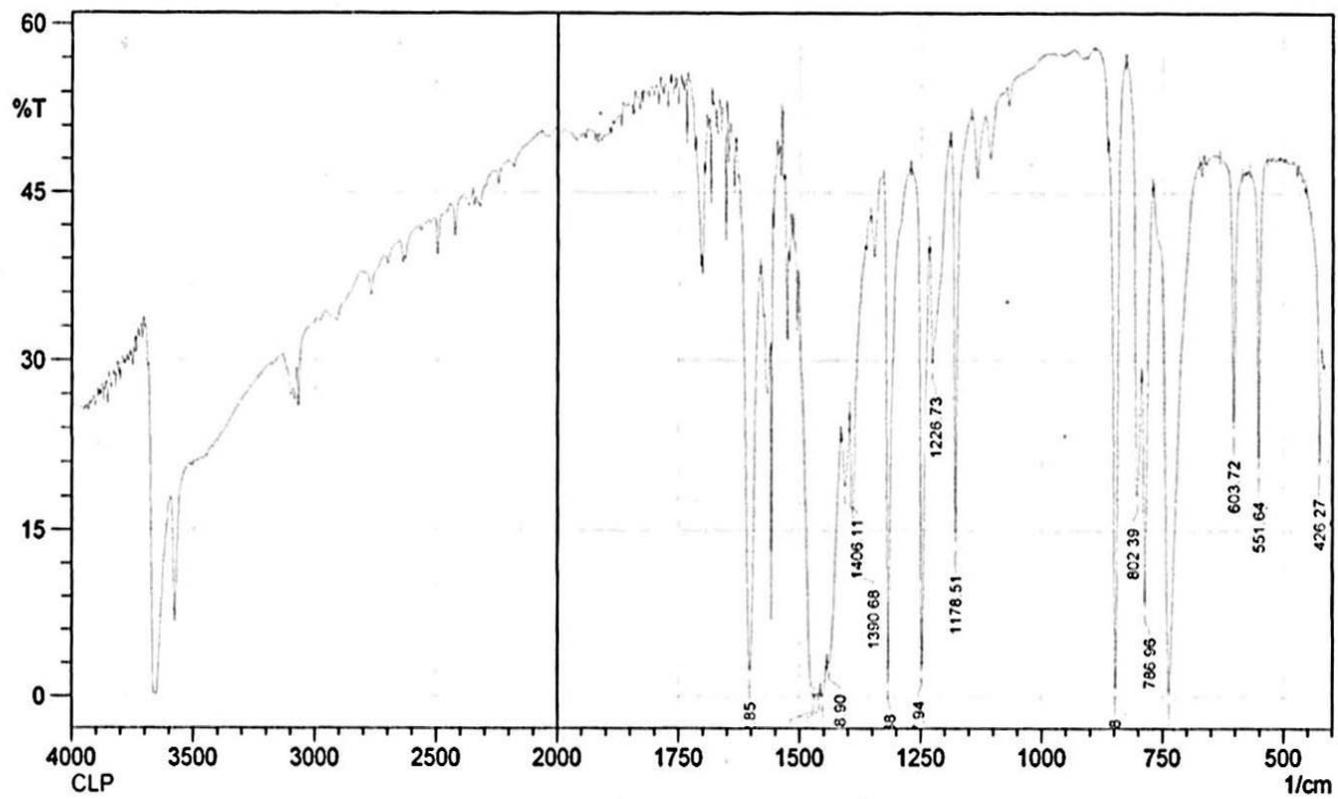


Figure 3.29. FTIR spectrum of CLP

2. Numune: CLP

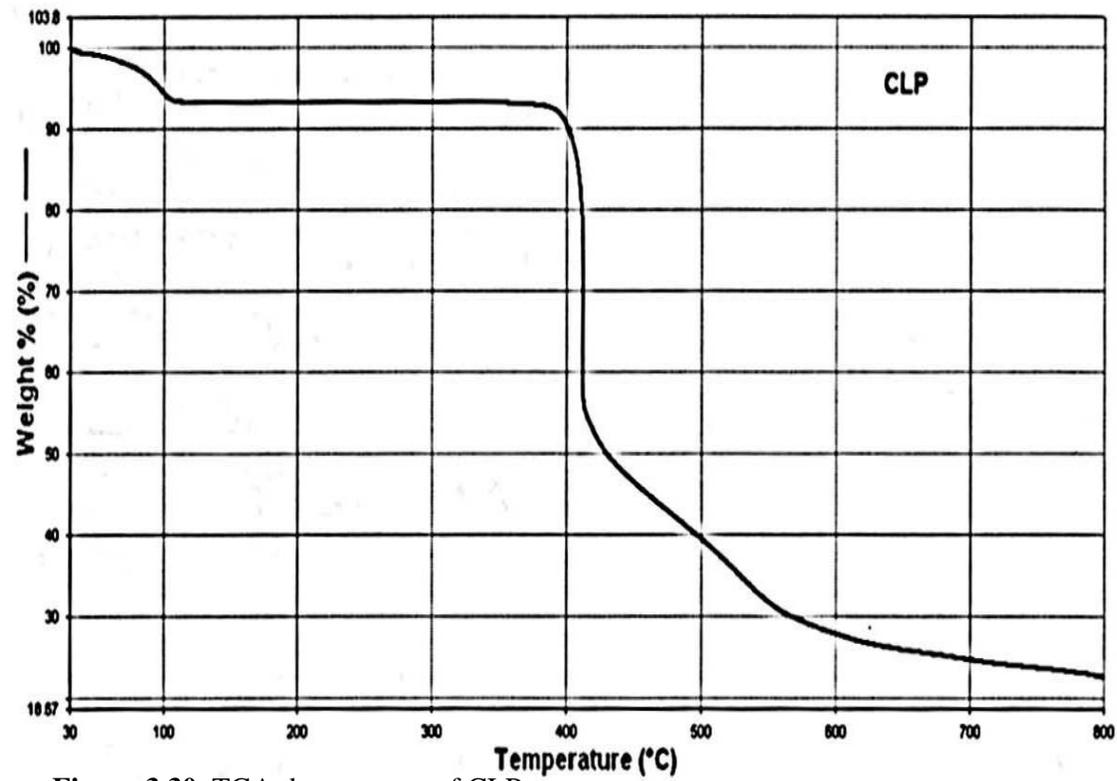


Figure 3.30. TGA thermogram of CLP

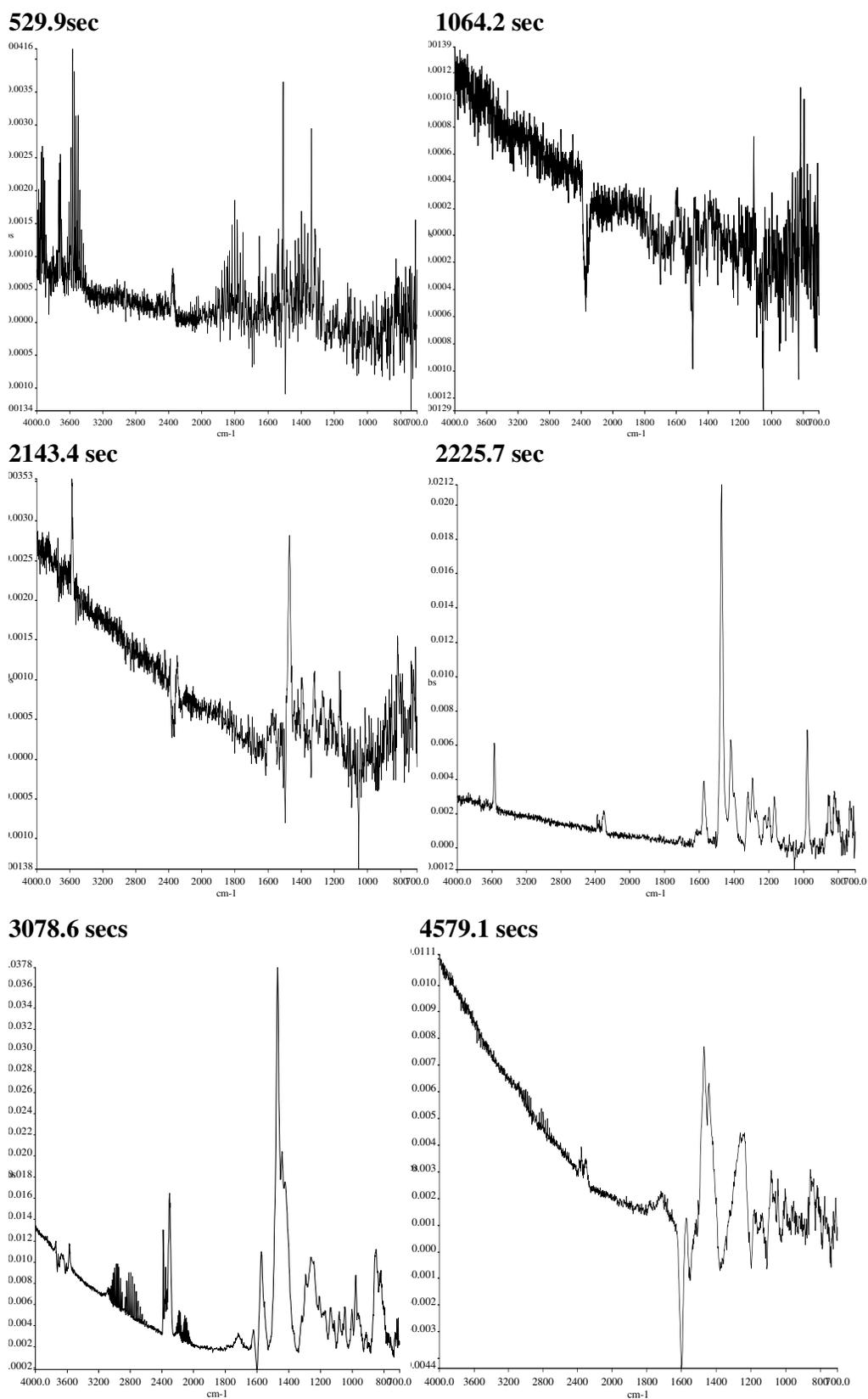


Figure 3.31. TGA-FTIR spectrums of CP.

Sample: CLP
Size: 7.0000 mg
Method: 10°C/MIN (25°C to 350°C)
Comment: RUN*2 (AT N2 ATM.)

DSC

File: OZDENOKYAY.7
Operator: SEVIM ULUPINAR
Run Date: 12-Dec-06 12:50

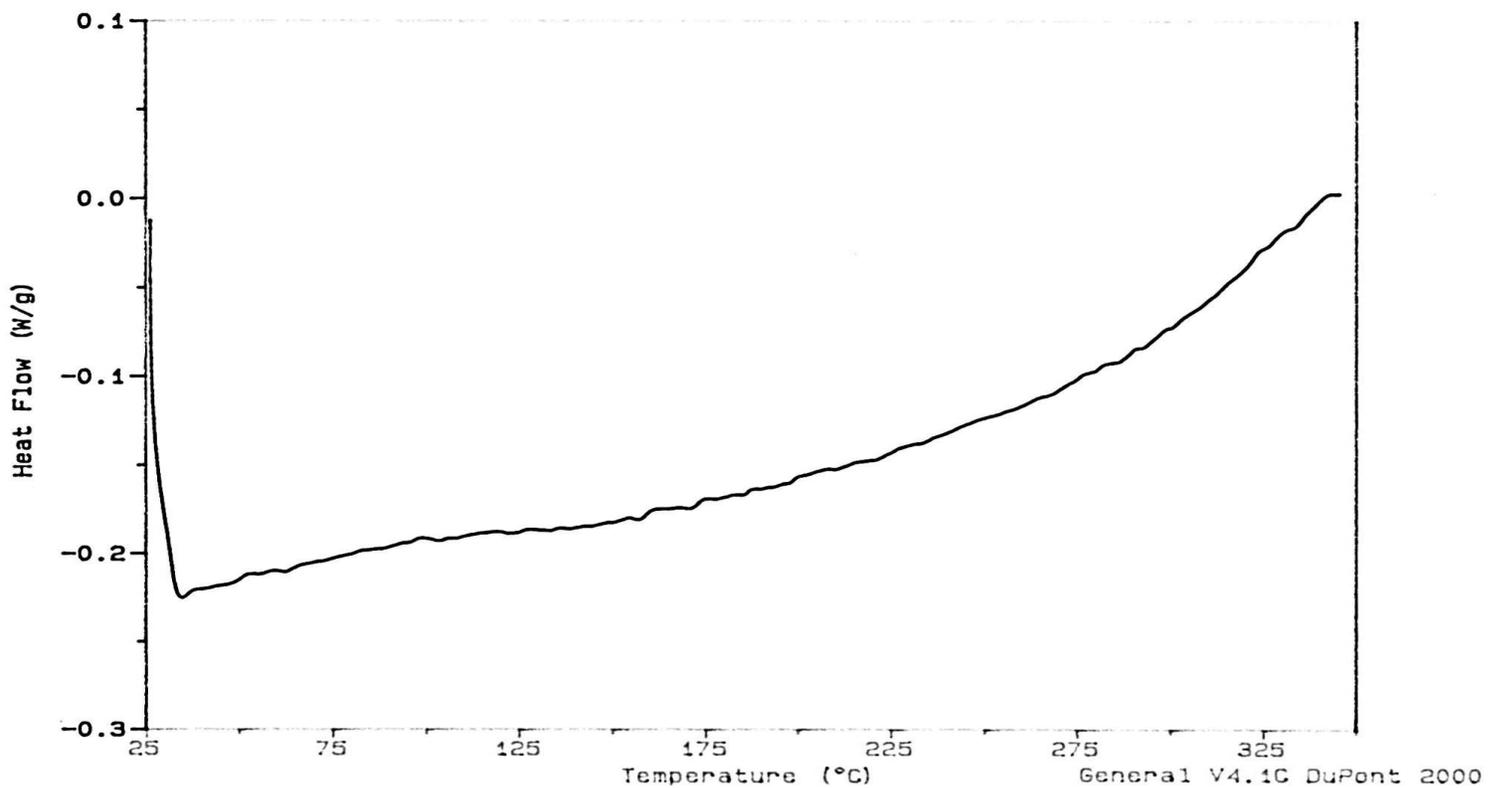


Figure 3.32. DSC thermogram of CLP

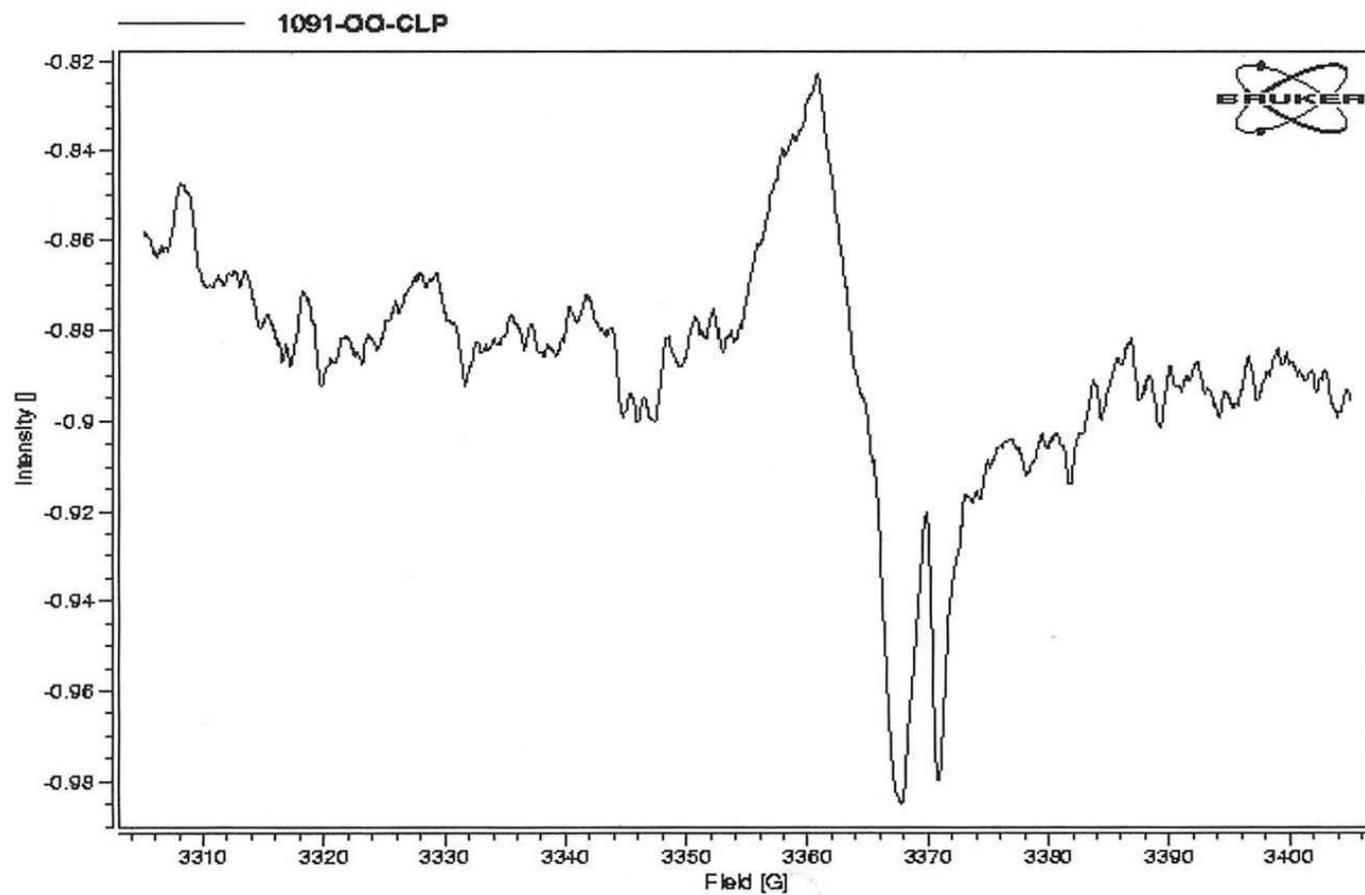


Figure 3.33. ESR spectrum of CLP

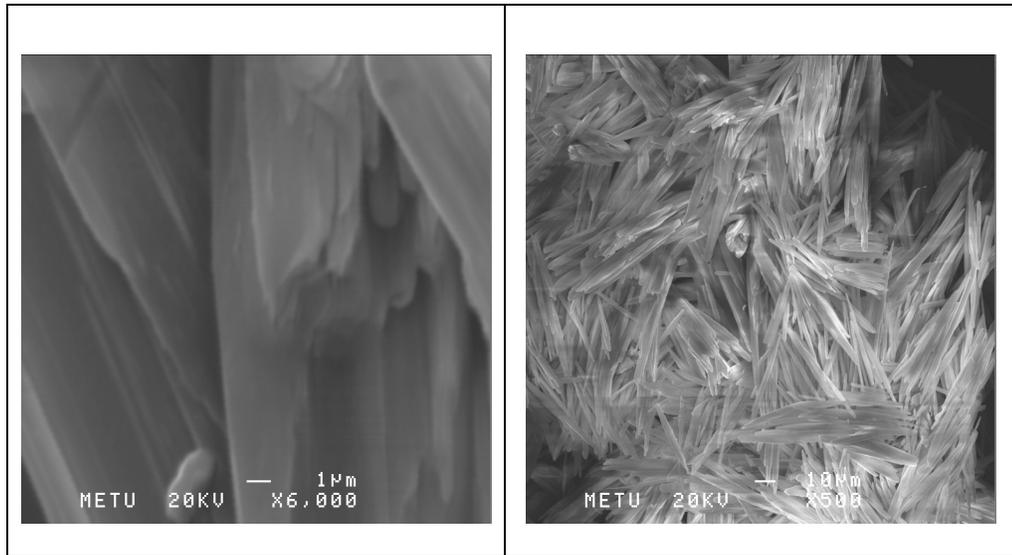


Figure 3.34. SEM micrographs of CLP

CHAPTER 4

CONCLUSION

Polymerization reaction is carried out by the reaction of 2,4,6 trichlorophenol with sodium hydroxide in the presence of water by microwave initiation.

Poly(dichlorophenylene oxide) and conducting polymer are successfully synthesized and characterized.

$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ results of poly(dichlorophenylene oxide) suggest that polymeric products prefer mainly 1-2, addition.

Maximum percent conversion to P is achieved at the end of 3 min having a value of 12.3 % at 180 Watt.

Highest conversion to the conducting polymer is obtained at 90 Watt at the end of 2 min.

By changing the amount of water between 1 cm^3 and 20 cm^3 , crosslinked polymer (CLP) and radical ion polymer (RIP) could be synthesized at various time intervals and various microwave energy levels.

This new technique is very time saving compared to previously used methods.

The following structure can be proposed for the conducting polymer due to result of elemental analysis, FTIR spectrum and TGA thermogram of conducting polymer.[36]

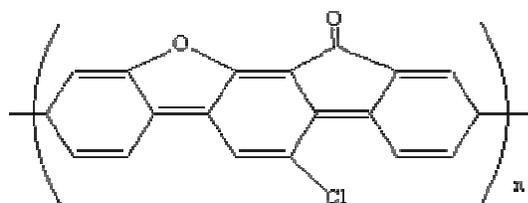


Figure 4.1. Structure of Conducting Polymer

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