ELECTROCHEMICALLY OBTAINED INSULATING AND CONDUCTING POLYMERS AND COMPOSITES OF ACRYLONITRILE

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Prof. Dr. Tayfur Öztürk
Director

I certify that this thesis satisfies all the requirements as athesis for the degree of Doctor of Philosophy.

Prof. Dr. Erdal Bayramlı
Chairman of Department

This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy.

Prof. Dr. Levent Toppare
Co-supervisor

Prof. Dr. Ural Akbulut
Supervisor

Examining Committee Members:

Prof. Dr. Zuhal Küçükyavuz (Chairman)
Prof. Dr. Ural Akbulut (Supervisor)
Prof. Dr. Levent Toppare (Co-supervisor)
Prof. Dr. Ali Gökmen
Prof. Dr. Ahmet Önal

ABSTRACT

ELECTROCHEMICALLY OBTAINED INSULATING AND CONDUCTING POLYMERS AND COMPOSITES OF ACRYLONITRILE

Yılmaz (Yurttaş), Berrin
Ph.D ; Department of Chemistry
Supervisor : Prof. Dr. Ural Akbulut
Co - Supervisor : Prof. Dr. Levent Toppare

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Acrylonitrile was polymerized by constant potential electrolysis technique. The reduction peak potential of acrylonitrile was determined by cyclic voltammetry and the polymerization potential was based on this reduction peak. The kinetics of polymerization was followed by gas chromatography analysis. The effect of temperature on conversion, yield and viscosity was determined. Characterization of electrolysis products were made by IR analysis. Electrochemically obtained polyacrylonitrile and a commercially available polyacrylonitrile were heat treated to improve their conductivities. The parameters chosen for heat treatment conditions were the temperature, the treatment medium (vacuum or air) and the doping agent. The conductivities of all heat treated polymers were measured. The sensitivity and the reproducibility of heat treated polyacrylonitrile samples toward water vapor were determined by subsequent exposing and disposing of the polymer to water vapor. The characterization of the heat treated polymers were made by IR analysis.

The composite films of polyacrylonitrile with polypyyrole and polythiophene were electrochemically prepared at different compositions. The change in conductivity of composites were analyzed as a function of the one of the insulating component. IR, DSC, TGA, SEM analyses were used to characterize the polymer composites.

Keywords : Conducting Polymers, Composite Polymer, Electrochemical Polymerization, Electroactivity, Electrochromism, Water Vapor Sensing

ÖZ

ELEKTROKİMYASAL YÖNTEMLE ÜRETİLEN YALITKAN , İLETKEN AKRİLONİTRİL POLİMERLERİ VE KOMPOZİTLERİ

Berrin (Yurttaş) Yılmaz
Doktora ; Kimya Bölümü
Tez Yöneticisi : Prof. Dr. Ural Akbulut
Yardımcı Tez Yöneticisi : Prof Dr. Levent Toppare

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Akrilonitril monomeri sabit gerilim elektroliz yöntemi ile polimerleştirilmiştir. Polimerizasyon öncesinde monomerin indirgenme gerilimi dönüşümlü voltametri ile tesbit edilmiştir ve polimerleşme gerilimi bu değerde tutulmuştur. Polimerleşme kinetiği gaz kromatografi analizleri ile takip edilmiştir. Polimerleşme ortamı sıcaklığının dönüşüm, verim ve viskositeye etkisi irdelenmiştir. Ürün analizi IR tekniği kullanılarak yapılmıştır.

Elektrokimyasal yöntemle üretilen poliakrilonitril ve ticari bir poliakrilonitril, iletkenliklerinin artırılması amacı ile ısıl işleme tabii tutulmuşlardır. Isıl işlem esnasında, uygulanan sıcaklık, ortam ve dopant etkisi araştırılmıştır. Isıl işlem gören polimerlerin iletkenlikleri ölçülmüştür ve su buharına duyarlılıkları ve bu duyarlılığın sürekliliği saptanmıştır. Polimerlerin karakterizasyonu IR ile yapılmıştır.

Polipirol - poliakrilonitril ve politiofen - poliakrilonitril kompozit filmleri elektrokimyasal yöntemle bileşenlerin değişik konsantrasyonlarında hazırlanmıştır. Komposit malzemelerde iletkenliğin bileşen konsantrasyonu ile değişimi takip edilmiştir. Polimer filmlerin tanımlanmasına yönelik IR, DSC, TGA, SEM analizleri yapılmıştır.

Anahtar Sözcükler : İletken Polimer, Kompozit Polymer, Elektrokimyasal Polimerleşme, Elektroetkinlik, Elektrokromizm, Sensör Davranışları.

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INTRODUCTION

1.1. ELECTROCHEMICAL POLYMERIZATION

Electrolytically initiated polymerization or shortly electropolymerization generally means initiation by the electron transfer processes which occur at the electrodes of an electrolytic cell containing monomer and an electrolyte, in that by controlling electrolysis current or potential. It is possible to control the generation of initiating species by controlling the applied potential. Under appropriate conditions electropolymerization may proceed by free radical, anionic or cationic mechanism.

Three general applications of electrochemical techniques to polymerization processes may be formulated. (a) Electroinitiated polymerization may be defined as the polymerization by an initiator formed in an electrode reaction. The initiator may be an oxidized or reduced additive. The technique is generally confined to vinyl monomers and offers the advantage of control over polymerization process, and, hence, control of the molecular weight of the polymer. (b) Electrochemical alteration of the polymers is merely electrochemical oxidation or reduction of an electroactive moiety on a polymer. The technique may be used to add monomeric or polymeric substituents to a polymer or to deposit a polymeric film on the surface of an electrode from a solution. (c) Electrochemical condensation polymerization may be defined as polymerization which proceeds with the addition or removal of one or more electrons per electroactive unit of a monomer followed by bond formation among the oxidized or reduced species, or unreacted monomer [1, 2]. The electrode - monomer relationship was explained as the adsorption of the monomer on the surface of the electrode followed by an electron transfer. After reaching to a certain length, the growing chain was desorbed from the electrode surface to the bulk of the solution. The polymerization can proceed through the desorbed growing chain or can be terminated by some other species [3, 4].

The electroinitiated polymerization can be carried out by Constant Potential Electrolysis (CPE) or Constant Current Electrolysis (CCE). The main advantage of CPE is the selective polymerization through the monomers' reduction or oxidation potential, since the potential is kept constant. However, in CCE the potential is let to vary and therefore undesired electrochemical reactions may take place [5, 6].

1.2. POLYMERIZATION OF ACRYLONITRILE

Acrylonitrile has been established as one of the most important building blocks of the plastic industry. Its unique properties have resulted in broad applications for a number of important market areas. Acrylonitrile was discovered in 1893 but had limited industrial applications until the development of nitrile rubbers during World War II . Later in the 1950s, acrylonitrile found its greatest use in synthetic fibers. In the late 1950s plastics of acrylonitrile appeared in the market. [7]

Acrylonitrile homopolymer has little application except for fibers because the combination of high melting point, poor thermal stability, and high melt viscosity make melt processing very difficult. However, by copolymerizing acrylonitrile with other monomers, these deficiencies have been tempered and a large measure of the unusual properties of acrylonitrile have been incorporated into melt-processable resins [7]

Polymerization of acrylonitrile by electrochemical techniques have been investigated by many authors. One of the most important investigation was carried out by Funt et al. They polymerized acrylonitrile electrolytically in dimethylformamide (DMF) saturated with sodium nitrate ($NaNO_3$) by applying constant current in a two compartment cell with Pt electrodes. They suggested the chain initiation by direct electron addition to the double bond of monomer where the nature of chain initiation was investigated through polarographic measurements. The analysis indicated the simultaneous presence of free radical and ionic mechanism at the same electrode. The effects of current, time and monomer concentration were studied. The yield of polymer increased linearly with time at fixed current density and showed first order dependence on monomer concentration. The molecular weights of the polymers are remarkably independent of monomer concentration, rate and current density. Colored cathodic polymer and white anode polymer were obtained. The polymers did not show any stereoregularity [8]

Electrolytical systems contains supporting electrolyte and polymerization is usually thought to proceed in an ionic atmosphere arising from the ionic dissociation of the salt. The influence of electrolyte type on anionic polymerization of acrylonitrile in DMF was investigated. Various kinds of the quaternary alkyl ammonium perchlorate salts i.e. tetra-n-propylammomium perchlorate ($(n\text{-}C_3H_7)_4NClO_4$), tetraethyl ammonium perchlorate ($(C_2H_5)_4NClO_4$) and tetramethylammonium perchlorate ($(CH_3)_4NClO_4$) were used . They preferred these salts to study electroinitiated anionic polymerization, because their reduction potentials are rather high and direct reduction of vinyl monomers is possible at the cathodic surface. They applied constant current in a two compartment cell, the reaction temperature was adjusted to 0°C and the cathode compartment was stirred continuously. They suggested that the initiation is via radical anion and the polymerization proceeds through anionic mechanism at the cathode compartment. High molecular weight polyacrylonitrile is obtained in dry systems. The rate of polymerization and the molecular weight of polymer was found to increase with increasing size of alkylammonium ion of the supporting electrolyte. Taking the electron donating inductive effect of the alkyl group into consideration, it is presumed that a smaller alkyl group in the ammonium ions makes it more reactive. Thus, decreasing the size of alkylammonium ion caused a corresponding increase in the termination constants [9].

Kolthoff et al. used cumene hydrogenperoxide (CHP) compounds to initiate polymerization of acrylonitrile in aqueous sulfuric acid with and without Fe^{+3}. They reported that free radical intermediates formed by direct reduction of peroxo compounds at the cathode or by the reduction by Fe^{+2} ions formed in situ by cathodic reduction of Fe^{+3} ion, initiated the polymerization. The authors reported that polymer was formed in the presence of Fe^{+3} ion when CHP was used in aqueous H_2SO_4, whereas no polymer could be obtained when CHP was electrolyzed in aqueous H_2SO_4 in the presence of acrylonitrile [10].

The electropolymerization of acrylonitrile was investigated by using t-butyl hydroperoxide (tBHP) and CHP in aqueous medium with KCl as the supporting electrolyte [11]. They used H-shaped two compartment cell with Pt foil cathode and smooth cylindrical graphite anode. The suggested mechanism is the reduction of peroxide (ROOH) to form a radical $(RO\cdot)$ which attacks the monomer to initiate the polymerization. Higher rate of polymerization observed with tBHP as the initiator compared to CHP is due to higher reactivity of t-butoxy radical toward the monomer as compared to cumyloxy radical. In summary, the cathodic polymerization of acrylonitrile takes place via the reduction of hydroperoxides in aqueous KCl solution resulting in high average molecular weight polymer. The polymerization was heterogeneous.

1.3. HEAT TREATMENT OF POLYACRYLONITRILE

PAN is one of the precursor material used for the commercial production of carbon fibres. The reason for this is that a low temperature heat treatment of textured fibre leads to the formation of the thermally stable, highly oriented molecular structure which is not catastrophically disrupted during the carbonization treatment [12, 13]. It was also known that when subjected to special heat treatment PAN acquires semiconducting properties.

The heat treatment includes first an oxidative stabilization of precursor fibers to prevent melting or fusing together. Second, a carbonizing heat treatment to drive off the majority of non-carbon elements takes place. Third, an optional high temperature treatment, often called graphitizing is designed to improve the mechanical properties of the carbon fibre. The temperature for three steps for PAN heat treatment is 220°C, 1000-1500°C and above 3000°C, respectively.

Acrylonitrile polymerizes through the carbon - carbon double bond, producing a linear macromolecule containing nitrile side groups. Since the nitrile groups are unsaturated there exists the possibility of an additional polymerization reaction through them. This reaction may be induced by simply heating the polymer. The stabilization through nitrile polymerization results in a thermally stable cyclized structure. Stabilization is accompanied by the color change of fibre from white through shades of yellow late turning to reddish brown and finally black arising from the formation of chromophore in the cyclized nitrile structure.

It has been found that to produce high performance carbon fibres it is generally better to polymerize the nitrile groups in air rather than inert atmosphere where the final carbon yield is higher with improved mechanical properties. In inert atmosphere the ladder polymer must be produced at a very low rate in order to ultimately produce a carbon fibre with good mechanical properties.

Different type of chemical structures was proposed for the oxidized PAN. The most likely possible chemical structures of PAN fibres pyrolized at 220°C in air and in nitrogen atmosphere were proposed by Grassi [14] (Figure 1). It appears that the principle structural difference between oxidative and non-oxidative treatments is that the former results in fully aromatic heterocycles carrying hydroxyl groups while the latter produces hydrogenated heterocycles containing carbon-nitrogen conjugation. Oxidative heat treatments result, therefore, in more thermally stable molecular structures than in the case of inert heat treatments.

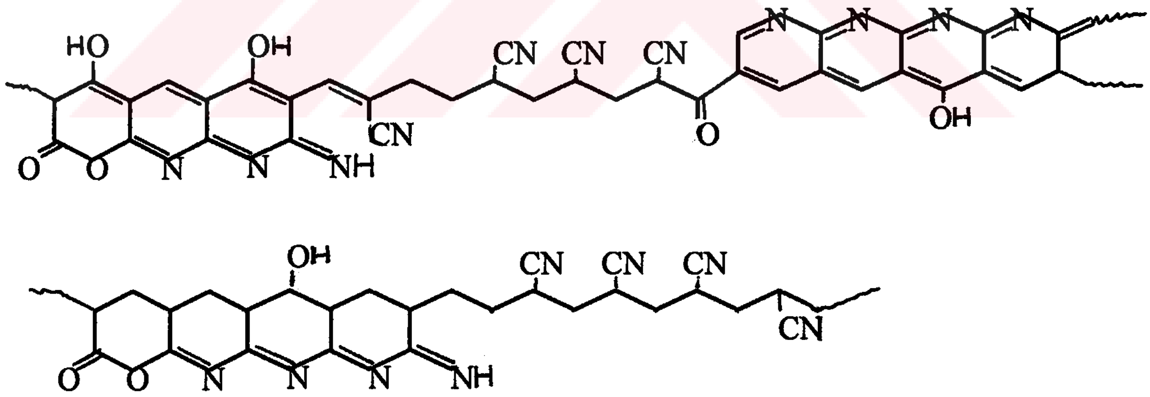


Figure 1. Possible Chemical structure of Courtelle Fibers after heat treatment at 220°C in air and under nitrogen atmosphere

The parameters influencing stabilization process include furnace temperature, time of stabilization, furnace environment and the precursor fibre characteristics.

It was found that the presence of Lewis acids increase the rate at which a thermally stable structure is formed. The polymerization can be assumed to be ionic rather than free radical and the Lewis acid should play a role in the mechanism. The following complex between the nitrile and the Lewis acid should be produced [13].

$$—C \equiv N + SnCl_4 \longrightarrow —C \equiv N - - - SnCl_4$$

Carbonization of the stabilized fibre is achieved by exposing it to high temperatures such as 1200-1500°C in an inert atmosphere. Although there is no fixed point of transition, the process at temperatures around 1700°C is termed as carbonization whereas a subsequent processing up to 3000°C is termed graphitization. The presence of oxygen results in oxides of carbon. A nitrogen environment is commonly used for temperatures up to 2000°C. Argon is used as the inert medium above this temperature because nitrogen reacts with carbon to form cyanogen. A steady flow of the inert gas is maintained within the furnace to flush out the released gases and to exclude oxygen from inside the furnace. It was reported that well stabilized fibres have a lower weight loss during carbonization than fibres with inadequate stabilization.

Heat treatment of PAN evolves mainly ammonia, hydrogen cyanide, water, nitrogen, hydrogen, oxides of carbon, hydrocarbons and nitriles. The gases evolved during heat treatment of PAN fibre is given in Figure 2 [13].

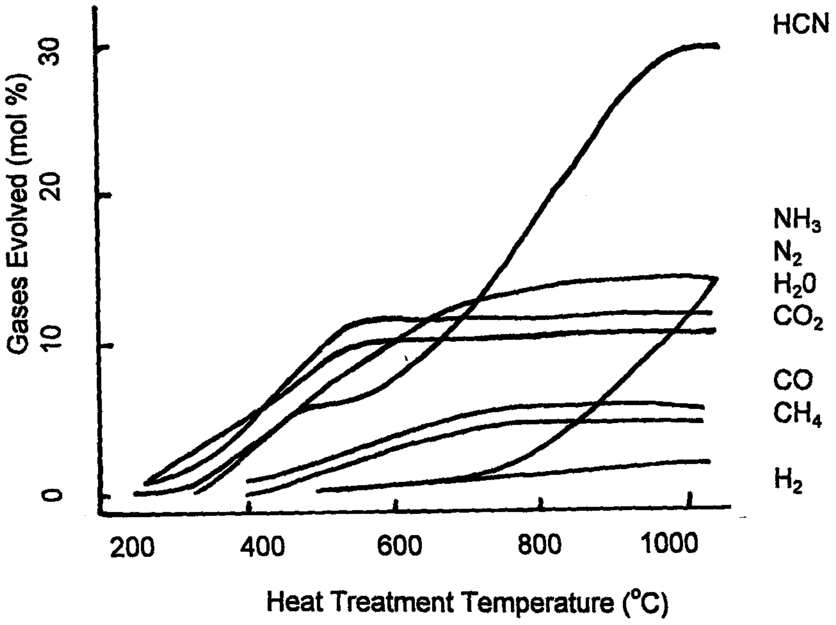


Figure 2. Gases released during high temperature treatment of PAN fibres

During stabilization, cyclization reaction of nitrile groups includes mainly evolution of hydrogen cyanide and ammonia. At temperatures above 270°C a large amount of hydrogen cyanide was produced. However, if the heating was carried out very slowly and up to the temperatures below 220°C, the hydrogen cyanide evolution was reduced [14,15]. For instance, after 5 hours heating at 220°C in vacuum, homopolymer fibres yield only 3 moles hydrogen cyanide per 100 moles of AN. In short, at these temperatures and under these conditions very little carbon-carbon unsaturation develops. The polymer becomes red owing to carbon-nitrogen conjugation. Termination reactions involving the repeated attact of growing free radical by hydrogen and meeting of two propagating ends have been put forward to explain evolution of ammonia. The reaction of HCN with water has also been suggested [16, 17, 18].

In case of carbonization , evolution of water as a result of the formation of intermolecular links between ladder sequences was proposed. These crosslinks contribute to the thermal stability of the structure during the subsequent processing and have been advanced as the chief reason for the importance of oxygen incorporation during stabilization. Reaction involving chain termination oxygen incorporation during stabilization. Reaction involving chain termination have been stated as the reason for the formation of ammonia. This could occur either by formation of ammonia from active chain ends or by the end to end joining of two ladder structures. Mechanism for evolution of hydrogen cyanide results from intermolecular reactions involving ladderized structures assumed to occur at higher temperatures. Nitrogen and hydrogen evolution at temperatures above 600°C was explained by inter-molecular reactions. [12, 13]. One of the proposed mechanism is given in Figure 3.

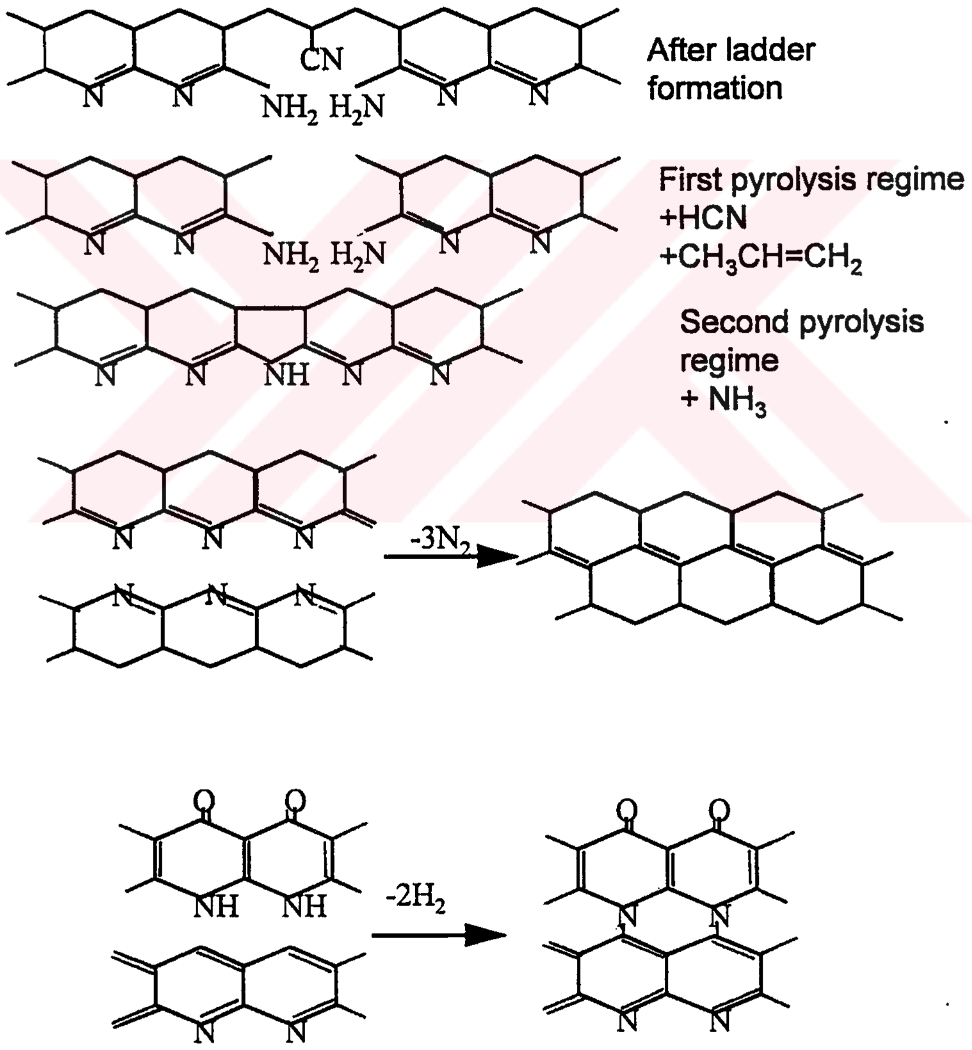


Figure 3. Mechanisms for evolution of gases during carbonization heat treatment

Besides direct heat treatment of PAN, Berlin et al [19] investigated the possibility of carrying out the heat treatment in dilute solutions. In these circumstances they expected that interactions between the polymer chains would be negligibly small, consequently crosslinking of the polymer would be avoided and it would thus be possible to obtain a soluble product. The solutions of 1 % PAN in DMF was heated in the presence of O_2 or air where in both case the gradual color change of polymer was observed. As the concentration of PAN was increased to 2-3%, the polymer precipitated in the early stages of heating. The heated polymer is soluble in DMF but not in ordinary solvents. As a result of this treatment of PAN degradation of the polymer occurs as well as oxidative dehydrogenation with formation of conjugated section in the polymer molecules. The products of heat treatment of PAN in DMF are distinguished by high heat resistance; they withstand heat up to 350-400°C. The spectral analysis of heat treated solution PAN indicate the absence of cyclization through the triple bond of — CN group which has an absorption signal at 2250 cm^{-1}. They suggested that the results indicate the probable formation of a complex between PAN and DMF.

The catalytic activity of pyrolyzed PAN has also been investigated [20]. White PAN was pyrolized at 230°C for a certain time followed by heating under nitrogen atmosphere at 450° C and the color changes slowly via yellow to brown. It is assumed that pyrolized PAN contains condensed pyridine ring, known to be a strong hydrogen acceptor, being capable of dehydrogenating olefinic compounds in vapor phase at elevated temperatures. The polymer becomes deactivated due to hydrogenation and needs to be reactivated. The reactivation was successful by air oxidation at 140°C. The catalytic activity of pyrolyzed PAN was observed in the oxidation of propanol-2 into acetone, cyclohexanol into cyclohexanone, cyclohexene into benzene. The polymer also causes cis - trans isomerizations in olefinic systems like butene-1 into butene-2.

The mechanism of hydrogen transfer from substrate to catalyst was considered as in the form of hydrogen atom or partly in the form of hydride ion.

The dielectric behavior of pyrolized PAN was investigated by Beek [21]. Acrylonitrile was polymerized chemically and the product was pyrolized for 5 hours at 170, 220 and 300°C under nitrogen atmosphere and compressed. The dielectric measurements were carried out between 0.1-300 kHz at 20°C. Pure PAN has a very broad dielectric loss region at 70 Hz which was ascribed to — CN groups. The 170°C pyrolized PAN has the same behavior to that of unpyrolyzed PAN. On the other hand 220 and 300°C pyrolizates did not show any disappearance which attributed to the formation of the conjugated chains by linking of — CN groups above 220°C.

Pyrolyzed PAN (PANP) is well known for its high electrical conductivity (up to 20 S/cm). Fibres of PAN may also be transformed to electrically conductive PANP giving highly conducting woven material [22]. The electrical resistivity of PAN fibers was established as high as $\approx 10^6$ Ωcm whereas that of carbon fibers is low as 10^{-2}-10^{-4} Ωcm, but never as low as well ordered graphite (4×10^{-5} Ωcm). The authors have found that the major decrease in resistivity occurs below 1000°C, possibly with a greatest rate of decrease at ≈600°C [12].

Recent studies on cast films of PAN (mol.wt.485,000 or 15,000) resulted in PANP formed at temperatures of 390-435°C which have conductivity as high as $5\ \Omega^{-1}\,\mathrm{cm}^{-1}$.

It is possible to introduce PANP with n- and p- type conductance, depending on the conditions of preparation. Pyrolysis in vacuum at temperatures 340°C and 710 °C leads to PANP with a n-type conductance. Probably, owing to an absorbed oxygen. p-type conductance of PANP can be achieved at temperatures 500°C and 700°C [22, 23].

1.4 . ELECTRICALLY CONDUCTING POLYMERS

One of the fundamental properties of the polymers is that they are insulators to the flow of electric current. Although there is some charge transfer in most polymeric materials the resistance level is normally in the order of 10^{17} Ω. Up to late 1970's polymer physicists and chemists thought that organic polymers did not and could not conduct electricity at any appreciable level.

Although conductive rubber has been known since the latter part of the nineteenth century, it was not major interest until about 1930, when several patents described the use of the conductive compounds for the prevention of corona discharge in cables. Most of the early workers employed large quantities of graphite or other coarse carbon-blacks or powdered metals to achieve conductivity. The conductivity obtained by the addition of conducting filler to an insulating polymer is a result of intimate contact of the filler with each other.

The other class conductive synthetic materials are the polymers whose backbone are responsible for the generation or propagation of charge carriers. The introduction of acetylene black and later other conductive materials led to the production of rubbers having appreciable conductivity. The mechanical properties of early stage conducting polymers were poor but, later generations have mechanical properties approaching to insulating polymers. Sometimes, products which were intended to be insulating were found to have a significant conductivity [24]. To date only few polymers; polyaniline, polypyrrole, polyacetylene and their derivatives have been commercialized due to their environmental stability and level of conductance in plastic battery electrodes, static dissipation films etc.

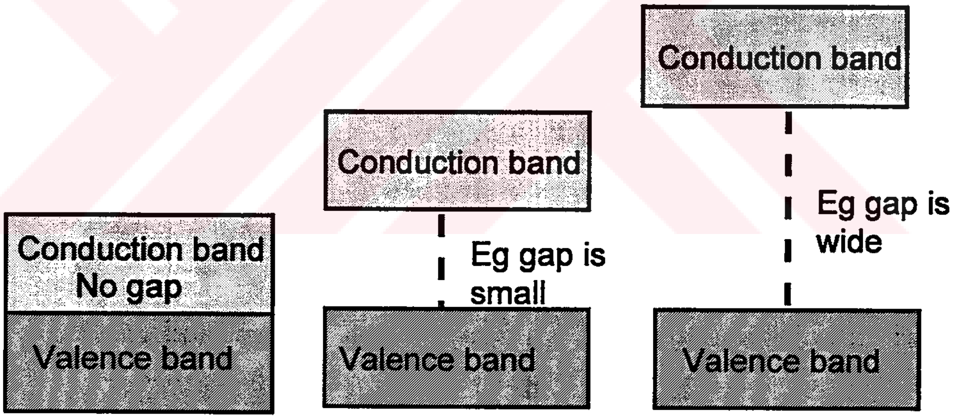
Regarding the conductivities of some materials, those having a conductivity of about 10^{-18} - 10^{-7} S.cm^{-1} are named as insulators, conductivities about 10^{-7} - 10^{-2} S.cm^{-1} are named as semiconductors, conductivities 10^{-2} - 10^{6} S.cm^{-1} are high conductivity materials [25]. The comparison of conductivities of various different substances including metals, conductive polymers and insulators are given in Table 1 [26].

Table 1. Conductivity Values of Some Materials.

Conductivity group	**Material**	**Conductivity (S/cm)**
Metals	Copper	1.5×10^{6}
	Gold	1.2×10^{6}
Conducting Polymers	Polyacetylene	1.0×10^{5}
	Polypyrrole	8.0×10^{3}
	Polyaniline	1.0×10^{3}
Semiconductors	Germanium	10^{-2}
	trans $(CH)_x$	10^{-4}
	Silicon	10^{-5}
Insulators	DNA	10^{-14}
	Diamond	10^{-14}
	Quartz	10^{-18}

1.4.1. BAND THEORY :

The theory often used to explain the electrical conduction of metallic materials is called band theory [25]. This theory simply states that in solids the orbital energies of the individual atoms are spaced closely together with a range of energies to form a wide band of closely spaced energy levels. The highest energy band containing electrons is named as the valence band and the next band is called as the conduction band. The valence and conduction bands are separated by an energy gap. If these bands are completely filled with electrons or completely empty no conduction occurs. If, however, an electron is promoted from a full band to an empty band then the previously filled band now has a hole and the electron in the higher energy, empty band, is free to move or delocalize over the band. Electrons moving in and out of the hole or delocalized over the higher band allow conduction to occur (Figure 4).



a : Metal b : Semiconductor c : Insulator

Figure 4 . Energy Level Diagrams for three types of solids.

In metals there is little or no separation in the energy between bands and the application of potential promotes electrons into the unoccupied bands and conduction occurs.

However, in insulators appreciably higher energy gap between bands prevents the promotion of electrons upon application of potential.

Semiconductors have a lower energy difference between bands and electrons can be promoted from valence to conduction band in the presence of energy applications.

1.4.2. INTRINSIC SEMICONDUCTORS :

There are two types of semiconductors being as intrinsic and extrinsic semiconductors.

The resistivity of intrinsic semiconductive polymers depends exponentially upon temperature. The excitation of electrons in valence band takes places into the conduction band at ambient temperatures. This excitation leaves a hole in the valence band. The excited electrons and holes are called as carriers in this case. The total conductivity (σ) results from the movement of both kinds of carriers. Most of the inherently semiconductive polymers contain conjugated structures.

1.4.3. EXTRINSIC SEMICONDUCTORS

The conductivity of polymeric systems can be changed by oxidizing or reducing the polymer chain. The oxidizing and reducing agents introduced to polymeric systems and their counter ions are referred to as the ‘dopant’ ion. If the polymer backbone is oxidized the system is p-doped where the p stands for the positive charge on the polymer backbone caused by the oxidation and subsequent loss of electrons. If, however, polymer backbone is reduced, the system is n-doped where n stands for negative charge on backbone.

The role of the counter ions of the oxidizing and reducing species is to stabilize the oxidized or reduced polymer by offsetting the charges formed on the polymer backbone. In many cases additional ionic species may be added to offset the charges on the polymer backbone. These ions are also referred as dopants.

Examples of oxidative and reductive doping of polyacetylene in the presence of either iodine or sodium ions are given in Figure 5.

$(CH)_n + I_2 \longrightarrow (CH)_n^{+} (I_3^{-})_{.33} + I^{-}$ oxidative doping (p-type)

$(CH)_n + xNa \longrightarrow (Na^{+})_x(CH)_n^{x-}$ reductive doping (n-type)

Figure 5. Schematic representation of p and n type doping

The smaller counter ions I_3^- and Na^+ dopants act simply as bystanders offsetting the positive or negative charge of the polymer backbone but not directly affecting the electrical conductivity of the polymer. In a purely chemical sense the dopped conductive polymer is a salt composed of oppositely charged ions.

A unique property of this system is the ability to turn the conductance on and off, that is changing from an insulator to conductor, by changing the concentration of dopant ion. This can be accomplished by applying an electric potential to the polymer causing the dopant ions to diffuse in or out of the polymer matrix depending on the oxidation state of the polymer and whether the applied potential is negative or positive in sign.

1.4.4. THEORY OF CONDUCTING POLYMER SYSTEMS

The conductivity (σ) in a polymer system is a function of charge carriers as given in below equation.

$\sigma = nq\mu$

where ; n is the total number of carriers
q is the charge on the carrier
μ is the mobility of carriers.

Charged carriers can either be electrons (negative carriers) or holes (positive carriers). It is generally recognized that for an organic polymer to support electronic conduction, the polymer must contain an overlapping set of molecular orbitals to provide reasonable carrier mobility along the polymer chains. In addition, since most organic polymers do not have intrinsic charge carriers, appropriate charge carriers must be provided by some extrinsic means, i.e. dopants.

In conductive polymers simple band theory (Section 1.4.1.) does not explain conductance since these polymers can conduct electricity without partially empty or partially filled bands. In that case the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of polymer systems participate in conduction. Normally the difference between the HOMO and LUMO orbital bands is around 4 to 5 electron volts in the insulator stage and less than one electron volt in the conduction stage [27, 28]. Upon doping, i.e. oxidation or reduction of polymer backbone, the band gap between HOMO and LUMO of the polymer system is reduced by forming new conduction bands of polarons or bipolarons in between above mentioned molecular orbitals. Electrons can move into these polaron, or in the case of two new bands being formed, bipolaron energy levels leaving holes in the HOMO level and a new conduction path in the polaron bands which may or may not overlap with the LUMO energy levels. The conduction mechanism in these materials are still complicated and are an active area for scientists.

1.4.5. FORMATION OF POLARONS AND BIPOLARONS :

In conductive polymers the actual charge carriers on the polymer backbone are called polarons or bipolarons. Polarons and bipolarons are formed by the concerted oxidation and doping of the polymer. This involves removing electrons from the polymer in the case of oxidation and the diffusing of the dopant ions into the polymer to offset the positive charge. An example of polaron structure and the charge propagation in polyacetylene is given in Figure 6 26, 29.

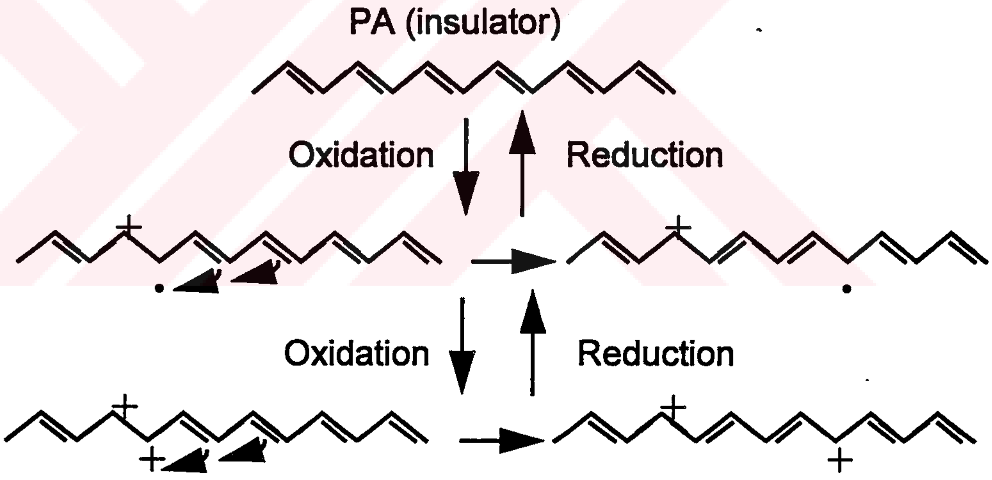


Figure 6 . Polaron and Bipolaron Formation.

1.4.6. HOPPING PROCESS

At the conceptual level the earlier assumptions in this area has been that a conjugated backbone is a prerequisite for a polymer to become electronically conducting. However, later investigations indicated that the charge transfer capability should not be limited to conjugated polymer systems alone. The conductivity in nonconjugated systems were attributed to the availability of some other type charge transfer named as hopping[30].

Movement of electronic charge in a polymer theoretically must involve at least three steps as given in Figure 7.

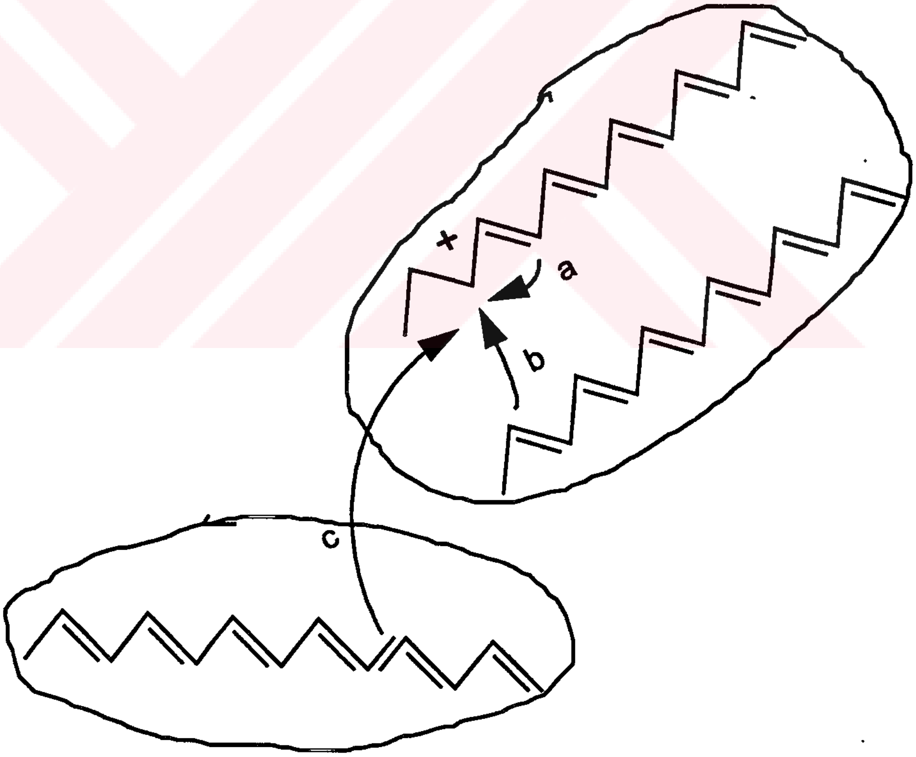


Figure 7. Movement of electronic charge in a polymer: (a) along the conjugated chain within a crystallite(b) from chain to chain in a crystallite(c) from chain to chain in an amorphous region

1.5. POLYMERIZATION OF PYRROLE

The electrochemical preparation of conducting polymers dates back to early attempts of Dall'Olio and coworkers [31] who obtained "pyrrole black" as it was called at that time,on electrochemical oxidation of Pyrrole (Py) in aqueous H_2SO_4 as powdery insoluble precipitate on Pt electrode. Elemental analysis of the product showed that, the pyrrole black consisted of 76% polypyrrole (PPy) the remainder being sulfate ions, therefore the polymer was cationic. It was found to have an electrical conductivity of 8 $S.cm^{-1}$.

Good quality films were first obtained by Kanazawa et al. [32, 33] and Diaz et al [34] using a modification of the electrochemical technique pionered by Dall'Olio et al [31].

Preparation of PPy has been performed in an aqueous solution of Py and cuppersulfate ($CuSO_4$) in one compartment cell equipped with two electrodes [35]. A convenient choice would be cupper for cathode and Pt or Indium-tin oxide coated glass side for the anode. A bronz to blue black film of PPy sulfate formed at the anode when , 0.5 V is placed across the electrodes using a battery. Under these circumstances, the counter electrode reaction was the deposition of metallic cupper on the cathode. During the preparation, the pH of the solution decreased, consistent with the elimination of the alpha protons. The PPy sulfate films can be readily removed from anode and have good mechanical properties. This aqueous technique can be used to introduce a variety of inorganic anions as well as some large organic anions such as tetrasulfonated cupper phtalocyanines, dodecylsulfate and polystrene sulfonate. The electrical properties of these films are acceptable, where dodecylsulfate films have conductivities higher than 100 $S.cm^{-1}$ but they contain significant amounts of excess oxygen. Although this aqueous technique may prove to be the method of choice for the industrial preparation of large films, or continuous ribbons of film, the poor stoichiometry of the resulting films makes them difficult to be characterized.

The technique described by Diaz et al [34] used 99% aqueous acetonitrile solutions of tetraalkylammonium salts as the electrolyte in a two electrode cell to grow films of PPy which adhere to the surface. Although these films were poorly characterized, their conductivities with two probe method were higher (40-100 $S.cm^{-1}$) than the grown in aqueous media.

A modification of this technique is to use carefully dried and deoxygenated acetonitrile solutions of $AgClO_4$ as the electrolyte in a dry box [36]. Ag^+ play the same roll as the cupper ions in aqueous preparation, providing a facile cathode reaction which does not interfere with the film forming reaction at the anode. This technique leads to extremely smooth films of good stoichiometry and eliminates the problem of excess oxygen; however, the films, like all other PPy films reported so far, still contain excess hydrogen, the origin of which is not understood. Despite their improved stoichiometries, these films have no better electrical conductivities than the previous films.

Py can be oxidatively polymerized in both solution and vapor phase [27, 37. Though chemical oxidation usually leads to powders, films can be obtained by allowing the oxidation to take place at a solid or liquid surface [38]. However, these films are of poor quality. In some cases there is no evidence that these chemically prepared films have much in common with what is now meant by PPy, indeed, they are not even conducting.

The solvent in electropolymerization has a very strong influence on the formation of good films. The effect of different solvent-electrolyte couple on the polymerization of Py has also been investigated. But, in the majority of cases, the films are produced so readily that the only serious limitations are the nucleophilic nature of the solution and the nature of the working electrode. As can be seen from examples in Table 2, a wide variety of aprotic solvents can be used, as long as the nucleophilic character of the solvent is poor [39]. If the nucleophilic character of the solvent is enhanced, film formation is minimized. This can be seen from the results of adding small amounts of pyridine to the acetonitrile solution. Films are not produced in the nucleophilic aprotic solvents such as DMF, dimethylsulfoxide and hexamethly phosphoramide, unless the nucleophilicity of solution is reduced by addition of aprotic acid. In solvents with nucleophilic characteristics intermediate between water and aprotic solvents, such as alcohol and mixed aqueous-aprotic solvent mixture, films can be prepared with intermediate conductivity values and good physical strengths. The quality of these films can be improved by adding a protic acid to the reaction solution in order to reduce its nucleophilic character.

Table 2 . Solvent Effects of the Quality of Generated Polypyrrole Films (Pyrrole 0.01 M was oxidized on a Pt electrode)

Solvent / Electrolyte (0.1 M)	**Film Quality**	**Conductivity (S/cm)**
Acetonitrile / tetraethylammonium tetrafluoroborate	good film	50
Acetonitrile / tetraethylammonium tetrafluoroborate plus 1.0 M pyridine	no film	-
Methylene chloride / tetrabutylammonium tetrafluoroborate	good film	50
Dimethylformamide /tetraethylammonium tetrafluoroborate	no film	-
Dimethylformamide / toluenesulfonic acid	good film	20

A wide variety of anions have been used to prepare thick free standing films in electrochemical preparation of conducting PPy films [39]. The conducting films contain 10-35% anion by weight. The amount of anion found is the characteristics of each film. For instance, anion content of PPy is 25 - 30 % whereas that of PTh is 7 - 25 %.

The properties of the films can be conveniently altered by changing the anion. Since the anion in the film is incorporated from the electrolyte salt in the preparative solution, the modifications can be made by simply changing the electrolyte salt of the solution. Few examples are given in Table 3 to show the influence of anion in PPy conductivities. Poorly nucleophilic tetraalkylammonium salts were used in the preparation of these films. Anion influence on the topology and the electroactivities of the films were observed [39, 40].

Table 3 . Polypyrrole films with different anions

Anion	**Conductivity (S/cm)**
Tetrafluoroborate	30 - 100
Hexafluoroarsenate	30 - 100
Perchlorate	60 - 200
Fluorosulfonate	0.01
Trifluoroacetate	12

The electrical properties of PPy are quite stable in air at room temperature. In case of unprotected films, the conductivity decreases only by about 20% in a year. By appropriate protection, considerable improvement in stability can be expected. At elevated temperatures PPy is stable to 100-200°C, depending on the nature of the anion. PPy is quite stable to acids, but bases can cause some partially reversible loss of conductivity [33].

1.6. POLYMERIZATION OF THIOPHENE

Thiophene provides a system closely related to Py and thus PPy, but in certain respect it is easier to study. Polythiophene (PTh) exhibit high chemical and electrochemical stability, doping level and a highly regular backbone which are all required criteria for their properties. The commercial availability of a wide variety of substituted thiophenes is a distinct advantage of Th. However, not all thiophene monomers yield conducting amorphous polymer films.

Polythiophene and its derivatives can be chemically or electrochemically synthesized . By chemical or electrochemical oxidation or reduction of the polymer the electrical conductivity of films can be varied.

Th and substituted Th show irreversible oxidation peaks and give rise colored solution upon electrooxidation. It was known that, like PPy, films are electroactive and can be cycled repeatedly between the oxidized conducting state and the neutral state, an event which is accompanied by a reversible color change from green-black to pale orange, respectively [39].

PTh films were thought to be more stable with respect to PPy film. This was explained as a consequence of rather high oxidation peak potential for PTh. Therefore, unlike PPy films, neutral or electrochemically oxidized PTh films can be exposed to air and even passed under stream of oxygen. Yet, it was later found out that when oxygen and humidity are present together, the polythiophene was reduced back to insulating regime. Analysis of neutral films do reveal the presence of bonded oxygen at the surface of these films [28, 41].

The effect of temperature on electrochemical polymerization of Th was studied by cyclic voltammetry under N_2 atmosphere [42]. Polymerization solvent

- electrolyte system was $LiClO_4$-CH_3CN working and counter - reference electrodes were Pt and SCE respectively. The increase in temperature from 0°C to 20°C, promotes a faster surface polymerization process with each potential cycle and as a result thicker polymer layers are obtained with a lower number of potential cycles. But at higher temperatures like 40°C, the monomer oxidation take place on the same potential region, but thin polymer films were obtained without any conductivity.

PTh and substituted PTh electrochemically generated as thin adhesive films or as thick powdery deposits. The electrochemical medium involving acetonitrile, tetrabutylammoniumperchlorate, Pt or gold electrodes were used. The thickness of the films was an important parameter on morphology and conductivity. Thin films having a thickness of 10^{-3} - 10^{3} A° have a conductivity of $2x10^{3}$ $S.cm^{-1}$. But as the film thickness is increased to 3500-5000 A°, type of coupling of Th units are changed and conductivity became 10 $S.cm^{-1}$. The morphology of the films changes with the thickness [43].

1.7. COMPOSITE POLYMER FILMS

Most commonly faced problem in conducting polymers is the poor mechanical properties which creates processing problems. Recent studies and this report are concentrated on the obtaining conducting polymers and polymer blends. One of the applied technique is to produce polymer blends of an insulating matrix and a conducting component. By that way, it is claimed that the mechanical property of the conducting component is improved [44, 46]. The conducting property of the blend is kept almost the same level of conducting one by determining the threshold point. In this work in terms of blends we are concentrated on the blends of Py and Th with PAN.

1.7.1. POLYPYRROLE BLENDS

Recently, deposition of PPy within a matrix of insulating polymer, or copolymerization yielded conducting polymers with improved properties.

Lindsey and Street [27] have demonstrated that PPy sulfate can be electrochemically deposited from an aqueous electrolyte solution into a polyvinyl alcohol film. Thin films of this composite polymer material had conductivities as high as 10 $S.cm^{-1}$ and excellent mechanical properties permitting it to be folded without cracking.

Another example is the electrochemical polymerization of Py on an electrode covered with an insulating film such as polyvinyl chloride (PVC) and vinylidene fluoride - trifluoroethylene copolymer [44]. They observed that, incorporation of PPy into the film greatly increases the electrical conductivity of film, where PVC/PPy alloy films has a conductivity of 0.2-1.5 S/cm, PVDF-TnFE/PPy alloy film has a conductivity of 15 S/cm. The percolation process, did not change the mechanical property of the insulating component and improved the thermal stability of the film in a high-temperature region.

Another versatile approach to systematic modification of the mechanical properties of PPy is via copolymer formation. Nazal and Street [27] have prepared Py-Styrene copolymer films varying in their properties, depending on the ratio of styrene to Py. Films with a high concentration of styrene were rather tough like Polystyrene , but with electrical conductivities of about 10 S/cm similar to PPy. Films with a low concentration of styrene had higher conductivities, about 50 S/cm, but their mechanical properties were similar to PPy tetrafluoroborate. Thus, either by appropriate choice of the anion or electrode material or composite formation, very satisfactory mechanical properties can be achieved for PPy.

The electrochemical preparation of blends of the conducting polypyrrole and polythiophene with the insulating host polymer, polystyrene and polycarbonate resin have been reported [45] The authors observed threshold conductivities at ca. 18 % for both conducting polymers in blends with polystyrene. With polycarbonate resin blends, polythiophene exhibits a threshold at ca 12 %, and polypyrrole exhibits a threshold at ca. 7 %. This low threshold conductivity of composites was attributed to the blend homogeneity enhanced by hydrogen bonding.

Electrochemical preparation of composites of PPy with an insulating polymer, polyamide was also carried out by Selampýnar [46] . They obtained a composite in which there exists H-bonding between the two polymers and a possible grafting to a certain extent. Polyamide film was dipcoated from chloroform solution and placed in TBAFB-CH_3CN_3 electrode system containing Py monomer and electrolyzed. They observed 4 $S.cm^{-1}$ conductivity when Ppy % was 24 and increased up to 19 $S.cm^{-1}$ when Ppy % was 62. The measured the conductivity of pure PPy was 25 $S.cm^{-1}$ via four probe method.

An investigation about PAN - PPy composite films has been carried out by Bhat et al. PAN was used as the polymeric matrix that was prepared by dissolving PAN in DMF and followed by addition of $FeCl_3$ as an oxidizing agent. A few drops of this solution was poured on a glass plate and dried. This film was exposed to pyrrole vapor at room temperature. Formation of composite film of PAN-PPy was established by IR and thermal analysis. The films showed improved thermal stability and electrical conductivity. The resistivity of PAN was determined as 16 MΩ cm and decreased gradually up to 20 KΩ cm with increasing incorporation of PPy (5.8 wt%PPy). The strength of the composite film decreased as compared to pure PAN [23].

1.7.2. POLYTHIOPHENE BLENDS

Conducting polymer composites of PTh and polyamide as the insulating matrix were prepared via electrochemical methods. The characterization analysis and conductivity measurements reveal the resultant composites have different properties from the simple mechanical mixture of two polymers [47].

The synthesis of conducting polymer composites of PTh with insulating natural and synthetic rubber was achieved [48]. The composites were prepared by CPE. The working electrode was dip coated with insulating polymer from toluene solution and immersed into the electrolysis cell containing Th. The characterization analysis and conductivity measurements proved that the resultant composites have different properties compared to Pth. It was attributed to the interaction of the synthetic or natural rubbers with electrochemical polymerization of Th. The authors observed 1x10^{-1} S/cm conductivity at 65 % PTh and 6x10 -1 S/cm conductivity at 95 % PTh for synthetic rubber - PTh composite films. Natural rubber - PTh composite has 3x10 $^{-1}$ S/cm conductivity at 80 % PTh and 3.7x10 -1 S/cm at 95 % PTh.

1.8. APPLICATIONS OF CONDUCTING THIOPHENE AND PYRROLE BLENDS

Serious attention has been given to their applications as the active element in display devices which would take advantage of color change that accompanying electrochemical switching of the polymers between the conducting and insulating regimes.

PPy appears to be seriously considered as a battery material but its nonfibrous structure is a disadvantage. The reversible doping and undoping process of PTh makes them good candidates for secondary battery electrodes.

A number of workers pointed out that both PPy and PTh can serve as pacifying layer of semiconductors, particularly n-type semiconductors in photoelectrochemical solar cells, where a thin layer of the polymer effectively inhibits photocorrosion [28, 49].

A PPy membrane has been used as an ion gate, which offers lower resistance to ion transport when the polymer is in the neutral form and a higher resistance when in the oxidized form [27].

In summary, for successful performance of these materials in various applications such as batteries, apart from the desirable electroactivity, the stability of films under different conditions becomes of paramount importance. For example, oxidized films placed in strong acid HCl or base NaOH, or in a solvent such as dichloromethane for a certain period of time, do not dissolve and they retain their electroactive properties when subsequently electrochemically cycled. Although the thicker films are less thermally stable to heating at 80°C and their conductivity is decreased, thin films has an extensive stability and they retained the conductivity [39].

CHAPTER 2

EXPERIMENTAL

2.1. PURIFICATION OF MATERIALS

2.1.1. ACRYLONITRILE (AN)

Acrylonitrile was washed several times with dilute H_2SO_4, then with dilute Na_2CO_3. After washing with H_2O, it was dried over CaH_2 for overnight and fractionally distilled under N_2. The purified AN distilate was collected at 74 °C. The distillate was kept in cold.

2.1.2 ACETONITRILE

Acetonitrile was dried over CaH_2 overnight and fractionally distilled over fresh CaH_2 under dry N_2 atmosphere.The details of purification was discussed in earlier reports [50].

2.1.3 TETRABUTYLAMMONIUMFLUOROBORATE (TBAFB)

This chemical is used as the electrolyte. It was prepared by the titration of tetrabutylammonium hydroxide with concentrated fluoroboric acid.

The precipitate is TBAFB and purified by recrystallization. The preparation and purification details of TBAFB were discussed in earlier reports (50)

2.1.4 DIMETHYLFORMAMIDE (DMF)

DMF was stirred with anhydrous $CuSO_4$ for 48 hours and then distilled under vacuum at 30°C and 4 torr.

2.1.5 ALUMINUM CHLORIDE ($AlCl_3$)

$AlCl_3$ was used without further purification.

2.1.6 HYDROQUINONE (HQ)

HQ was used without further purification.

2.1.7 COMMERCIAL POLYACRYLONITRILE (CPAN)

CPAN (Aldrich Chem.Comp.Inc.) was used without further purification. The bottle label informations of CPAN are : $Tg = 80^{\circ}C$, $T_m = 317^{\circ}C$, $nD_{20} = 1.5140$, density = 1.184, the molecular weight is about 80,000.

2.1.8 PROPIONITRILE (Pn)

Pn (Merck) was used without any further purification.

2.1.9. PYRROLE (Py)

Pyrrole was dried on CaH_2 for overnight and distilled under vacuum in the presence of CaH_2 at 10 mmHg and 42°C.

2.1.10. THIOPHENE (Th)

Thiophene was dried on CaH_2 and fractionally distilled at 83°C in the presence of CaH_2 . The first fraction of distillate was discarded.

2.1.11. DICHLOROMETHANE (DM)

Reagent quality dichloroethane (Merck) was dried overnight over CaH_2 and distilled at 36 °C.

2.2. APPARATUS

2.2.1. CYCLIC VOLTAMMETRY SYSTEM (CV)

The system is composed of a Tacussel potentiostat, Sefram XY-recorder and a CV cell with working and counter electrode and a Ag/Ag^+ reference electrode. Working electrode is a platinum bead on which the electrochemical reactions occur. Counter electrode (Pt) wire is coupled with working electrode to supply current flow. The reference electrode contains 0.01 M silver fluoroborate and 0.1 M TBAFB. The details of CV system was given in earlier reports [50].

2.2.2. CONSTANT POTENTIAL ELECTROLYSIS SYSTEM (CPE)

Except the cell the same instruments of CV system is used in CPE. The electrolysis cell contains three electrodes being as working, counter and reference electrodes. Working and counter electrode compartments are separated by a sintered glass disc. The working and counter electrodes are Pt foils with 2 cm^2 area. The reference electrode is the same as the CV system. The details and the shape of CPE system is given elsewhere [50).

2.2.3. INFRARED SPECTROPHOTOMETER (IR)

A Perkin Elmer 177 grating type and Nicolet 510 FT spectrometer were used.

2.2.4. GAS CHROMATOGRAPHY (GC)

A Hewlett - Packard 5890A gas chromatography with a columns of Porapak Q was used. The dimensions of the column is 1.5 m length and 3.2 mm outer diameter.

2.2.5. VISCOMETER

Viscosities of samples were measured in DMF at 25 °C by capillary Ubbelohde viscometer.

2.2.6. HEAT TREATMENT OF POLYACRYLONITRILE

Heat treatment of PAN was carried out in test tubes (Figure 8). PAN was used as pelletized form for all treatments. Treatments under atmospheric conditions and in the absence of dopant were carried out in the test tube given in Figure 8.a. The tube containing pelletized PAN was placed into the oven. Treatments under vacuum and in the absence of dopant were carried out in isolated tubes (Figure 8.b). Before the isolation the set up was connected to the degassing vacuum line. Treatments of PAN in the presence of dopant were carried out by using a pair of test tube connected to each other (Figure 8.c, d). Direct contact of doping agent with PAN was avoided.

Those which were carried out under vacuum were degassed and isolated before treatment (Figure 8.d).

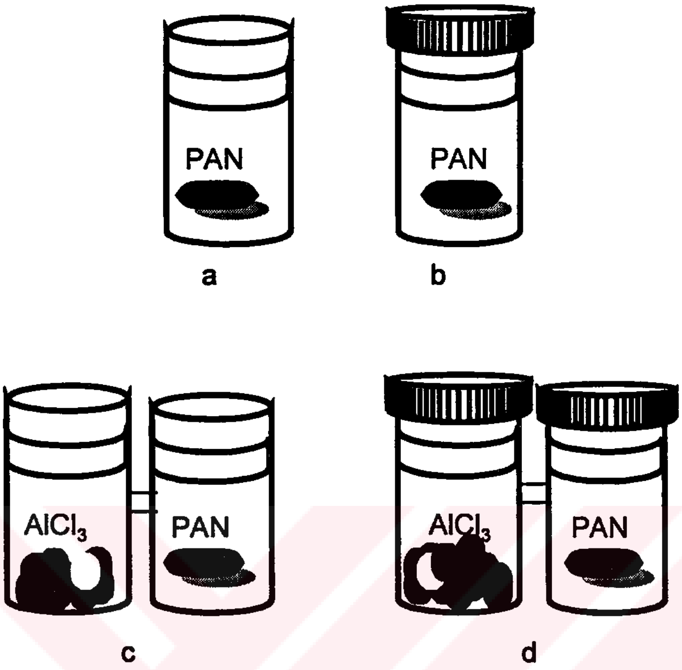
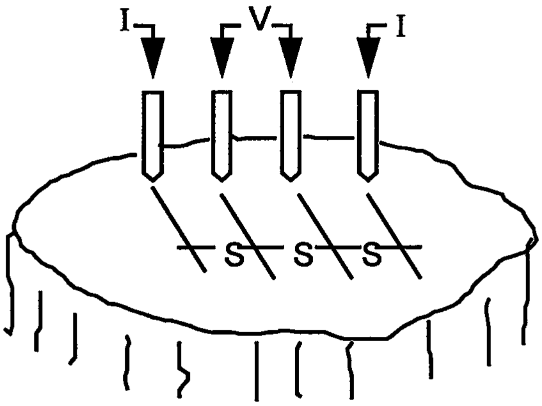


Figure 8 . Heat treatment system (a) : PAN under atmospheric conditions, (b) : PAN under vacuum, (c): PAN under atmospheric conditions and in the presence of dopant, (d) : PAN under vacuum and in the presence of dopant.

2.2.7. CONDUCTIVITY MEASUREMENT SYSTEM

The conductivity measurement of polymers was done by using four probe method. As explained in earlier reports in this method four equally spaced osmium tips are placed on the surface of the sample. The current is passed through the outer tips, the voltage drop is measured across the other two (Figure 9).



$\rho = (V/I) \times 2\pi S$

where

ρ : resistivity
V : potential difference
I : current
S : probe spacing

Figure 8. Schematic diagram of four probe method

2.2.8. MOISTURE SENSITIVITY ANALYSIS

The sensitivity of PAN and heat treated PAN to moisture were measured by means of the set up given in Figure 10. The whole set up was placed into a constant temperature bath. The temperature of water in the balloon was monitored by a thermometer. The sample was attached by conducting adhesive to the tips of two cupper wires. The wires were connected to a two probe digital multimeter.

The moisture sensor analysis was performed by two probe technique where the sample dimension is in consideration (Figure 11). The change in resistance of sample was determined. The probes were fixed by a conducting electrodag paste.

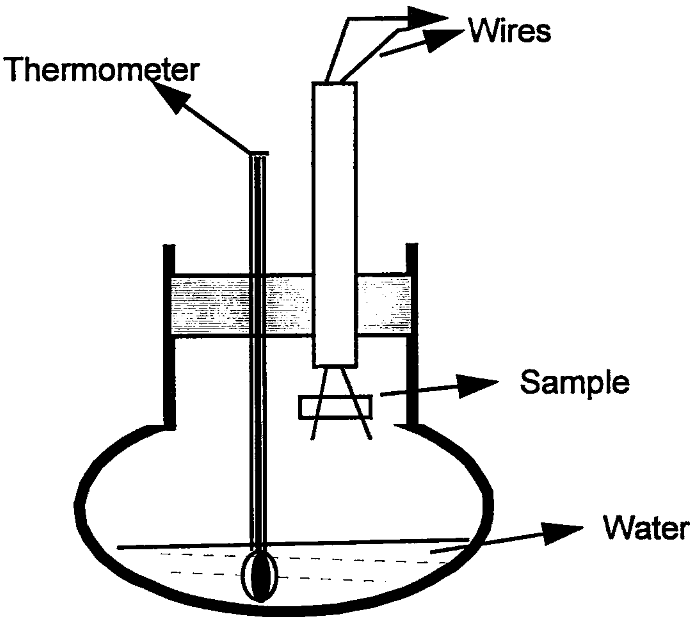
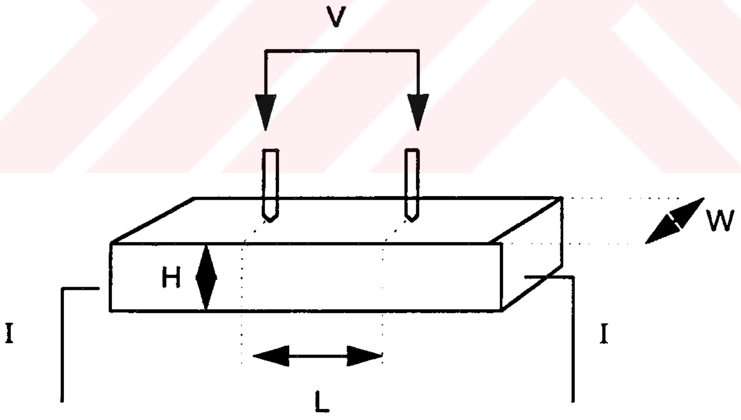


Figure 10. Schematic presentation of moisture sensitivity measuring system



where :

W : width of the sample

H : height of the sample

L : length of the sample

ρ, V, I are specified in Figure 9.

Figure 11 . Schematic diagram of two probe method

2.2.9. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DSC V2.A DuPont 9900 type DSC was used.

2.2.10. THERMAL GRAVIMETRIC ANALYSIS (TGA)

TGA V2.0B DuPont 9900 type instrument was used.

2.2.11. SCANNING ELECTRON MISROSCOPE (SEM)

JEOL JSM 840A type SEM was used for surface analysis. The samples were coated by gold and secondary electron image was determined.

2.3. PROCEDURE

2.3.1. CYCLIC VOLTAMMETRY

Prior to electrolytic polymerization, the voltammetric oxidation or reduction potentials of monomers were determined by CV in acetonitrile as the solvent and under inert N_2 atmosphere. The concentration of monomers was in the order of 10^{-3} M while the supporting electrolyte TBAFB was 0.1 M. N_2 gas is passed through the solution to deaerate the system. During potential scanning the solution was kept quiet. The potential of working electrode is scanned to either anodic and cathodic potential and than back to the starting point. Always a background scan of solvent - electrolyte was run to check the impurities in the system.

2.3.2. POLYMERIZATION OF ACRYLONITRILE

Dry supporting electrolyte TBAFB was dissolved in freshly distilled acetonitrile (approximate volume is 30 mL). The solution was introduced into electrolysis cell. The cell was purged with N_2 and kept under N_2 atmosphere. Acrylonitrile monomer (2.0 mol/L) was added. The cell is placed in a constant temperature (ethanol) bath. After temperature equilibration, N_2 inlet of working electrode compartment was turned off and the gas is allowed to pass through the auxiliary electrode compartment during electrolysis.

Just before the application of polymerization potential, 10 μL of samples were removed from each compartment and subsequently transferred into the 100 μL of methanol (MeOH) containing 3 μL of internal standard (propionitrile). The final solution was used to determine the initial concentration of monomer by gas chromatography analysis.

The potential determined by CV system was applied by switching on the potentiostat after above mentioned zero point sampling. The current was followed from the recorder as a function of time.

During the electrolysis, at definite time intervals 10 μL of aliquots of anolyte and catholyte were removed from the cell and transferred separately into MeOH (100 μL), propionitrile (3 μL) mixture to follow up the kinetics by GC technique. The samples were kept in cold.

The kinetics of polymerizations were followed for 2 hours. The contents of each compartment were separately introduced into methanol to precipitate the polymer. The precipitated polymer was filtered, washed and dried under vacuum. The polymerization yield was obtained by gravimetric method. The IR and viscometry measurements were done by using the precipitated and the dried polymer.

In order to check the mechanism of polymerization in the anolyte, a radical inhibitor hydroquinone (HQ) was added to the electrolysis cell. The same polymerization method and kinetic study were applied.

The polymerization of PAN was carried out at -2.60 V ($E_{p,c}$) vs Ag^{o}/Ag^{+} and at three different temperatures namely -10.0, 0.0, +10°C.

2.3.3. GAS CHROMATOGRAPHY

The kinetics of polymerization was followed by determining initial and unreacted monomer concentration in the electrolysis sample transferred into MeOH and propionitrile mixture.

For each polymerization, before gas chromatography analysis, a standart solution was prepared to determine the response factor (RF) of the monomer. RF solution contained propionitrile (3μL), acrylonitrile (3μL), acetonitrile (20μL) and methanol (100μL). The response factor was evaluated according to the following formula ;

$$RF = \frac{H_1 / H_2}{W_1 / W_2}$$

where

H_1 is the peak height of monomer acrylonitrile
H_2 is the peak height of internal standart propionitrile
W_1 is the weight of monomer acrylonitrile
W_2 is the weight of internal standart propionitrile

Once RF was determined from the standart mixture, W_1 was calculated for each sample removed from the cell.

The conditions of GC were as follows. The column used Porapak Q 80/100 has a dimension of 1.5 m long, 3.2 mm outer diameter was a crosslinked polymer and stable up to 250°C. The mobile phase N_2 gas flow rate was 10 mL / 22 sec (27.3 mL/min). The oven temperature was 175 °C, the injection and detector temperatures were 200 °C. The injection volume of samples was 1μL.

2.3.4 INFRARED ANALYSIS (IR)

The structural analysis of polymers were carried out by Perkin Elmer IR. The polymers were pelletized with KBr and their IR spectra were obtained.

2.3.5. MOLECULAR WEIGHT DETERMINATION

The intrinsic viscosities of homopolymers were determined in DMF and at 25°C. The flow time of a specific volume of solution and solvent were measured. Four different concentrations of polymer solution were tested. From the solution - solvent flow times the specific viscosity was calculated. The plot of 'specific viscosity/concentration' vs concentration was drawn and from the intercept the intrinsic viscosity was determined.

2.3.6. HEAT TREATMENT OF POLYACRYLONITRILES

2.3.6.1. HEAT TREATMENT OF CATHOLYTE PAN

PAN samples were pelletized at 1000 psi for 7 minutes prior to heat treatment. The pellets were placed in a suitable glass tube. Samples which will be treated under atmospheric conditions was directly placed in the oven. However, those which will be treated under vacuum first connected to vacuum line for degassing purposes. The sealed samples were than placed in the oven.

The heat treatment of PAN were carried out mainly at three different temperatures 200, 400 and 600°C. The oven temperature was increased gradually and kept constant at desired temperature for two hours. In case of multiple step heat treatments, such as 200 and 400 °C, the sample was kept at 200 °C for two hours and then the temperature of oven was increased to 400 °C gradually. The sample was let to stay at that temperature for another two hours.

The effect of dopant at different temperatures and environmental conditions was also investigated. For that purpose $AlCl_3$ was used as the dopant. Pelletized PAN and $AlCl_3$ were placed in separate tubes that are connected to each other, but there was no physical contact between the dopant and the polymer.

The details of heat treatment procedure and the conditions were summarized on Table 4.

The conductivity measurements, moisture sensitivity analysis and IR analysis of the heat treated samples were carried out.

Table 4. Heat Treatment conditions of catholyte PAN and commercial PAN.

SAMPLE CODE	HEAT TREATMENT CONDITIONS								
	STEP 1			STEP 2			STEP 3		
D	200°C	VACUUM	-	-			-		
F	200°C	AIR	-	-			-		
G	200°C	AIR	$AlCl_3$	-			-		
H	200°C	VACUUM	$AlCl_3$	-			-		
I	200°C	AIR	-	400°C	VACUUM	$AlCl_3$	-		
J	200°C	AIR	$AlCl_3$	400°C	AIR	$AlCl_3$	-		
K	200°C	VACUUM	$AlCl_3$	400°C	VACUUM	$AlCl_3$	-		
E (1)	200°C	AIR	-	-			-		
L	200°C	AIR	-	400°C	AIR	-	-		
M (2)	200°C	AIR	-	-			-		
N	200°C	AIR	$AlCl_3$	400°C	AIR	$AlCl_3$	600°C	AIR	$AlCl_3$
O	200°C	VACUUM	$AlCl_3$	400°C	VACUUM	$AlCl_3$	600°C	VACUUM	$AlCl_3$

(1) : Commercial PAN, heat treating time was 6 hours
(2) : Heat treating time was 6 hours.

2.3.6.2. HEAT TREATMENT OF COMMERCIAL WHITE PAN

The heat treatment of commercial white PAN was carried out at 200°C and open to atmospheric conditions for 6 hours.

2.3.7. CONDUCTIVITY MEASUREMENT

The conductivity of polymers were determined by 4 probe method and the following calculations were applied.

$V = I R$

$I = \text{constant}$

$V_s / R_s = V_r / R_r \quad \Rightarrow \quad R_s = V_s \times R_r / V_r$

$\sigma = 1 / 4.53 \times t \times R_s$

where

V_s is the potential of sample

R_s is the resistance of sample calculated from above equation

V_r is the potential of reference

R_r is the resistance of reference being as 10.000, 1000, 100 and 10Ω.

σ is the conductance in S/cm^{-1}

t is the thickness of the sample film in cm.

Prior to measurements the thickness of samples were determined. At different reference resistance values the potential of sample and reference were obtained from voltmeter.

2.3.8. MOISTURE SENSITIVITY MEASUREMENTS

Since two probe technique was applied in case of moisture sensitivity analysis the distance between electrodes and the dimensions of the samples gain importance. Same as 4 probe technique at known reference resistance values, the potential of sample and reference were measured (Figure 11). The sample resistance was calculated. The relation between the R_s and the conductance is given below .

$$R_s = \rho\, l / A$$

$$\sigma = 1 / \rho$$

where

ρ is the specific resistance of the sample in Ω.cm.

l is the distance between two electrodes adhered to the surface of sample in.

A is the crossectional area of the electrodes contact points in cm^2. (A = the contact length of electrodes (W) x thickness of the sample).

σ is the conductance in S/cm or $\Omega^{-1}.cm^{-1}$.

250 ml of distilled water in a balloon was placed in a constant temperature water bath at 40°C and waited for thermal equilibrium. The sample equipped with electrodes was purged with water vapor without getting any contact with liquid water . The sample was kept at that position for a certain time and then removed. When the samples were exposed and removed the

potential of sample and reference were continuously measured. After repeated cycle of that adsorption and desorption cycles the sensitivity to moisture and its stability was determined.

2.3.9. DIFFERENTIAL SCANNING CALORIMETRY (DSC)

A known amount of sample was weighed and introduced to the sample holder of the instrument. The temperature was increased from 30°C to 470 °C by 20 °C/min ramps. The output plots were reported as heat flow versus temperature.

2.3.10. THERMAL GRAVIMETRIC ANALYSIS (TGA)

A known amount of sample was weighed and the weight loss of the sample was determined in the range of 20 - 850 °C. The temperature was increased from room temperature to 600 °C under nitrogen atmosphere. The temperature was kept constant at 250 °C for 25 min. From 600 °C to 850 °C the temperature was increased under air condition. The temperature increase rate is 20 °C /min.

2.3.11. PREPARATION OF POLYMER BLENDS

Different electrolysis conditions were applied during the blend preparation. The electrolysis conditions were summarized in Table 5 for PAN-PPy blend and in Table 6 for PAN-PTh blend.

PAN-PPy and PAN-PTh composites were prepared by the electrochemical polymerization of Py and Th onto a PAN coated electrode separately. The constant potential electrolysis was carried at the oxidation potential of Py or Th. Dichloromethane was used as polymerization solvent and

TBAFB was used as the electrolyte. The remaining components of the electrolysis cell were Pt foil (2 cm ^{2}) working and counter electrodes and a Luggin capillary Ag^o / Ag^+ reference electrode. The electrolysis cell was purged with N_2 throughout the polymerization. In the case of blend syntheses, (10^{-3}M) monomer Py or Th was introduced into the cell. The polymerizations were carried out at room temperature. Electrochemically prepared (yellow) polyacrylonitrile was dissolved in acetonitrile. The working electrode (anode) was dip coated from this solution. The coated electrode was placed in the electrolysis cell and N_2 gas was allowed to pass through the counter electrode compartment. The potential was switched on and the electrolysis was allowed to proceed till obtaining desired conducting polymer percentage. After electrolysis, anode was removed from the cell and immersed into dichloromethane and acetonitrile for quick washing process (samples P in Table 5 and V in Table 6). The film on the electrode surface was peeled off for further gravimetric, conductivity, thermal and FTIR, SEM analysis. The electrochemical behavior of dip coated PAN was analyzed by running the electrolysis in the absence of Py or Th in the electrolysis cell to rule out the possibility of oxidation of the insulating component. No change was observed on the polymer electrode.

The second group experiments cover the possibility of obtaining polymer blends when both acrylonitrile and pyrrole (or thiophene) were present in the electrolysis medium. First, the acrylonitrile component was considered. Therefore acetonitrile was used as the solvent and the reduction peak potential of acrylonitrile was applied (samples R in Table 5 and V in Table 6). Second, the oxidation peak potential of pyrrole (or thiophene) was applied where the working electrode was anode and the solvent was dichloromethane (samples S in Table 5 and Z in Table 6). Those two synthesis were done in separate systems.

In the third group experiments, the heterocyclic monomers were polymerized at their oxidation potentials in dichloromethane until conducting polymer electrode films were formed. As soon as the film reaches to a certain thickness, the electrochemically coated electrode was removed and immersed in an another electrolysis cell. This new cell contains acrylonitrile monomer, and the solvent was acetonitrile. The polymerization potential was the $E_{p,c}$ of the acrylonitrile (samples T and X). Another version of that group experiment was the addition of acrylonitrile monomer to the polypyrrole or polythiophene system while conducting electrode film formation. After addition of acrylonitrile to the cell the potential was reversed to the $E_{p,c}$ of the acrylonitrile (samples U and W).

Polymerization of pure PPy and PTh were carried out in the same three electrode system under controlled potential. The cell equipped with Pt foils (2 cm ^{2}) as working and counter electrodes and a capillary Ag^{o} / Ag^{+} as the reference electrode. Dichloromethane was used as the solvent and TBAFB as electrolyte. Monomers, either Py or Th (10^{-3} M) was charged into the electrolysis cell. N_2 gas was passed through both compartments, after the application of potential, only catholyte compartment was purged. The polymerization was carried out at room temperature and oxidation potential of either Py or Th. The electrolyses were allowed to proceed untill obtaining sufficiently thick films. The electrode was removed from the cell, polymer film was peeled off from the electrode surface. Polymer films were washed with dichloromethane.

The percentage of polyacrylonitrile, polypyrrole and polythiophene in blends were determined gravimetrically.

The conductivity, IR, thermal and SEM analyses of the blends were done.

Table 5. Electrolysis conditions of PPy-PAN blends.

SAMPLE NO	STEP 1		STEP 2	
	POLYMER or MONOMER	ELECTRODE COATING METHOD or ELECTROLYSIS CONDITON	POLYMER or MONOMER	ELECTRODE COATING METHOD or ELECTROLYSIS CONDITON
P	Catholyte PAN	Dip coated (in CH_3CN)	Py and dip coated electrode	E_{pol} = + 1.6 V ((in CH_2Cl_2)
R	AN and Py together	E_{pol} = - 2.6 V (in CH_3CN)	-	-
S	AN and Py together	E_{pol} = + 1.6 V (in CH_2Cl_2)	-	-
T	Py	E_{pol} = + 1.6 V (in CH_2Cl_2)	AN (added to Py containing electrolysis cellin step 1)	E_{pol} = - 2.6 V (in CH_2Cl_2)
U	Py	E_{pol} = + 1.6 V (in CH_2Cl_2)	AN (in separate cell, solvent CH_3CN)	E_{pol} = - 2.6 V (in CH_3CN)

Table 6. Electrolysis conditions of PTh-PAN blends.

SAMPLE CODE	STEP 1		STEP 2	
	POLYMER or MONOMER	**ELECTRODE COATING METHOD or ELECTROLYSIS CONDITON**	**POLYMER or MONOMER**	**ELECTRODE COATING METHOD or ELECTROLYSIS CONDITON**
V	Catholyte PAN	Dip coated (in CH_3CN)	Th and dip coated electrode	E_{pol} = + 1.9 V ((in CH_2Cl_2)
Y	AN and Th together	E_{pol} = - 2.6 V (in CH_3CN)	-	-
Z	AN and Th together	E_{pol} = + 1.9 V (in CH_2Cl_2)	-	-
X	Th	E_{pol} = + 1.9 V (in CH_2Cl_2)	AN (added to Th containing electrolysis cell in step 1)	E_{pol} = - 2.6 V (in CH_2Cl_2)
W	Th	E_{pol} = + 1.9 V (in CH_2Cl_2)	AN (in separate cell, solvent CH_3CN)	E_{pol} = - 2.6 V (in CH_3CN)

CHAPTER 3

RESULTS AND DISCUSSION

3.1 CYCLIC VOLTAMMETRY OF PAN

In earlier reports the advantage of Constant Potential Electrolysis (CPE) was explained in detail. One of the most important advantage is that the polymerization proceeds selective to monomer, especially in the initiation step, if a suitable potential is applied. For that purpose, prior to polymerization the electrochemical behavior of monomer was determined by CV.

The electrochemical behavior of acrylonitrile was determined in acetonitrile - TBAFB (0.1 mol/L) solvent - electrolyte system which is totally electroinert in the potential range of ± 3.0 V vs Ag^o/Ag^+. Only one irreversible reduction peak for acrylonitrile was observed at - 2.60 V vs Ag^o/Ag^+ at room temperature (Figure 12.a). Scanning through the oxidation or reduction sides did not affect the place and the number of this potential in this solvent - electrolyte range.

The cyclic voltammogram of acrylonitrile in acetonitrile - TBAFB system (Figure 12) indicates that the polymerization can be initiated selectively through the monomer. In that system solvent - electrolyte couple discharge occurs at - 3.0 V vs Ag^o/Ag^+ where $E_{p,c}$ of acrylonitrile appears at - 2.6 V vs Ag^o/Ag^+. By adjusting the polymerization potential to - 2.6 V vs Ag^o/Ag^+, ($E_{p,c}$ for acrylonitrile), initiation is primarily through the monomer, i.e. initiation occurs by direct electron transfer.

In literature, the electroinitiated anionic polymerization of acrylonitrile has also been carried out [8] depending on the half wave potential of the monomers obtained by polarography. They determined $E_{1/2}$ of acrylonitrile as - 1.69 V vs Hg pool and that of $NaNO_3$ as -1.55 V vs Hg pool in dimethylformamide (DMF) - tetramethylammoniumiodide (TMAI) system. Although they suggested direct electron transfer to monomer, it is obvious that $NaNO_3$ discharge occurs before acrylonitrile. If compared to our solvent - electrolyte system, the DMF - $NaNO_3$ system (Figure 12.c) shows a reduction potential of Na^+ at -1.5 V vs Ag^o/Ag^+ and solvent - electrolyte discharge potential at about - 1.60 V which can be attributed to the presence of trace amount of water in our system. Thus, in the DMF - $NaNO_3$, a direct electron transfer to monomer is not found to be possible. Also in the acetonitrile - $NaNO_3$ couple, a similar reduction peak of Na^+ occurs before the $E_{p,c}$ of acrylonitrile whereas still solvent - electrolyte discharge occurs at around - 3.0 V vs Ag^o/Ag (Figure 12.d.). Thus, the nature of the initiating species can not be easily determined by CCE.

The reduction peak potential of monomers can be correlated with the lowest unoccupied molecular orbitals (LUMO) (Figure 13). After a short time of electrolysis, the energy band of working electrode, in this case the cathode, becomes comparable to the LUMO of the monomer and as a consequence, an electron transfer occurs from the electrode to the LUMO of the monomer. The electrochemically created active form of the monomer, either a radical anion or dianion, propagates polymerization.

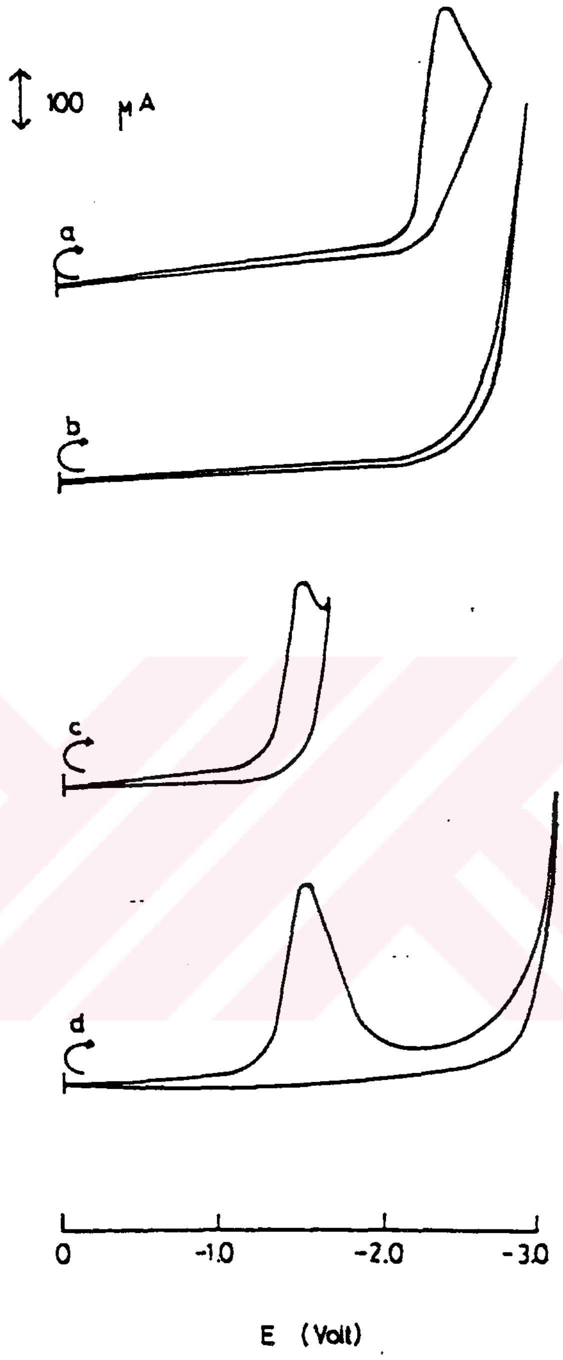


Figure 12. (a) The cyclic voltammogram of Acrylonitrile (1.0 mmole/lt) in CH_3CN - TBAFB, (b) Background voltammogram of Acetonitrile in the presence of TBAFB, (c) Cyclic voltammogram of DMF in the presence of $NaNO_3$, (d) Cyclic voltammogram of Acetonitrile in the presence of $NaNO_3$.

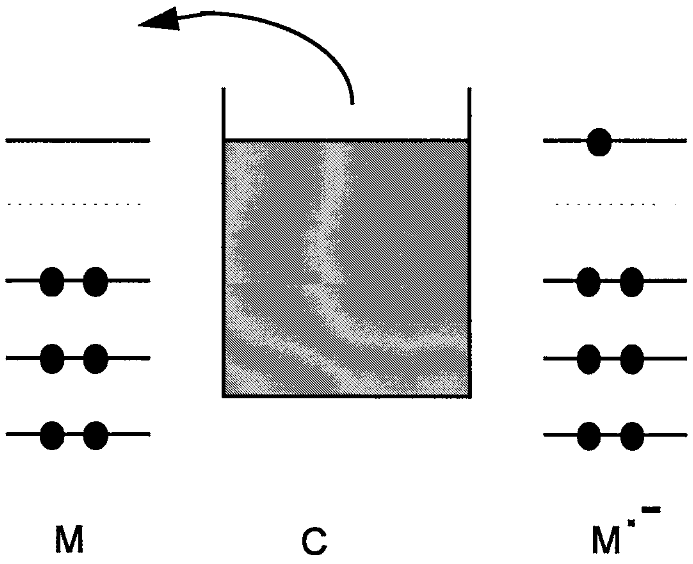


Figure 13. Schematic representation of molecular energies of the monomer (M), the radical anion of the monomer ($M^{\cdot -}$), and the energy band of the cathode (C) for electroinitiated anionic polymerization

3.2. ELECTROINITIATED ANIONIC POLYMERIZATION OF ACRYLONITRILE

The polymerization was carried out at the cathodic peak potential ($E_{p,c}$) of the monomer, i.e. -2.60V vs Ag^o/Ag^+ . Since the reduction peak potential of monomer is in the solvent-electrolyte range the polymerization proceeds via direct electron transfer. Three different polymerization temperatures were employed , namely, -10, 0 and +10°C.

The monomer conversion, given by ($([M_t] / [M_o])x100$), was obtained from gc data. Unreacted monomer concentrations were calculated by evaluating gc data, which were further used to determine monomer consumption in each cell compartment. In our previous studies [51 - 54] gc sampling was done by removing equal amounts of solution from each compartment of electrolysis cell. This procedure enables one to follow the conversion points in the gc measurements rather accurately. During the electrolysis, depending on the consumption rate of the monomer, there occurs monomer passage between the two compartments through the sintered glass disk. Therefore sampling from only one side results in erroneous kinetic curves. However, in this study since we observed polymer formation both in anolyte and catholyte compartments, the samples removed from each compartment were added into separate methanol tubes. By this way we were able to follow up the kinetics in both compartments. Additionally, in order to obtain reproducible kinetic results, the average of several experiments were taken.

Acrylonitrile molecule is derived from ethylene by substituting one hydrogen atom for a nitrile group; the result is a vinyl monomer (vinyl cyanide). The nitrile group has a high polar character which makes acrylonitrile unique in the sense that it is appreciably soluble in water. Additionally, the nitrile group withdraws electrons from the vinyl double bond leaving it with positive character. As a result polymerization through the vinyl group may be accomplished with free radical or reductive initiators while oxidative initiators are inactive [12].

$$CH_2{=}\,CH - C \equiv N \quad \longleftrightarrow \quad \overset{+}{C}H_2 - \; CH = C = \overset{-}{N}$$

Referring to the applied polymerization potential , $E_{p,c}$ = -2.60V vs Ag^{o}/Ag^{+}, based on CV measurements, the initiation at cathode compartment is the electron transfer from cathode to the monomer. As a consequence, formation of radical anion initiating the polymerization was expected (Figure 14). The propagating chain end can be terminated by one of the species present in the system or by self termination such as cyclization. The polymer chains desorbed from the electrode surface can propagate the polymerization in the bulk of the solution.

$$M + e \xrightarrow{k_i} M^{\dot{-}}$$

$$M^{\dot{-}} + M \xrightarrow{k_p} \cdot MM^{-}$$

$$\sim\sim M^{-} \xrightarrow{k_t} P$$

$$\sim\sim M^{-} + M \xrightarrow{k_t'} P$$

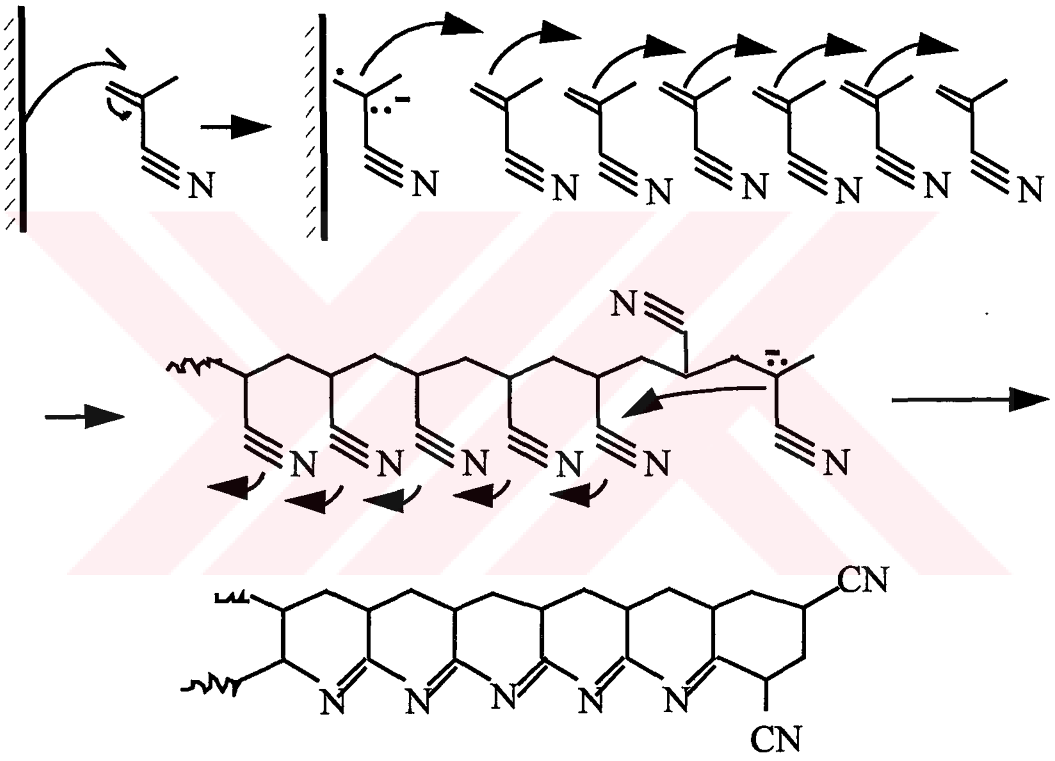


Figure 14. The suggested polymerization mechanism of acrylonitrile

The results of gc analysis of electrolysis at three different temperatures were given in Tables 7, 8 and 9. The values given in these tables were plotted as % monomer consumption vs time (Figures 15 and 16). Since the sampling and gc analysis from catholyte and anolyte was performed separately, the related data were reported and plotted separately.

Table 7. Results of gas chromatographic analysis of electroinitiated anionic homopolymerization[a] of acrylonitrile at -10°C and - 2.60 V[b].

Time (min)	[M]unreacted (mol/L)	[M]reacted (mol/L)	% Conversion
CATHOLYTE			
0	2.160	0.000	0.0
2	2.153	0.006	0.3
3	2.137	0.022	1.1
10	2.104	0.055	2.6
15	2.093	0.066	3.1
20	2.069	0.090	4.2
30	2.052	0.107	4.9
45	2.008	0.151	7.0
60	1.947	0.212	9.8
90	1.867	0.292	13.5
120	1.839	0.320	14.9
ANOLYTE			
0	2.102	0.000	0.0
5	2.062	0.039	1.9
15	2.025	0.076	3.6
20	1.982	0.119	5.7
30	1.983	0.118	5.6
120	1.849	0.252	12.1

a: In Acetonitrile containing 0.1 M TBATFB
b: versus Ag^o/Ag^+ on 5 cm^2 Pt foil.

Table 8. Results of gas chromatographic analysis of electroinitiated homopolymerization[a] of acrylonitrile at 0°C and - 2.60 V.

Time (min)	[M]unreacted (mol/L)	[M]reacted (mol/L)	% Conversion
<u>CATHOLYTE</u>			
0	2.223	0.000	0.0
1	2.182	0.040	1.8
2	2.170	0.051	2.3
3	2.142	0.08	3.6
5	2.121	0.101	4.6
10	2.042	0.180	8.1
15	1.977	0.245	11.1
20	1.963	0.259	11.7
30	1.340	0.288	12.9
45	1.856	0.366	16.5
60	1.790	0.432	19.5
90	1.753	0.469	21.1
120	1.691	0.531	23.9
<u>ANOLYTE</u>			
0	2.353	0	0.0
2	2.086	0.267	11.3
3	2.077	0.276	11.7
7	1.987	0.366	15.5
15	1.973	0.380	16.1
30	1.973	0.38	16.2
60	1.863	0.49	20.8
120	1.824	0.529	22.5

a: In Acetonitrile containing 0.1 M TBATFB

b: versus Ag°/ Ag^+ on 5 cm^2 Pt foil.

Table 9. Results of gas chromatographic analysis of electroinitiated homopolymerization[a] of acrylonitrile at +10°C and - 2.60 V[b].

Time (min)	[M]unreacted (mol/L)	[M]reacted (mol/L)	% Conversion
CATHOLYTE			
0	2.549	0.000	0.0
2	2.496	0.053	2.1
3	2.476	0.072	2.8
5	2.371	0.177	6.9
7	2.32	0.228	8.9
10	2.283	0.265	10.4
15	2.238	0.31	12.2
20	2.166	0.382	15.0
30	0.128	0.42	16.5
45	2.061	0.487	19.1
60	1.983	0.565	22.2
90	1.902	0.646	25.3
120	1.902	0.646	25.3
ANOLYTE			
0	2.549	0.000	0.0
1	2.124	0.424	16.7
7	2.089	0.459	18.0
15	2.072	0.476	18.7
20	2.066	0.483	18.9
30	2.066	0.483	18.9
45	2.002	0.546	21.4
60	1.986	0.563	22.1
90	1.918	0.63	24.7
120	1.91	0.638	25.0

a: In Acetonitrile containing 0.1 M TBATFB
b: versus Ag°/ Ag$^+$ on 5 cm^2 Pt foil.

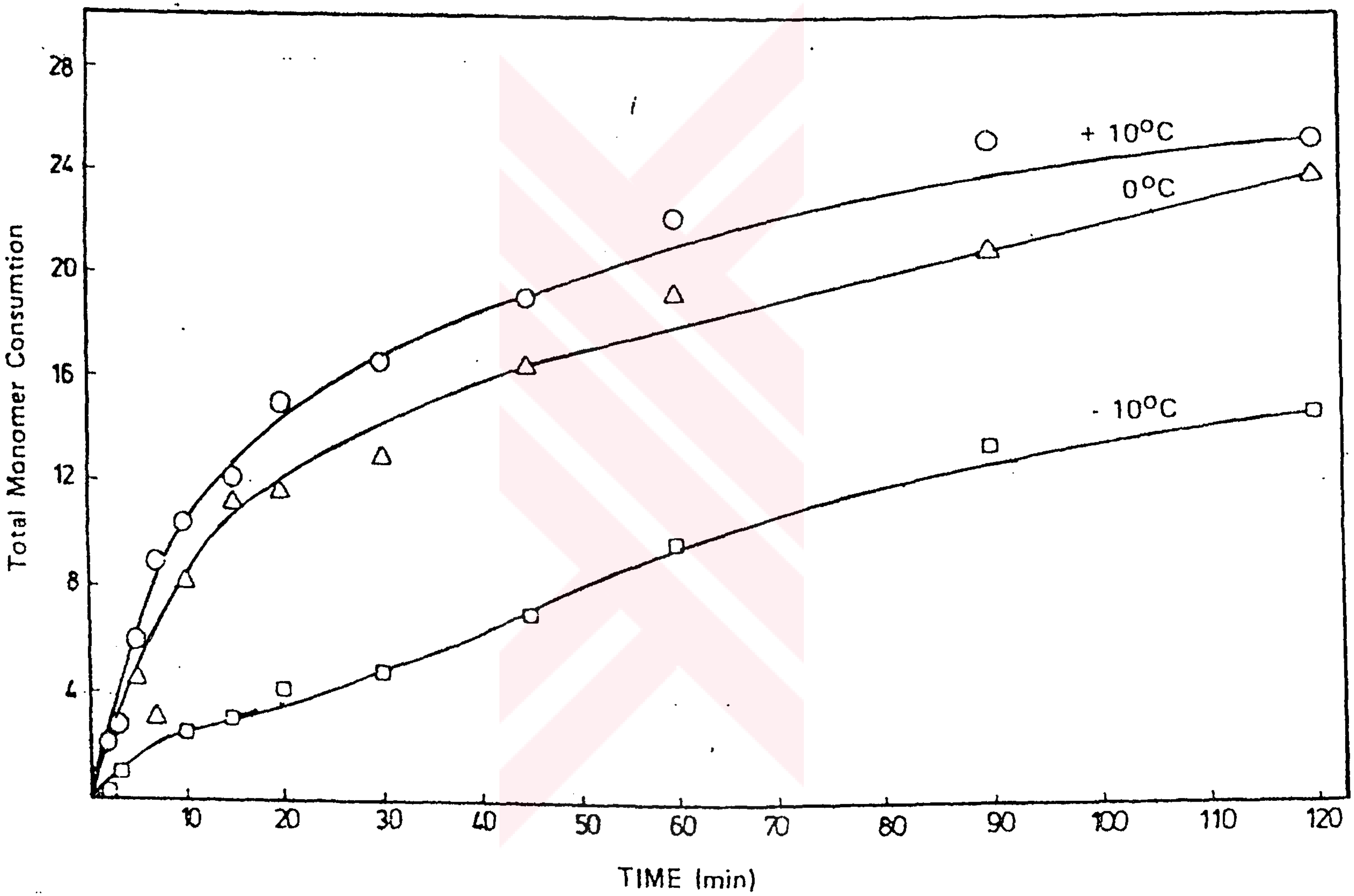


Figure 15. Percent monomer conversion in catholyte versus time (□) -10.0 °C, (Δ) 0.0 °C, (o) +10.0°C.

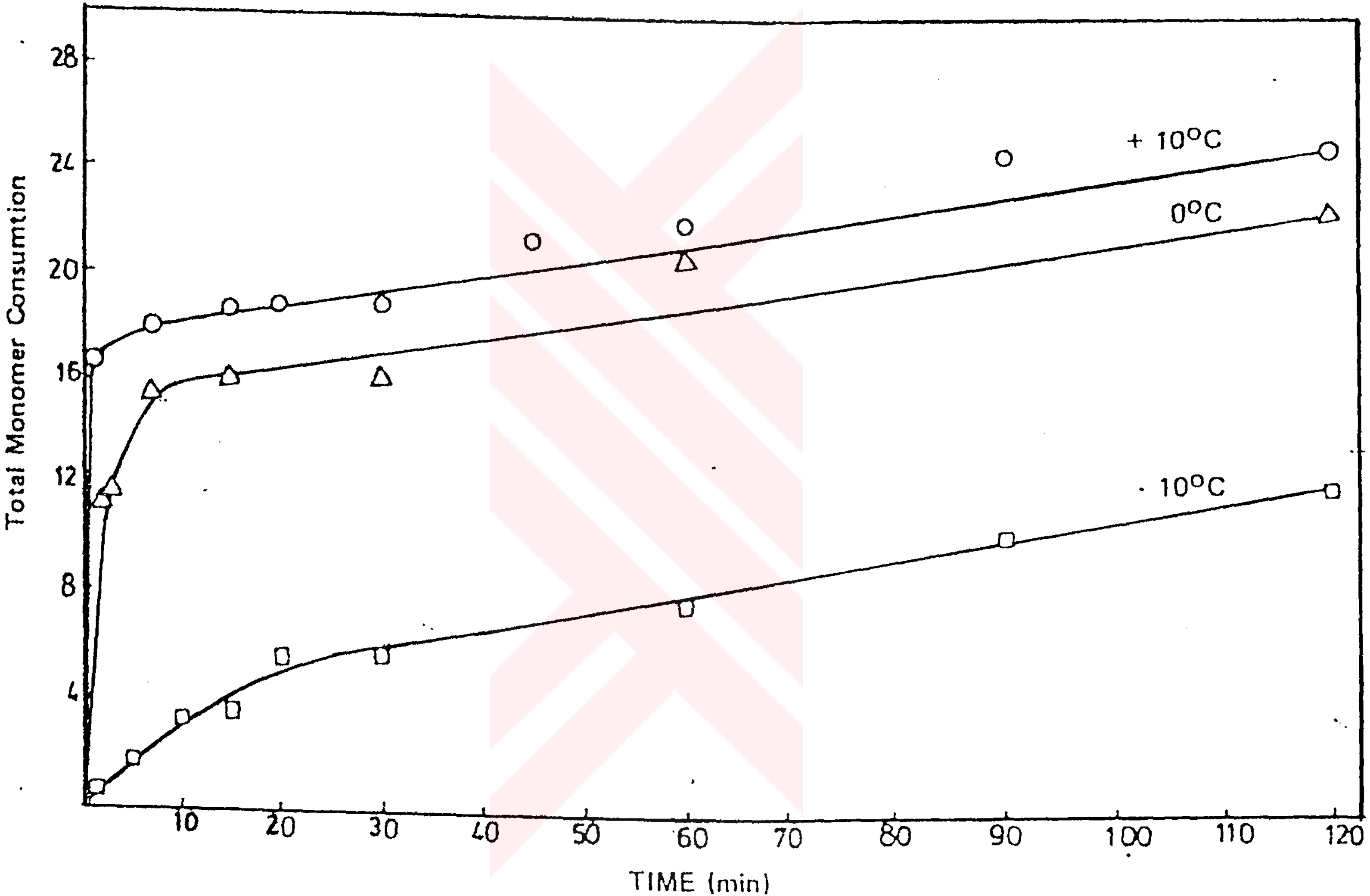


Figure 16. Percent monomer conversion in anolyte versus time (□) -10.0 °C, (Δ) 0.0 °C, (o) +10.0°C.

It was observed that as the polymerization temperature increases the rate and the reacted monomer concentration, as a result of polymerization conversion increases. In both anolyte and catholyte compartments the same type of behavior was observed. In a short time of electrolysis (ca. 10 minutes), the conversion increases very sharply and reaches to a plateau in 120 minutes of electrolysis (Figure 15 and Figure 16). Initial conversions in anolyte at +10°C and 0°C are rather sharp than that of the catholyte whereas comparable initial conversions are observed at -10°C. The total monomer consumption was very close to each other with a small advantage of catholyte.

At the very beginning of the electrolysis the color of catholyte compartment solution was changed to light yellow and got darker with the electrolysis time. When the two compartments were compared, the color in the catholyte was more obvious. Almost at the 10th minute of electrolysis light yellow polymer precipitation was observed when the catholyte samples removed from cell and added to methanol tube. On the other hand, the anolyte polymers were observed later.

The type of polymerization in the anolyte compartment was examined by adding 10^{-3}M HQ radical inhibitor to the anolyte compartment at the beginning of electrolysis. The kinetics of this reaction was also followed by gc analysis and the results are given in Table 10. Figure 17 represents the monomer consumption in the cell. In catholyte compartment no appreciable monomer consumption change was observed. On the other hand, in the anode compartment the presence of inhibitor makes an important difference up to 30 min. of electrolysis. Thereafter, due to electrolytical decomposition of HQ, the reaction rate increases. During the electrolysis since the cathode potential was kept constant at - 2.60 V, the anode potential can be as high as 10 V, depending on the reaction conditions, IR drop, the substrate concentration, etc.

No inhibitor or any solvent electrolyte or substrate can stand to that high potential. This shows an indirect radical type of initiation occurs in the anolyte.

The anolyte and catholyte solution were completely transferred into methanol to precipitate the polymer at the end of 2 hours of electrolysis. The polymers were filtered, washed and vacuum dried. The color of catholyte polymer was apparently darker yellow than the anode polymer. The polymers were weighed and the percent yield was calculated. The characterization analyses were carried out by using these polymers.

The results of electrochemical polymerization were summarized in Table 11. A discrepancy between % conversion and yield in anolyte and catholyte was observed. This discrepancy can be explained as the diffusion of monomer through the sintered disk of electrolysis cell from either anolyte to catholyte or vice versa.

The differences in overall % conversion, i.e. anolyte and catholyte, and the yield values are most probably due to oligomeric products of very low molecular weight which do not precipitate in methanol.

The viscosities of catholyte polymers were determined in DMF at 25°C. The polymers have very low molecular weights referring to their intrinsic viscosities. The intrinsic viscosities increase with the decrease of electrolysis temperature (Table 11)

The physical appearance and IR spectra of polymers permit some comments on the structure. Insoluble, crosslinked and colored polymers were obtained on the cathode surface. The polymers obtained from cathode and anode compartments can be distinguished. The cathode material was darker, yellow to orange, whereas the anode material was light yellow. The coloration of

Table10. Results of gas chromatographic analysis of electroinitiated anionic homopolymerization[a] of acrylonitrile at 0°C and - 2.60 V in the presence of hyroquinone inhibitor.

Time (min)	[M]unreacted (mol/L)	[M]reacted (mol/L)	% Conversion
CATHOLYTE			
0	2.353	0.000	0.0
1	2.285	0.068	2.9
2	2.139	0.213	9.1
3	2.111	0.241	10.3
10	1.909	0.443	18.9
15	1.848	0.504	21.5
30	1.834	0.518	22.0
60	1.767	0.585	24.9
120	1.764	0.588	25.0
ANOLYTE			
0	2.107	0.000	0.0
2	2.086	0.020	0.9
6	2.097	0.009	0.4
10	2.037	0.690	0.3
15	1.973	0.133	0.6
30	1.972	0.134	0.6
60	1.863	0.243	11.6
120	1.632	0.474	22.5

a: In Acetonitrile containing 0.1 M TBATFB

b: versus Ag^o/ Ag^+ on 5 cm^2 Pt foil.

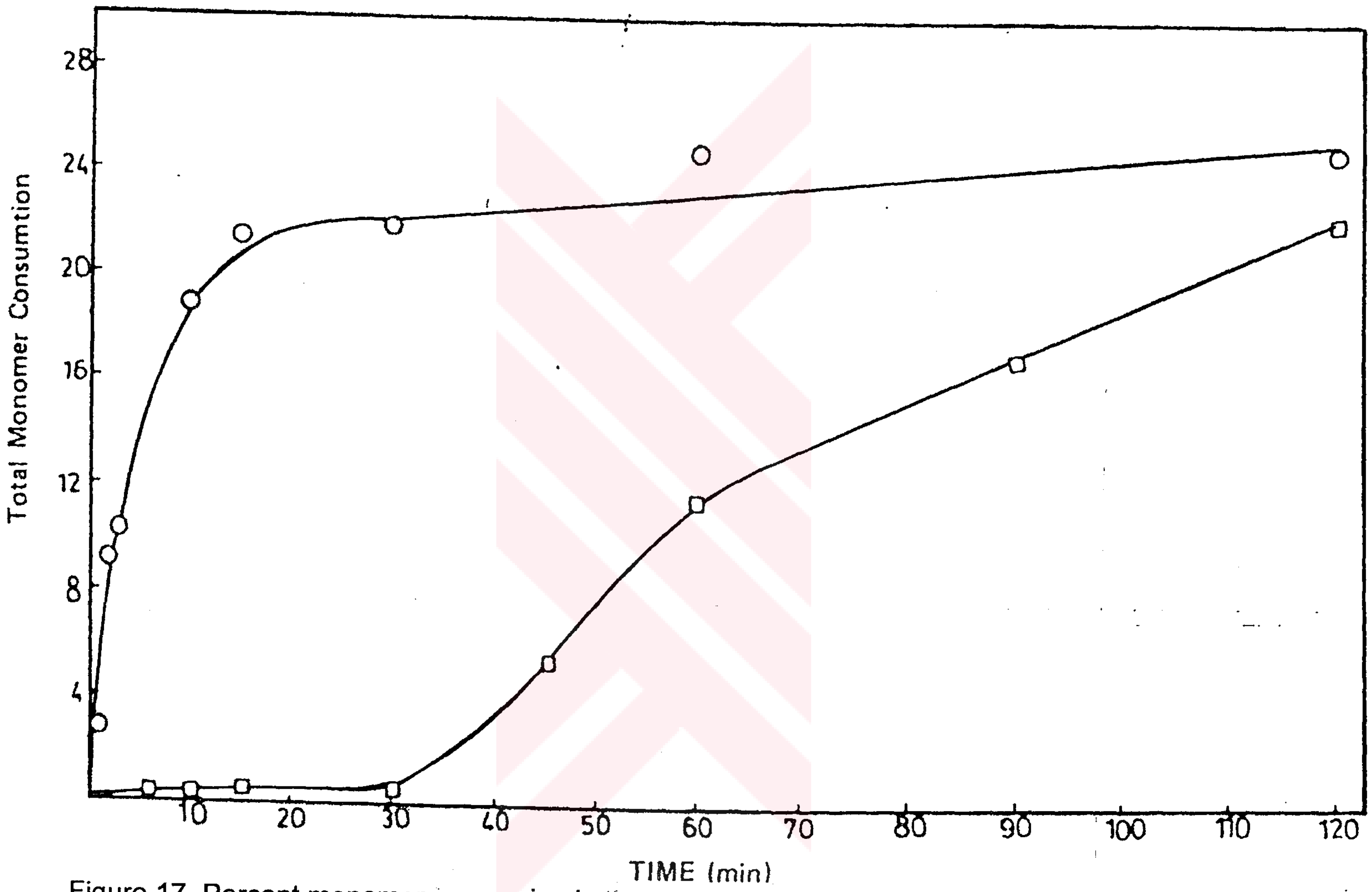


Figure 17. Percent monomer conversion in the presence of radical inhibitor (hydroquinone) versus time (□) : anolyte, (o) : catholyte.

Table 11. Electroinitiated polymerization of acrylonitrile carried out by constant potential electrolysis at -2.60 V in acetonitrile on a Pt^{o} electrode.

Polymerization Temperature (^{o}C)	Conversion in anolyte[a], (%)	Conversion in catholyte[a], (%)	Yield in anolyte[b], (%)	Yield in catholyte[b], (%)	Total conversion (%)	Total yield (%)	[n], dL/g[c]
+10.0	25	25.3	9.3	30.4	50.3	39.7	0.041
0.0	22.5	23.9	11.1	25.1	46.4	36.2	0.072
-10.0	12.1	14.9	5.3	21.6	27	26.9	0.088

[a] The %conversion in the cell compartments, anode and cathode, were measured by gas chromatography at the end of 2 h of electrolysis, separately

[b] The % yields in anode and cathode compartments were obtained by precipitation of polymer solution at the end of 2 h of electrolysis, separately.

[c] at 25°C in DMF.

PAN was attributed to intermolecular cyclization [8, 9]. Linear polyacrylonitrile has a powdery appearance and is white in color.

Comparison of the IR spectra of the samples with the literature indicates that the colored polyacrylonitrile contains cyclic structures (Figure 18). The IR spectra of linear polyacrylonitrile showed mainly two intense peaks. These are the — C≡N vibrations at 2240 cm^{-1} and the — CH_2 — bending vibrations at 1450 cm^{-1} . On the other hand colored polyacrylonitriles have the same — C≡N absorption at 2240 cm^{-1} , but this peak splits into two due to the formation of cyclic sequences in the chains. In addition, the intensity of the 2240 cm^{-1} band is decreased. The changes in the intensities of — C≡N vibrations, broadening in the frequency range 1400 - 1700 cm^{-1} due to vibrations of —CH and —CH_2 groups are yet another indications of cyclization.

The IR spectra of anode and cathode materials have the same basic structure, except for the degree of cyclization. (Figure 18). Both have the 2240 cm^{-1} — C≡N band, but the intensity of this peak of the anolyte polymer is higher than that of the cathode material. This verifies the predominance of cyclic sequences in the cathodic polymer. As mentioned earlier, the color of cathodic polymer was darker, indicating that cathode polymer has more cyclic units, in agreement with the IR spectra.

3.3. HEAT TREATMENT OF POLYACRYLONITRILES AND DETERMINATION OF THEIR CONDUCTIVITIES

Polyacrylonitrile, is a precursor polymer of carbon fibers which has conducting properties up to a certain degree. The inter and intramolecular cyclization of polyacrylonitriles produce a conducting structure. In this study we have a certain degree of cyclization that was explained by yellow to brown

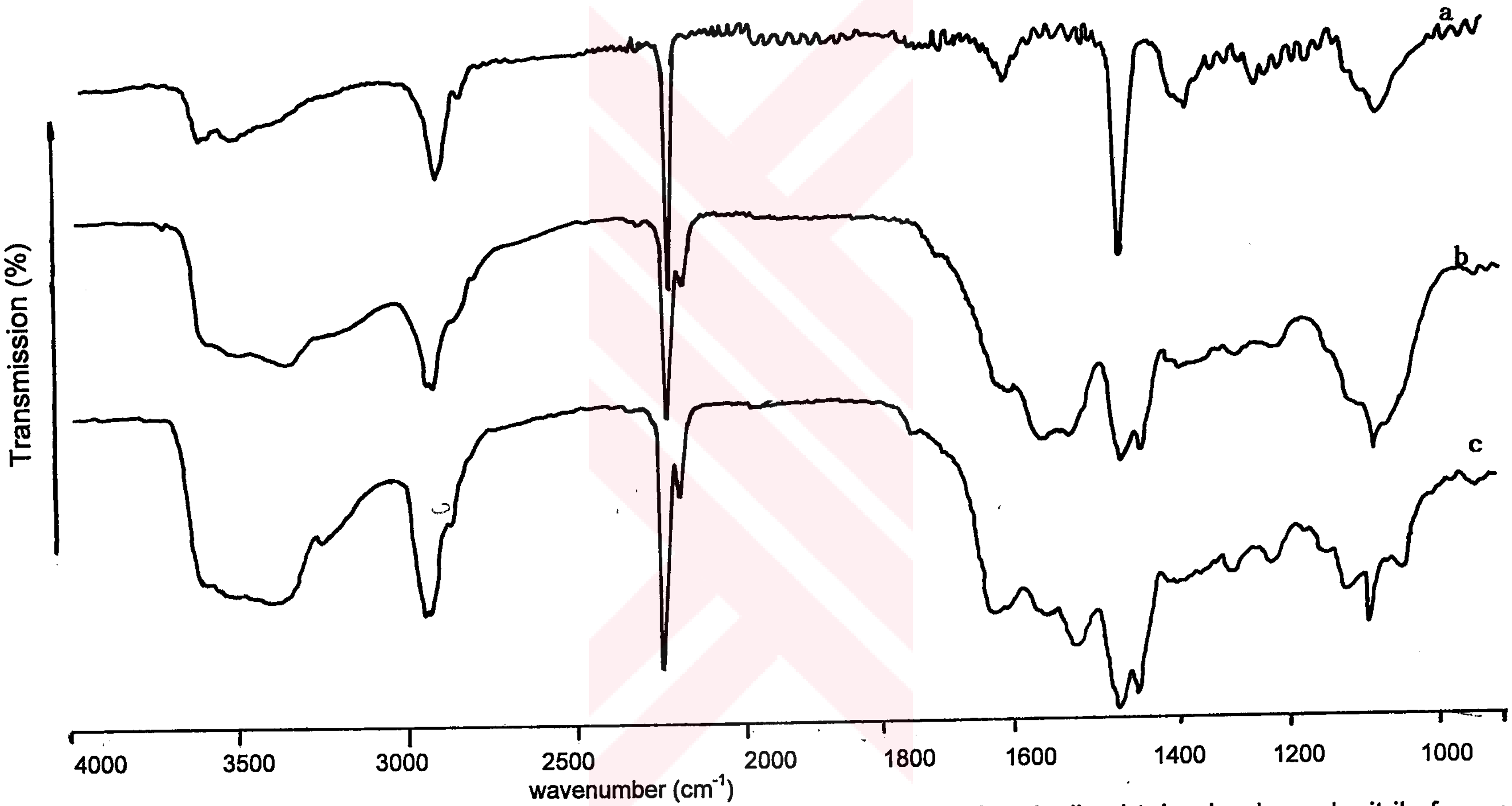


Figure 18. Infrared spectra of (a) linear polyacrylonitrile, (b) electrochemically obtained polyacrylonitrile from anode compartment, (c) same from cathode compartment (at -2.6 V vs Ag^{o} / Ag^{+})

coloration of polymers. The conductivity behavior of electrochemically obtained polymers was investigated.

Our aim was to obtain polyacrylonitrile films for further analysis. Therefore, colored catholyte polymer was heated up to 300°C under different pressures, but unfortunately no melting was observed. On the other hand, the color of polymer got darker (yellow to brown). The same procedure was applied to commercial white polyacrylonitrile. Same as electrochemical product, no melting but color change was observed. The degree of color change in the electrochemical product was higher. In other words, the rate of cyclization through nitrile groups were higher. The thermal analysis of these polyacrylonitriles supported this behavior which will be mentioned later.

Heat treatments of catholyte PAN, commercial white PAN was performed at different conditions. The conductivities of these polymers were measured. Electrochemical polymerization results in the polymerization through the carbon - carbon double bond and additional polymerization through unsaturated nitrile groups to some extent. The further (nitrile group) polymerization was enhanced by simply heating the polymer. As a consequence of heating, thermally stable cyclized structures which are often referred as ladder polymers are produced. In literature there are various proposals to the mechanism of cyclization.

During the heat stabilization of polymers ammonia and hydrogen cyanide were the principle gases evolved (Figure 2). Porous appearance of heat treated pellets was attributed to the above mentioned gas evolution. It was observed that as the heat treatment temperature was increased the porosity was also increased.

The results of four probe conductivity measurements of all heat treatment products are given in Table 12 and Figure 19. The commercial PAN (sample A) has a conductivity of about 10^{-8} S.cm^{-1} and the cathodic film (sample B) and the yellow catholyte polymer conductivity (sample C) values are in the order of 10^{-7}S.cm^{-1}. Thus, for the electrolysis products, although a considerable conductivity is not observed, the order of magnitude is higher than that of the commercial one.

Heat treatment of catholyte polymer at 200°C (open to atmosphere) for two hours (sample F) yields dark yellow to brown colored product having 10^{-7} S.cm^{-1} conductivity. Besides, under the same conditions the conductivity of commercial polyacrylonitrile was still in the order of 10^{-8} S.cm^{-1} where the color was not as yellow as the original catholyte polymer. The heat treatment time was increased to 6 hours which resulted in a conductivity of 10^{-7} S.cm^{-1} . At this circumstance, the conductivity of catholyte polymer is still little bit higher than the commercial one. Heat treatment of catholyte polymer at the same temperature , in vacuum for two hours, did not change the conductivity of the sample.

Heat treatment at 200°C in the presence of Lewis acid ($AlCl_3$) for two hours, led to an increase in conductivity. Those (sample G) which were heat treated open to atmosphere possessed a conductivity of about 10^{-6} S.cm^{-1}. The samples sealed in vacuum line (sample H, I, J, K) possessed a conductivity of 10^{-5} S.cm^{-1} . When compared to the heat treatment at the same temperature (in the absence of Lewis acid) the order of magnitude of conductivity was increased. The dopant effect of $AlCl_3$ was obvious. In literature, it was proposed that the presence of Lewis acid enhances cyclization reaction by forming a complex with nitrile groups.

The effect of higher temperatures in heat treatment was also investigated. The catholyte polymer was heat treated at 200^0 C open to the atmosphere for two hours in the first step. The pretreated sample was further heat treated in the presence of $AlCl_3$ under vacuum (sample I) and at 400^0 C for two more hours. The conductivity of the product was found to be 10^{-5} $S.cm^{-1}$.

Heat treatment at 200°C (open to atmosphere), in the presence of Lewis acid for two hours and further treatment of the same sample at 400°C (open to air) and in the presence of Lewis acid for two hours (sample J) did not further increase the conductivity level (10^{-5} $S.cm^{-1}$).

Heat treatment of the catholyte polymer at 200°C (under vacuum) in the presence of Lewis acid for two hours and further treatment of the same sample at 400°C, (under vacuum) in the presence of Lewis acid for two hours (sample K) did not bring any increase in conductivity where again the measured conductivity was about 10^{-5} $S.cm^{-1}$.

The conductivities of all these heat treatment processes were plotted in Figure 19. It was clearly observed that, the presence of Lewis acid increased the conductivity. Another observation is the positive effect of temperature . At high temperatures, namely 400°C, a maximum of 10^{-5} $S.cm^{-1}$ conductivity was observed.

In addition to above explained analyses some more experiments were also performed regarding to conductivity. For instance, for the following conditions either before or after the heat treatment the polymer lost its ability to form pellets. Therefore conductivity masurements were not carried out. Those conditions were the heat treatment at 200°C open to atmosphere for two hours followed by 400°C open to atmosphere for two hours (sample L); the heat treatment at 200°C open to atmosphere for six hours (sample M); the heat treatment at open to atmosphere and in the presence of $AlCl_3$ at 200°C for two hours, followed by 400°C for two hours, finally 600°C for two hours (sample N).

When heat treatment of pelletized catholyte polymer was carried out in a vacuum sealed tube and in the presence of $AlCl_3$ at 200°C for two hours, followed by 400°C for two hours, finally 600°C for two hours the sealed tube breakage was observed (sample O). Repeated analysis of that conditions resulted the same tube breaking. This can be attributed to the increased dopant concentration which increases the cyclization rate and evolution of more gaseous products.

As mentioned previously cathodic PAN film has a certain conductivity without any heat treatment. But, the film was brittle. Heat treatment at 200°C was increased the brittlesness of the film. As a result of this we could not perform the conductivity measurements. Thus, the additional heat treatments were not conducted on these samples.

3.4. DETERMINATION OF MOISTURE SENSITIVITY OF HEAT TREATED POLYACRYLONITRILES

Moisture sensitivity of polymers were investigated by exposing the samples to water vapor. All samples listed in Table 12 almost revealed similar type of moisture sensitivity. During exposure (adsorption), the conductivity of sample increased whereas upon removal (desorption) the conductivity decreased.

Commercial polyacrylonitrile has negligibly small sensitivity toward moisture. The original conductivity was 10^{-8} $S.cm^{-1}$ and during water vapor exposure it was still 10^{-8} $S.cm^{-1}$ (Table 13 and Figure 20).

Electrolytic cathodic polyacrylonitrile film (sample B) has a certain sensitivity against water vapor. The original conductivity was in the order of

Table 12. The Conductivities of Heat Treated Polyacrylonitriles

SAMPLE CODE	POLYMER	HEAT TREATMENT CONDITIONS	CONDUCTIVITY (S/cm)
A	PAN, COMMERCIAL	Without Heat Treatment	4×10^{-8}
B	PAN FILM , CATHODIC	Without Heat Treatment	1×10^{-7}
C	PAN, CATHOLYTE	Without Heat Treatment	2×10^{-7}
D	PAN, CATHOLYTE	(200°C, Vacuum)	4×10^{-7}
E	PAN, COMMERCIAL	(200°C, Air)	5×10^{-7}
F	PAN, CATHOLYTE	(200°C, Air)	7×10^{-7}
G	PAN, CATHOLYTE	(200°C, Air, $AlCl_3$)	4×10^{-6}
H	PAN, CATHOLYTE	(200°C, Vacuum, $AlCl_3$)	2×10^{-5}
I	PAN, CATHOLYTE	(200°C, Air) ▶ (400°C, Vacuum, $AlCl_3$)	3×10^{-5}
J	PAN, CATHOLYTE	(200°C, Air, $AlCl_3$) ▶ (400°C, Air, $AlCl_3$)	4×10^{-5}
K	PAN, CATHOLYTE	(200°C, Vacuum, $AlCl_3$) ▶ (400°C, Vacuum, $AlCl_3$	4×10^{-5}

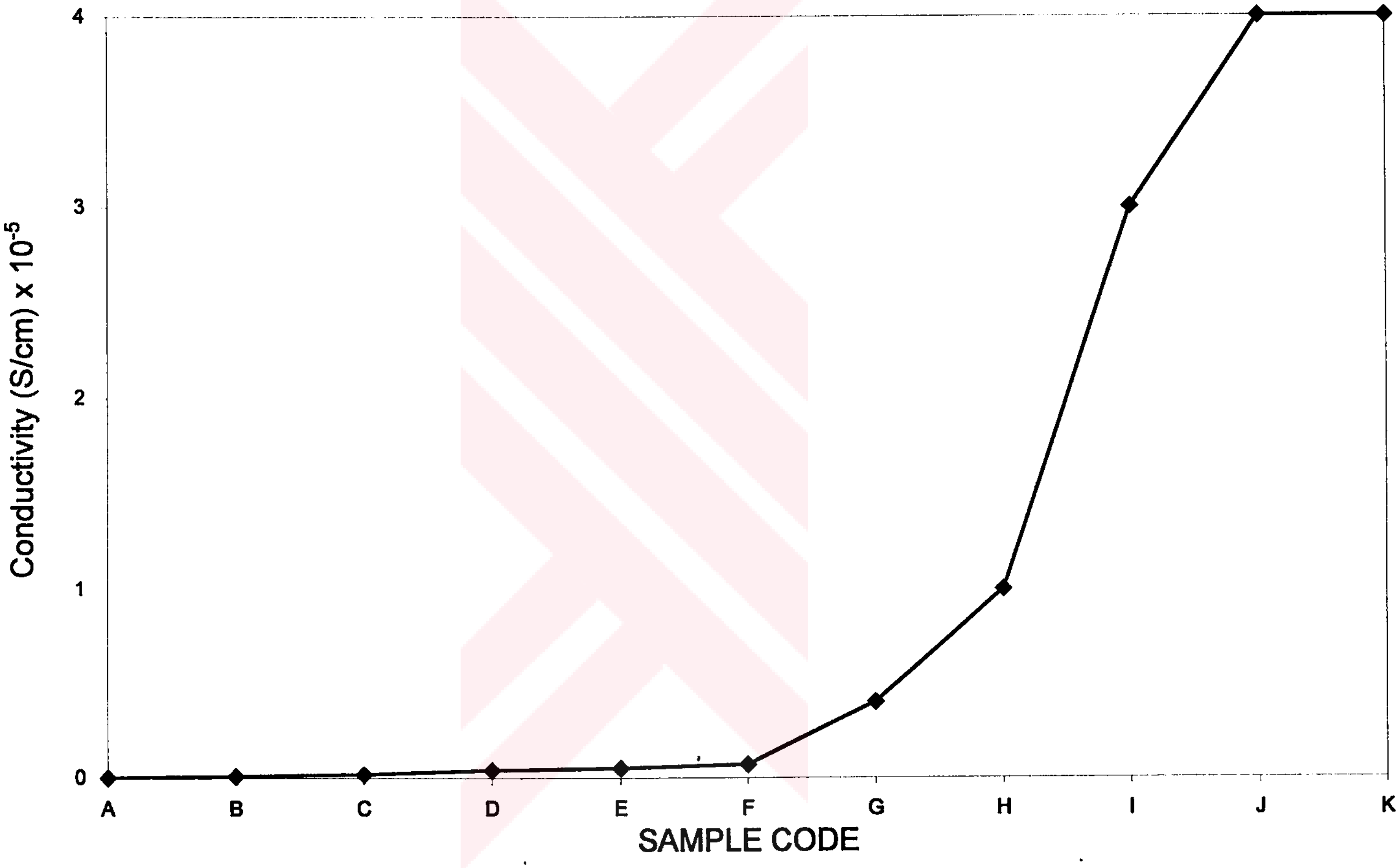


Figure 19. The conductivities of heat treated PAN

10^{-7} S.cm^{-1} where as the maximum conductivity achieved during adsorption and desorption process was 2 x 10^{-6} S.cm^{-1}. As evident from Table 14 and Figure 21, when cathodic PAN film is exposed to water vapor the conductivity increases and then decreases back when the film is opened to air. Figure 21 shows that, the conductivity increases as the number of successive adsorption - desorption steps increase.

Catholyte polymer (sample C) has higher gas sensing ability compared to the cathodic film. The maximum conductivity during gas sensing was around 6 x10^{-6} S.cm^{-1}. Reminding that the color of cathodic film was darker than the catholyte, and deepness of color was interpreted as the degree of cyclization, a little bit higher sensitivity was observed. That difference may be due to more physical compactness of the pelletized sample. The behavior of polymer toward adsorption desorption cycle was found to be reproducible (Table 15 and Figure 22).

When the catholyte polymer was heat treated at 200°C (open to atmosphere) (sample F) the gas sensitivity was increased and the conductivity was reached up to 3 x10^{-5} S.cm^{-1}(Table 16 and Figure 23). Heat treatment of commercial polyacrylonitrile under above mentioned conditions (sample E) caused an increase in the sensitivity. Maximum conductivity observed was 4 x10^{-6} S.cm^{-1} where an increasing trend in the response was observed (Table 17 and Figure 24). When compared to original form (the untreated), some sensitivity was acquired but yet not as high as the electrolysis product. When the heat treatment was carried out in vacuum (sample D), the gas sensing ability of catholyte was improved (maximum 5 x10^{-6} S.cm^{-1}) but not as much as the one observed for the sample open to atmospheric conditions. The sample which was exposed to cyclic adsorption - desorption processes lost some sensitivity (Table 18 and Figure 25). Heat treated polyacrylonitriles gained more sensitivity toward water vapor. That can be interpreted as inter or intramolecular cyclization through nitrile groups and as a consequence more conjugation in the structure was obtained.

For samples which are heat treated in the presence of the dopant ($AlCl_3$) (sample G) (open to atmosphere) no improvement in the water vapor sensitivity was observed compared to the ones treated in the absence of dopant. However, the positive effect of dopant was determined in sample H which was treated under vacuum. The former has $5x10^{-7}$ $S.cm^{-1}$ conductivity upon exposure whereas the latter has $1 x10^{-6}$ $S.cm^{-1}$ conductivity. The sensitivity was gradually decreased as the samples were cycled towards water vapor (Table 19, 20 and Figure 26, 27).

For the samples I, J, K which were obtained at higher treatment temperatures and in the presence of dopant the water vapor sensitivity was developed more. The order of conductivity was 10^{-4} $S.cm^{-1}$. Sample I has a little bit lower sensitivity compared to the others. (Table 21 and Figure 28). Sample J and K acquired almost the same sensitivity where the maximum observed conductivity was around $1 x10^{-3}$ $S.cm^{-1}$ within 6 minutes of exposure (Tables 22, 23 and Figures 29, 30).

The increased sensitivity in case of last three samples was attributed to the further treatment of polyacrylonitrile at high temperatures, resulting in more ladder like structure and dopant effect.

In summary, all of the heat treated samples possessed some sensitivity toward water vapor which were determined by resistance changes. The comparison of moisture sensitivity of all samples were given in Figure 30. The samples show rapid and reversible response. The background resistance remains almost constant indicating that doping and undoping processes are very rapid and reversible. The most drastic changes in sensitivity were

Table 13. Results of Moisture Sensitivity Analysis of Commercial PAN (sample A)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^8$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^8$)	CONDUCTIVITY (S /cm) ($x10^{-8}$)
ADS-1	1	5.25	0.74	1.36
	2	5.63	0.79	1.27
	3	4.63	0.65	1.54
	4	3.15	0.44	2.27
	5	2.72	0.38	2.63
	6	2.19	0.31	3.26
DES-1	1	3.28	0.46	2.18
	2	3.58	0.50	1.99
	3	3.58	0.50	1.99
	4	3.58	0.50	1.99
	5	3.28	0.46	2.18
	6	3.15	0.44	2.27
ADS-2	1	5.63	0.79	1.27
	2	7.88	1.10	0.91
	3	6.56	0.92	1.09
	4	4.92	0.69	1.45
	5	3.15	0.44	2.27
	6	2.02	0.28	3.54
DES-2	1	4.38	0.61	1.63
	2	6.56	0.92	1.09
	3	6.56	0.92	1.09
	4	6.56	0.92	1.09
	5	6.56	0.92	1.09
	6	6.56	0.92	1.09
ADS-3	1	6.56	0.92	1.09
	2	7.16	1.00	1.00
	3	6.56	0.92	1.09
	4	5.25	0.74	1.36
	5	3.75	0.53	1.90
	6	2.32	0.32	3.08

ADS: Adsorption
DES: Desorption

Table 13. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) (x10^8)	SPECIFIC RESISTANCE (ohm.cm) (x10^8)	CONDUCTIVITY (S /cm) (x10^{-8})
DES-3	1	4.63	0.65	1.54
	2	4.92	0.69	1.45
	3	4.92	0.69	1.45
	4	4.92	0.69	1.45
	5	4.92	0.69	1.45
	6	4.92	0.69	1.45
ADS-4	1	6.06	0.85	1.18
	2	6.56	0.92	1.09
	3	5.63	0.79	1.27
	4	4.15	0.58	1.72
	5	2.81	0.39	2.54
	6	1.97	0.28	3.63
DES-4	1	5.63	0.79	1.27
	2	6.56	0.92	1.09
	3	6.56	0.92	1.09
	4	6.56	0.92	1.09
	5	6.56	0.92	1.09
	6	6.56	0.92	1.09
ADS-5	1	4.63	0.65	1.54
	2	6.06	0.85	1.18
	3	5.25	0.74	1.36
	4	4.15	0.58	1.72
	5	3.28	0.46	2.18
	6	2.63	0.37	2.72
DES-5	1	5.25	0.74	1.36
	2	6.56	0.92	1.09
	3	6.06	0.85	1.18
	4	6.06	0.85	1.18
	5	6.06	0.85	1.18
	6	6.06	0.85	1.18

ADS: Adsorption
DES: Desorption

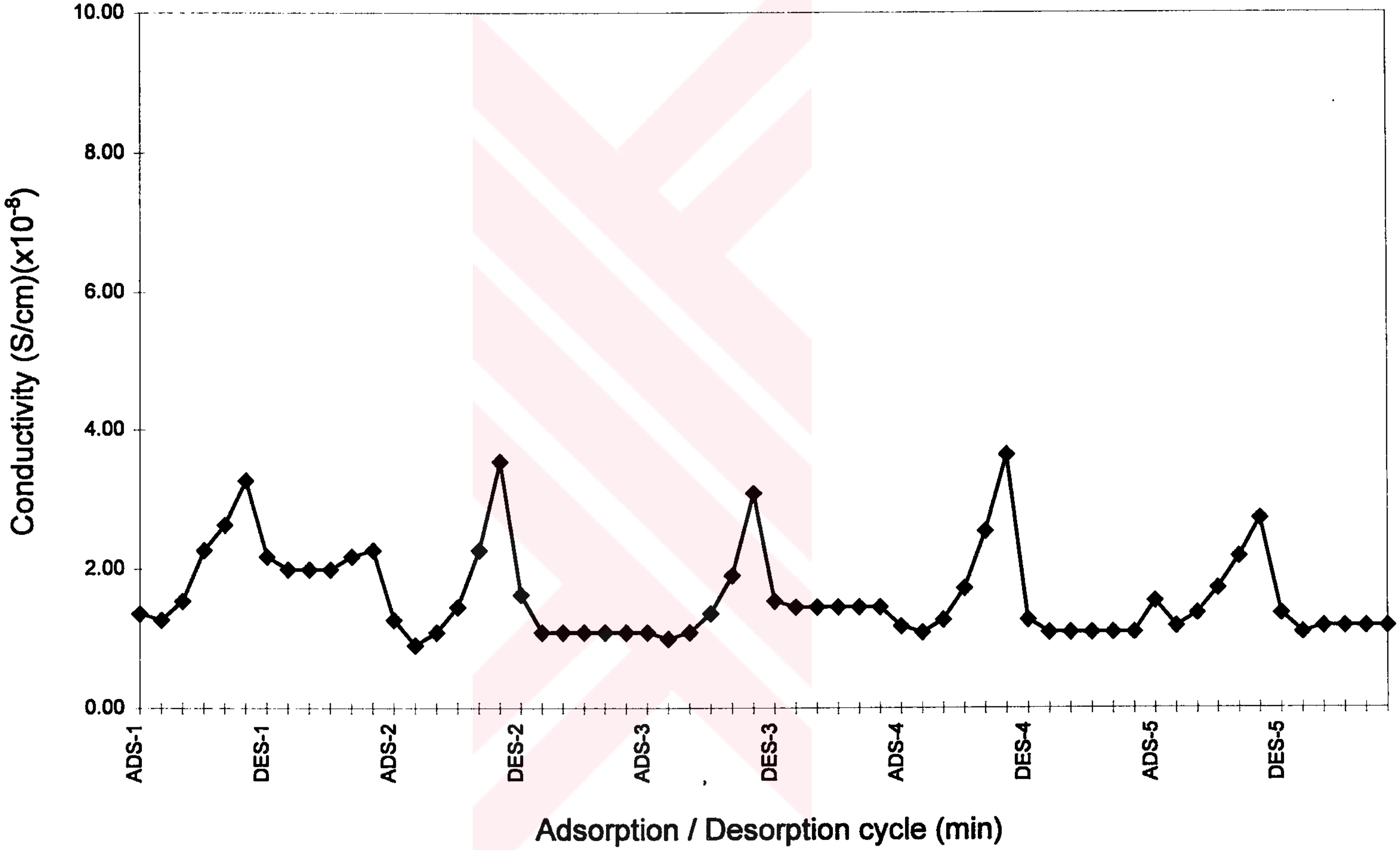


Figure 20. Sensitivity of commercial PAN to moisture (sample A)

Table 14. Results of Moisture Sensitivity Analysis of Cathodic PAN Film (sample B)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^8$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^6$)	CONDUCTIVITY (S /cm) ($x10^{-7}$)
ADS-1	1	1.77	3.18	3.14
	2	1.34	2.41	4.15
	3	1.05	1.89	5.28
	4	0.82	1.47	6.79
	5	0.63	1.14	8.81
	6	0.50	0.90	11.07
DES-1	1	1.64	2.94	3.40
	2	1.92	3.46	2.89
	3	1.92	3.46	2.89
	4	2.01	3.61	2.77
	5	2.01	3.61	2.77
	6	2.01	3.61	2.77
ADS-2	1	1.92	3.46	2.89
	2	1.84	3.31	3.02
	3	1.23	2.21	4.53
	4	0.82	1.47	6.79
	5	0.57	1.03	9.69
	6	0.42	0.76	13.08
DES-2	1	1.58	2.84	3.52
	2	2.32	4.18	2.39
	3	2.45	4.42	2.26
	4	2.45	4.42	2.26
	5	2.60	4.68	2.14
	6	2.60	4.68	2.14
ADS-3	1	1.38	2.48	4.03
	2	1.38	2.48	4.03
	3	0.94	1.69	5.91
	4	0.62	1.12	8.93
	5	0.43	0.78	12.83
	6	0.31	0.56	17.86

ADS: Adsorption
DES: Desorption

Table 14. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(\times10^{8})$	SPECIFIC RESISTANCE (ohm.cm) $(\times10^{6})$	CONDUCTIVITY (S /cm) $(\times10^{-7})$
DES-3	1	2.10	3.79	2.64
	2	2.21	3.97	2.52
	3	2.21	3.97	2.52
	4	2.32	4.18	2.39
	5	2.32	4.18	2.39
	6	2.32	4.18	2.39
ADS-4	1	1.92	3.46	2.89
	2	1.38	2.48	4.03
	3	0.92	1.66	6.04
	4	0.57	1.03	9.69
	5	0.38	0.69	14.59
	6	0.28	0.50	20.13
DES-4	1	1.30	2.34	4.28
	2	2.21	3.97	2.52
	3	2.45	4.42	2.26
	4	2.76	4.97	2.01
	5	2.76	4.97	2.01
	6	2.76	4.97	2.01

ADS: Adsorption
DES: Desorption

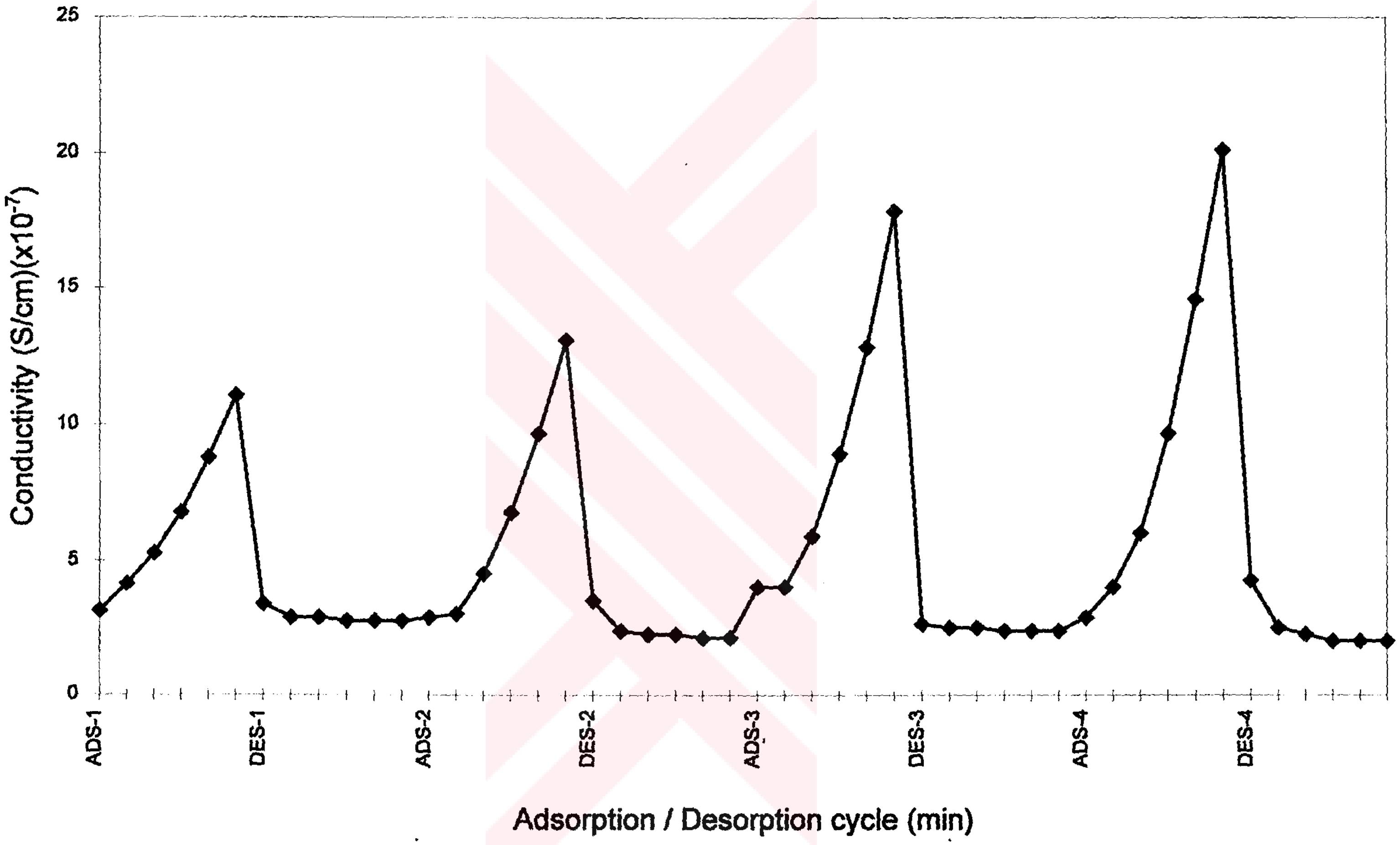


Figure 21. Sensitivity of cathodic PAN film to moisture (sample B)

Table 15. Results of moisture snsitivity analysis of catholyte PAN (Sample C)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(x10^8)$	SPECIFIC RESISTANCE (ohm.cm) $(x10^6)$	CONDUCTIVITY (S /cm) $(x10^{-7})$
ADS-1	1	2.94	5.14	1.95
	2	1.55	2.71	3.70
	3	0.52	0.92	10.89
	4	0.29	0.50	20.04
	5	0.19	0.33	30.74
	6	0.10	0.17	58.36
DES-1	1	1.96	3.43	2.92
	2	3.26	5.71	1.75
	3	3.26	5.71	1.75
	4	3.26	5.71	1.75
	5	3.26	5.71	1.75
	6	3.26	5.71	1.75
ADS-2	1	2.45	4.28	2.33
	2	1.34	2.34	4.28
	3	0.50	0.87	11.48
	4	0.20	0.35	28.98
	5	0.11	0.20	50.58
	6	0.11	0.19	52.52
DES-2	1	0.92	1.61	6.22
	2	2.45	4.28	2.33
	3	2.45	4.28	2.33
	4	2.45	4.28	2.33
	5	2.45	4.28	2.33
	6	2.45	4.28	2.33
ADS-3	1	2.45	4.28	2.33
	2	1.47	2.57	3.89
	3	0.73	1.29	7.78
	4	0.18	0.32	31.12
	5	0.10	0.17	58.36
	6	0.08	0.15	68.08

ADS: Adsorption
DES: Desorption

Table15. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(x10^8)$	SPECIFIC RESISTANCE (ohm.cm) $(x10^6)$	CONDUCTIVITY (S /cm) $(x10^{-7})$
DES-3	1	1.13	1.98	5.06
	2	2.45	4.28	2.33
	3	2.45	4.28	2.33
	4	2.45	4.28	2.33
	5	2.45	4.28	2.33
	6	2.45	4.28	2.33
ADS-4	1	2.45	4.28	2.33
	2	1.40	2.45	4.09
	3	0.65	1.14	8.75
	4	0.21	0.37	27.23
	5	0.15	0.26	38.91
	6	0.10	0.18	56.41
DES-4	1	0.82	1.43	7.00
	2	2.26	3.95	2.53
	3	2.26	3.95	2.53
	4	2.45	4.28	2.33
	5	2.45	4.28	2.33
	6	2.45	4.28	2.33

ADS: Adsorption
DES: Desorption

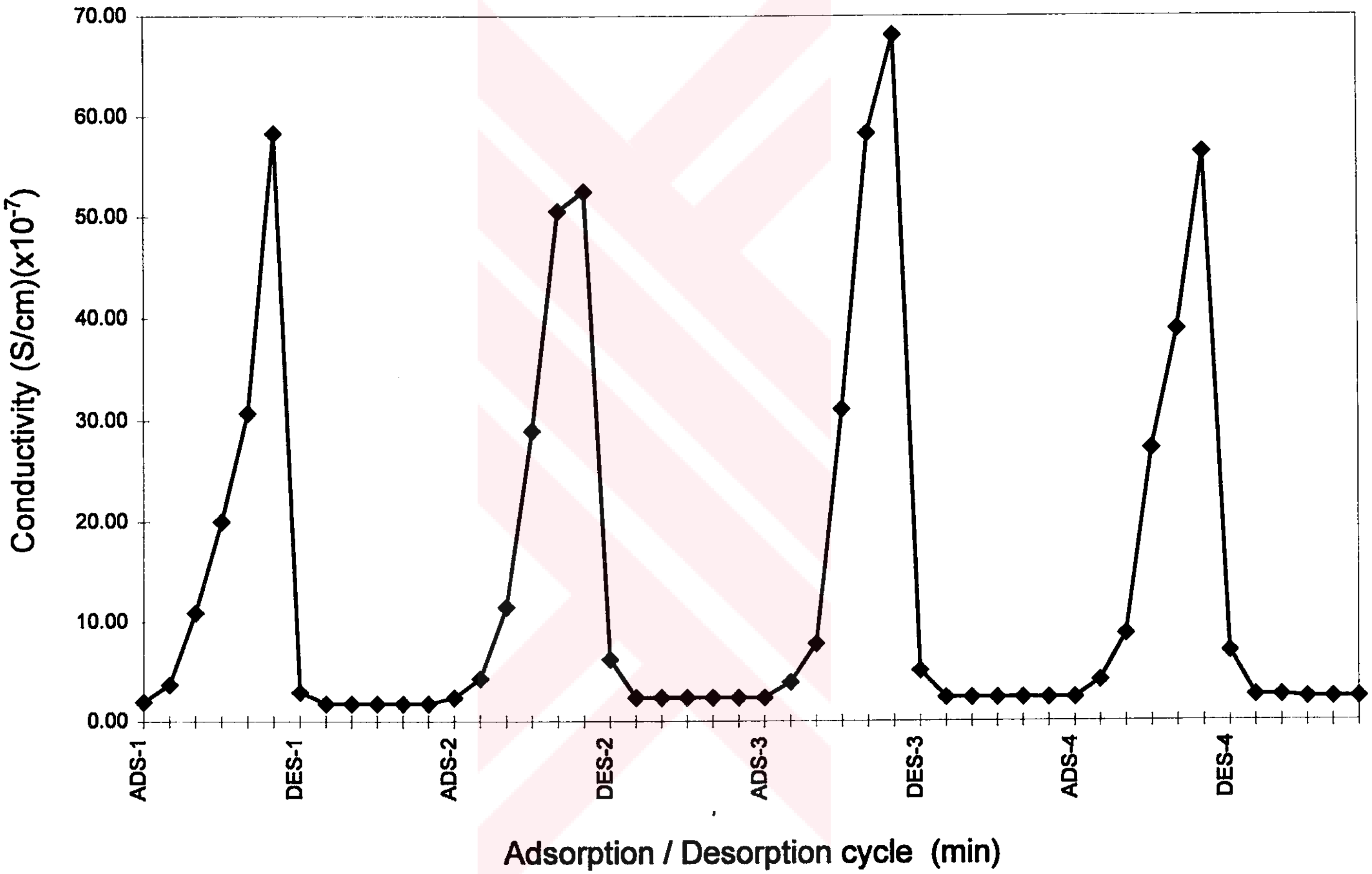


Figure 22. Sensitivity of cathodic PAN to moisture (sample C)

Table 16. Results of moisture sensitivity analysis of heat treated* PAN (sample F) (* 200^{o}C, Air)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) (x10^{8})	SPECIFIC RESISTANCE (ohm.cm) (x10^{5})	CONDUCTIVITY (S /cm) (x10^{-6})
ADS-1	1	1.84	1.09	1.09
	2	0.70	2.86	2.86
	3	0.35	5.65	5.65
	4	0.22	9.19	9.19
	5	0.14	14.16	14.16
	6	0.10	19.06	19.06
DES-1	1	2.67	0.75	0.75
	2	3.67	0.54	0.54
	3	3.67	0.54	0.54
	4	3.67	0.54	0.54
	5	3.67	0.54	0.54
	6	3.67	0.54	0.54
ADS-2	1	0.89	2.25	2.25
	2	0.36	5.58	5.58
	3	0.22	8.92	8.92
	4	0.15	13.41	13.41
	5	0.11	18.79	18.79
	6	0.08	24.71	24.71
DES-2	1	2.26	0.89	0.89
	2	2.67	0.75	0.75
	3	2.94	0.68	0.68
	4	2.94	0.68	0.68
	5	2.94	0.68	0.68
	6	3.26	0.61	0.61
ADS-3	1	0.84	2.38	2.38
	2	0.26	7.63	7.63
	3	0.18	11.30	11.30
	4	0.12	16.41	16.41
	5	0.10	20.90	20.90
	6	0.08	26.35	26.35

ADS: Adsorption
DES: Desorption

Table 16. (cont)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^8$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^5$)	CONDUCTIVITY (S /cm) ($x10^{-6}$)
DES-3	1	1.84	1.09	1.09
	2	3.67	0.54	0.54
	3	3.67	0.54	0.54
	4	3.67	0.54	0.54
	5	3.67	0.54	0.54
	6	3.67	0.54	0.54
ADS-4	1	0.30	6.60	6.60
	2	0.18	11.30	11.30
	3	0.13	16.00	16.00
	4	0.09	23.42	23.42
	5	0.07	26.69	26.69
	6	0.07	27.91	27.91
DES-4	1	1.34	1.50	1.50
	2	1.63	1.23	1.23
	3	1.63	1.23	1.23
	4	1.63	1.23	1.23
	5	1.63	1.23	1.23
	6	1.63	1.23	1.23

ADS: Adsorption
DES: Desorption

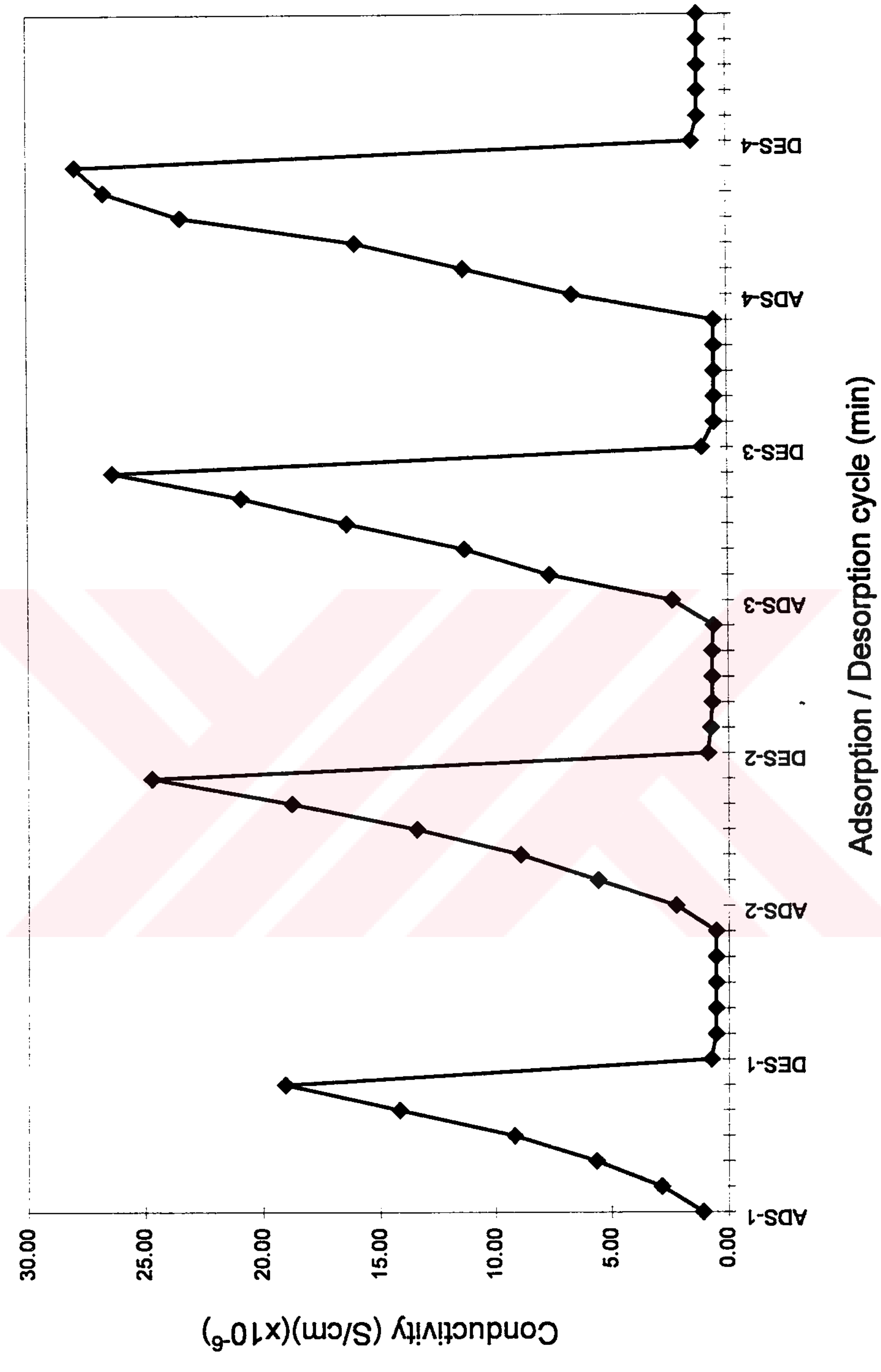


Figure 23. Sensitivity of heat treated PAN to moisture (sample F)

Table 17. Results of moisture sensitivity analysis of heat treated* commercial PAN (sample E) (*200°C, Vacuum)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^8$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^6$)	CONDUCTIVITY (S /cm) ($x10^{-7}$)
ADS-1	1	0.90	1.70	5.80
	2	0.90	1.90	5.30
	3	0.80	1.50	6.50
	4	0.60	1.30	8.00
	5	0.20	0.40	23.10
	6	0.20	0.40	24.00
DES-1	1	0.70	1.50	6.80
	2	1.00	2.00	4.90
	3	1.30	2.60	3.90
	4	1.50	2.90	3.40
	5	1.50	3.10	3.20
	6	1.60	3.30	3.10
ADS-2	1	0.50	0.90	10.50
	2	0.30	0.60	16.30
	3	0.30	0.60	17.50
	4	0.30	0.50	19.80
	5	0.20	0.50	20.20
	6	0.20	0.50	21.30
DES-2	1	1.40	2.80	3.60
	2	1.70	3.50	2.90
	3	1.80	3.70	2.70
	4	2.00	3.90	2.60
	5	2.40	4.90	2.00
	6	2.40	4.90	2.00
ADS-3	1	0.40	0.80	12.30
	2	0.30	0.60	16.90
	3	0.30	0.50	18.20
	4	0.20	0.40	24.70
	5	0.20	0.30	29.80
	6	0.20	0.30	31.60

ADS: Adsorption
DES: Desorption

Table 17. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^8$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^6$)	CONDUCTIVITY (S /cm) ($x10^{-7}$)
DES-3	1	1.50	2.90	3.40
	2	2.10	4.20	2.40
	3	2.40	4.90	2.00
	4	2.40	4.90	2.00
	5	2.40	4.90	2.00
	6	2.40	4.90	2.00
ADS-4	1	0.80	1.60	6.10
	2	0.30	0.50	19.40
	3	0.20	0.40	25.70
	4	0.20	0.30	31.30
	5	0.10	0.30	34.00
	6	0.10	0.30	35.70
DES-4	1	1.50	3.10	3.20
	2	2.00	3.90	2.60
	3	2.10	4.20	2.40
	4	2.40	4.90	2.00
	5	2.40	4.90	2.00
	6	2.40	4.90	2.00
ADS-5	1	1.20	2.40	4.30
	2	0.70	1.30	7.50
	3	0.50	0.90	10.60
	4	0.20	0.40	24.90
	5	0.20	0.30	33.20
	6	0.10	0.30	34.00
DES-5	1	1.60	3.30	3.10
	2	2.30	4.50	2.20
	3	2.40	4.90	2.00
	4	2.70	5.30	1.90
	5	2.70	5.30	1.90
	6	2.70	5.30	1.90

ADS: Adsorption
DES: Desorption

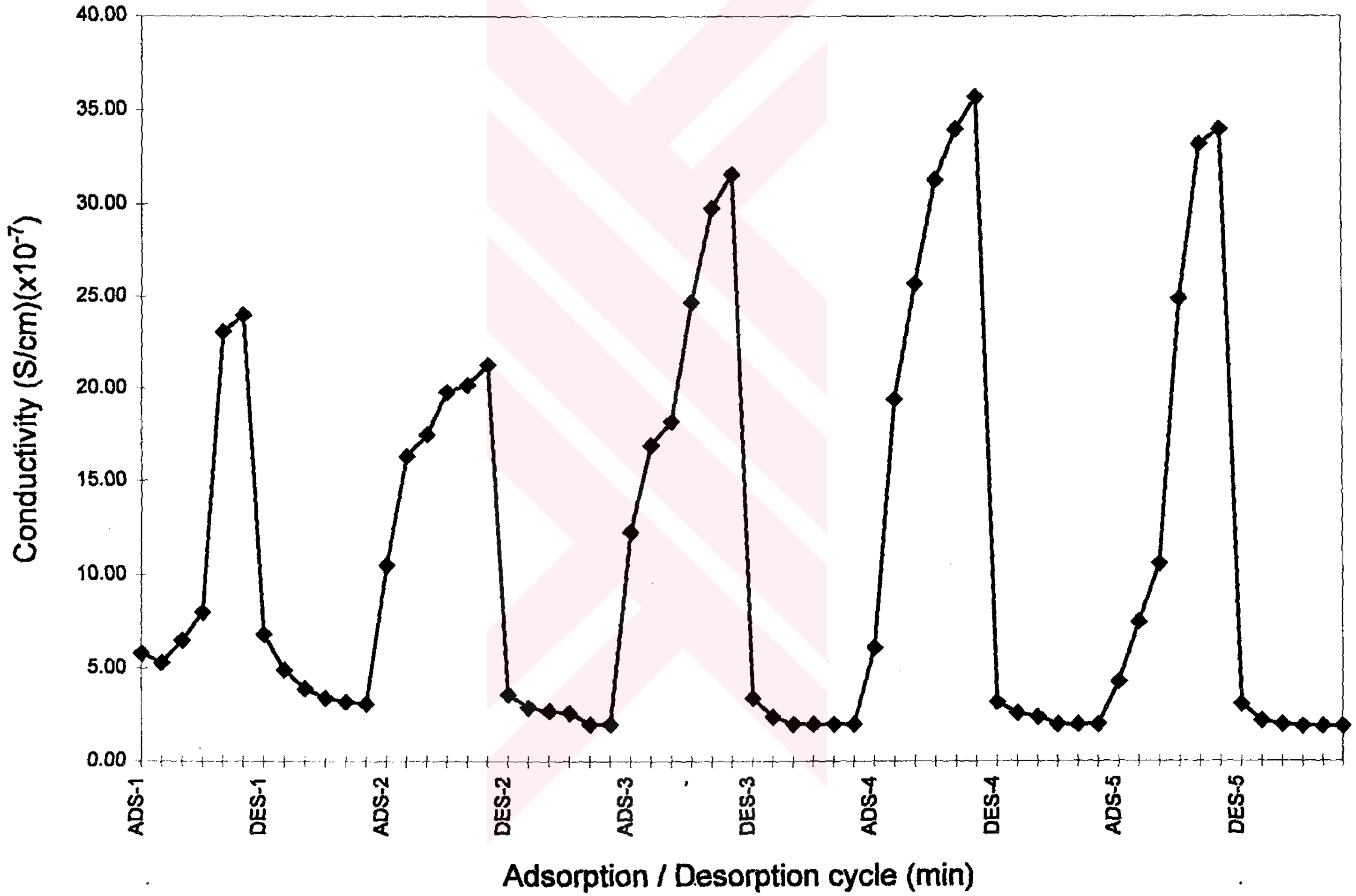


Figure 24. Sensitivity of heat treated commercial PAN to moisture (sample E)

Table 18. Results of moisture sensitivity analysis of heat treated* PAN (sample D) (200°C, Vacuum)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(x10^{7})$	SPECIFIC RESISTANCE (ohm.cm) $(x10^{6})$	CONDUCTIVITY (S /cm) $(x10^{-7})$
ADS-1	1	9.13	2.37	4.21
	2	4.00	1.04	9.62
	3	1.88	0.49	20.42
	4	1.47	0.38	26.08
	5	1.02	0.26	37.80
	6	0.88	0.23	43.86
DES-1	1	12.17	3.16	3.16
	2	15.37	4.00	2.50
	3	18.25	4.75	2.11
	4	17.18	4.47	2.24
	5	17.18	4.47	2.24
	6	17.18	4.47	2.24
ADS-2	1	11.23	2.92	3.42
	2	7.68	2.00	5.01
	3	3.56	0.93	10.80
	4	1.72	0.45	22.39
	5	1.39	0.36	27.66
	6	1.04	0.27	36.88
DES-2	1	11.23	2.92	3.42
	2	14.60	3.80	2.63
	3	15.37	4.00	2.50
	4	15.37	4.00	2.50
	5	15.37	4.00	2.50
	6	15.37	4.00	2.50
ADS-3	1	12.17	3.16	3.16
	2	9.13	2.37	4.21
	3	5.03	1.31	7.64
	4	2.73	0.71	14.09
	5	1.78	0.46	21.60
	6	1.12	0.29	34.25

ADS: Adsorption
DES: Desorption

Table 18. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^{7}$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^{6}$)	CONDUCTIVITY (S /cm) ($x10^{-7}$)
DES-3	1	11.23	2.92	3.42
	2	14.60	3.80	2.63
	3	14.60	3.80	2.63
	4	14.60	3.80	2.63
	5	14.60	3.80	2.63
	6	14.60	3.80	2.63
ADS-4	1	14.60	3.80	2.63
	2	10.81	2.81	3.56
	3	7.68	2.00	5.01
	4	3.70	0.96	10.41
	5	2.20	0.57	17.52
	6	1.36		28.19
			0.35	
DES-4	1	14.60	3.80	2.63
	2	17.18	4.47	2.24
	3	18.25	4.75	2.11
	4	18.25	4.75	2.11
	5	20.86	5.42	1.84
	6	20.86	5.42	1.84

ADS: Adsorption
DES: Desorption

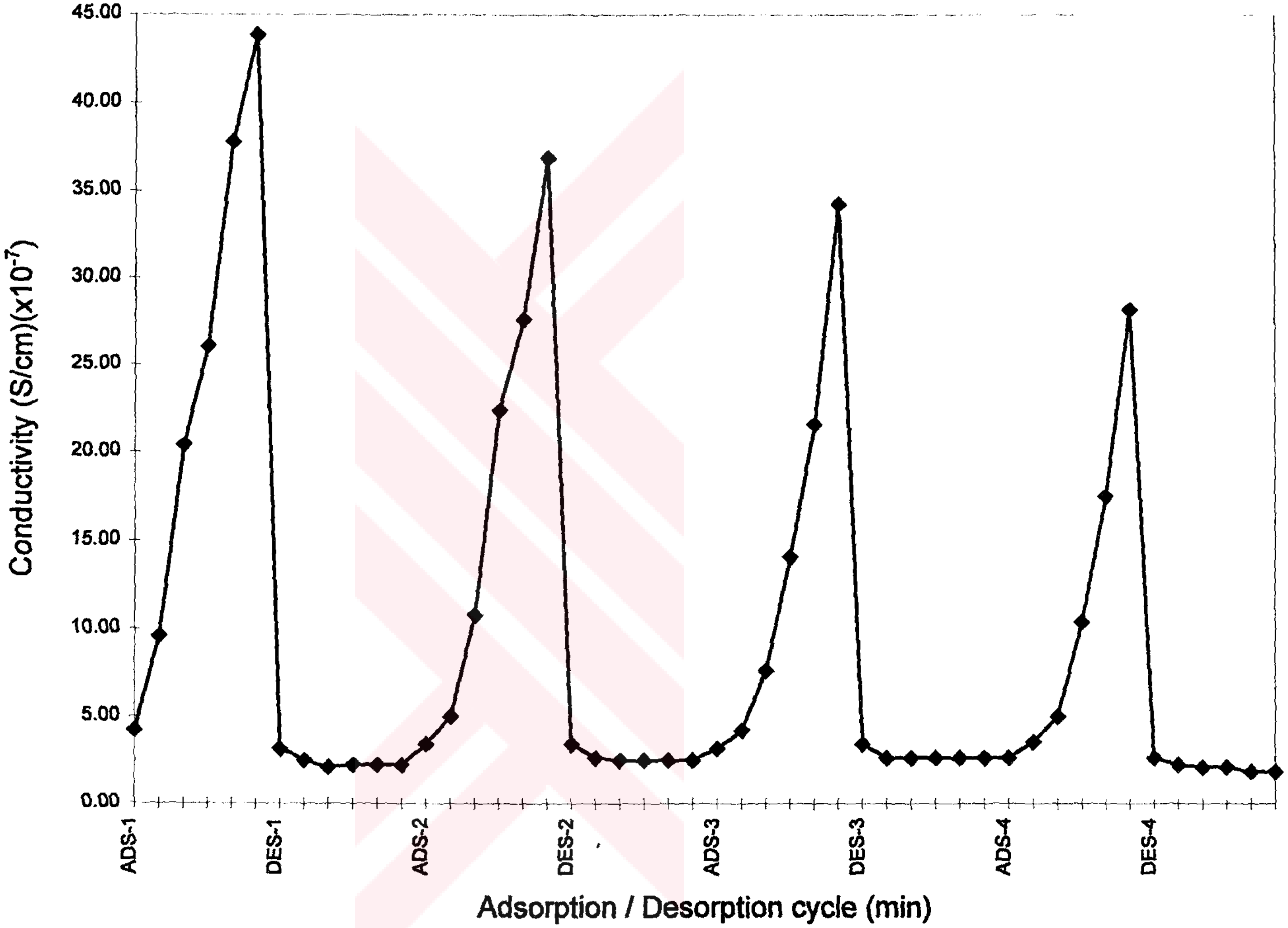


Figure 25. Sensitivity of heat treated PAN to moisture (sample D)

Table 19. Results of moisture sensitivity analysis of heat treated* PAN (sample G) (* 200°C, Air, $AlCl_3$)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(x10^5)$	SPECIFIC RESISTANCE (ohm.cm) $(x10^4)$	CONDUCTIVITY (S /cm) $(x10^{-6})$
ADS-1	1	7.73	1.47	6.81
	2	6.07	1.15	8.67
	3	5.76	1.09	9.14
	4	5.25	1.00	10.03
	5	5.13	0.97	10.27
	6	4.90	0.93	10.75
DES-1	1	23.50	4.47	2.24
	2	29.38	5.58	1.79
	3	50.65	9.62	1.04
	4	73.44	13.95	0.72
	5	98.91	18.79	0.53
	6	122.91	23.35	0.43
ADS-2	1	34.32	6.52	1.53
	2	8.44	1.60	6.24
	3	6.08	1.16	8.65
	4	5.47	1.04	9.62
	5	5.30	1.01	9.93
	6	5.41	1.03	9.73
DES-2	1	11.30	2.15	4.66
	2	42.21	8.02	1.25
	3	90.94	17.28	0.58
	4	135.37	25.72	0.39
	5	169.80	32.26	0.31
	6	219.22	41.65	0.24
ADS-3	1	89.56	17.02	0.59
	2	43.33	8.23	1.21
	3	9.57	1.82	5.50
	4	7.73	1.47	6.81
	5	7.06	1.34	7.45
	6	6.86	1.30	7.67

ADS: Adsorption
DES: Desorption

Table 19. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^5$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^4$)	CONDUCTIVITY (S /cm) ($x10^{-6}$)
DES-3	1	15.63	2.97	3.37
	2	55.63	10.57	0.95
	3	130.56	24.81	0.40
	4	212.86	40.44	0.25
	5	269.50	51.20	0.20
	6	341.57	64.90	0.15
ADS-4	1	139.22	26.45	0.38
	2	18.71	3.55	2.81
	3	12.14	2.31	4.34
	4	9.92	1.89	5.30
	5	8.64	1.64	6.09
	6	8.18	1.55	6.43
DES-4	1	42.95	8.16	1.23
	2	97.27	18.48	0.54
	3	194.54	36.96	0.27
	4	262.28	49.83	0.20
	5	386.52	73.44	0.14
	6	466.27	88.59	0.11

ADS: Adsorption
DES: Desorption

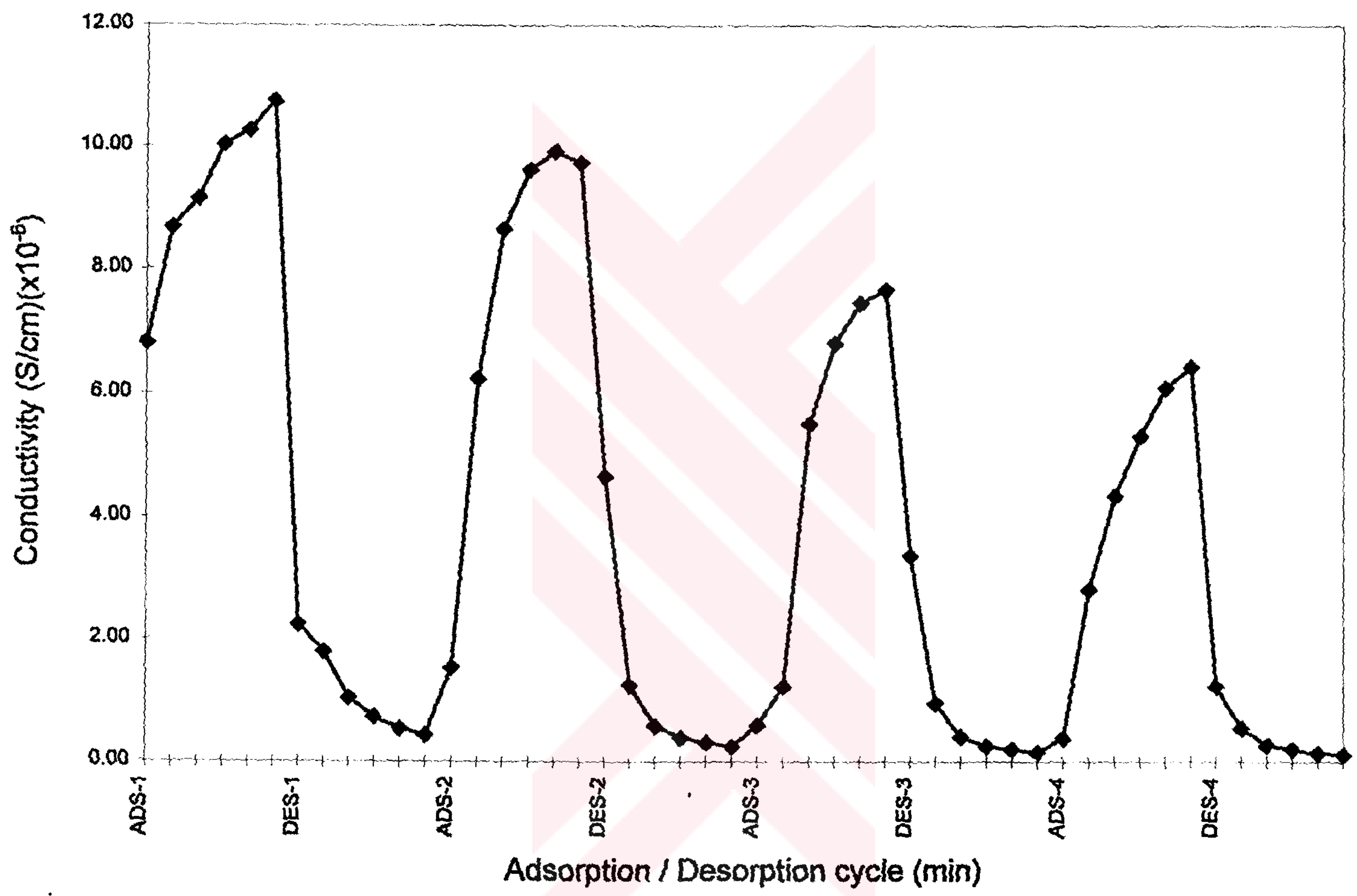


Figure 26.Sensitivity of heat treated PAN to moisture (sample G)

Table 20. Results of moisture sensitivity analysis of heat treated* PAN (sample H) (* 200°C, Vacuum, $AlCl_3$)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(\times 10^{6})$	SPECIFIC RESISTANCE (ohm.cm) $(\times 10^{4})$	CONDUCTIVITY (S /cm) $(\times 10^{-5})$
ADS-1	1	5.30	8.70	1.15
	2	1.63	2.67	3.74
	3	1.46	2.40	4.17
	4	0.90	1.48	6.77
	5	0.61	1.00	9.96
	6	0.59	0.96	10.38
DES-1	1	1.59	2.60	3.84
	2	1.98	3.26	3.07
	3	2.39	3.92	2.55
	4	2.62	4.30	2.32
	5	2.96	4.86	2.06
	6	3.16	5.18	1.93
ADS-2	1	3.38	5.54	1.81
	2	1.08	1.76	5.67
	3	0.87	1.43	6.97
	4	0.83	1.36	7.33
	5	0.81	1.33	7.51
	6	0.80	1.31	7.64
DES-2	1	6.26	10.27	0.97
	2	7.69	12.61	0.79
	3	9.04	14.82	0.67
	4	10.20	16.73	0.60
	5	11.30	18.53	0.54
	6	12.39	20.33	0.49
ADS-3	1	2.67	4.38	2.28
	2	1.12	1.83	5.46
	3	0.88	1.44	6.95
	4	0.82	1.34	7.47
	5	0.79	1.30	7.70
	6	0.78	1.27	7.87
DES-3	1	4.56	7.48	1.34
	2	6.88	11.28	0.89
	3	9.45	15.49	0.65
	4	11.39	18.67	0.54
	5	13.41	22.00	0.45
	6	14.47	23.73	0.42

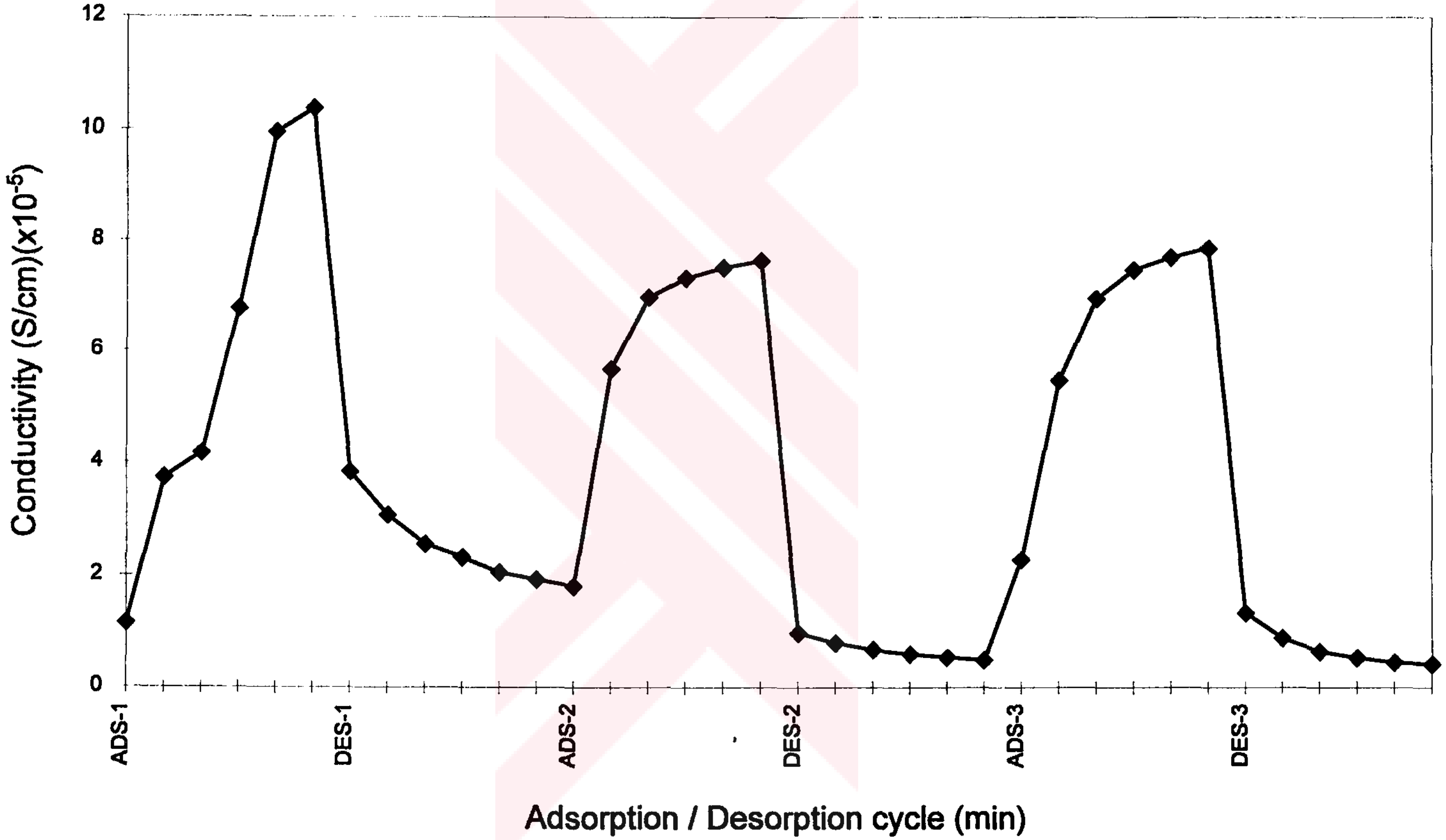


Figure 27. Sensitivity of heat treated PAN to moisture (sample H)

Table 21. Results of moisture sensitivity analysis of heat treated* PAN (sample I) (* 200°C,Air and 400°C, Vacuum, $AlCl_3$)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^6$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^3$)	CONDUCTIVITY (S /cm) ($x10^{-4}$)
ADS-1	1	1.96	9.32	1.07
	2	1.36	6.47	1.55
	3	1.21	5.76	1.73
	4	1.01	4.79	2.09
	5	0.84	3.97	2.52
	6	0.80	3.80	2.63
DES-1	1	0.82	3.90	2.57
	2	0.84	3.99	2.50
	3	1.74	8.28	1.21
	4	2.54	12.04	0.83
	5	3.06	14.52	0.69
	6	3.25	15.43	0.65
ADS-2	1	1.79	8.51	1.17
	2	1.19	5.68	1.76
	3	0.88	4.20	2.38
	4	0.73	3.47	2.88
	5	0.66	3.15	3.17
	6	0.71	3.38	2.96
DES-2	1	0.82	3.90	2.57
	2	0.84	3.97	2.52
	3	1.76	8.37	1.19
	4	2.52	11.95	0.84
	5	2.97	14.11	0.71
	6	3.18	15.12	0.66
ADS-3	1	2.75	13.09	0.76
	2	1.64	7.80	1.28
	3	1.13	5.35	1.87
	4	0.79	3.74	2.67
	5	0.76	3.61	2.77
	6	0.73	3.46	2.89

ADS: Adsorption
DES: Desorption

Table 21 (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^6$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^3$)	CONDUCTIVITY (S /cm) ($x10^{-4}$)
DES-3	1	1.01	4.81	2.08
	2	1.21	5.74	1.74
	3	2.21	10.51	0.95
	4	2.94	13.97	0.72
	5	3.85	18.29	0.55
	6	4.21	20.02	0.50
ADS-4	1	2.00	9.50	1.05
	2	1.39	6.61	1.51
	3	0.95	4.52	2.21
	4	0.86	4.10	2.44
	5	0.79	3.74	2.67
	6	0.76	3.59	2.79
DES-4	1	1.09	5.20	1.92
	2	1.27	6.02	1.66
	3	2.34	11.14	0.90
	4	3.32	15.76	0.63
	5	4.00	18.99	0.53
	6	4.21	20.02	0.50
ADS-5	1	2.40	11.39	0.88
	2	1.61	7.65	1.31
	3	1.15	5.47	1.83
	4	0.94	4.48	2.23
	5	0.88	4.16	2.40
	6	0.80	3.81	2.63
DES-5	1	1.19	5.68	1.76
	2	1.79	8.51	1.17
	3	2.15	10.22	0.98
	4	3.00	14.24	0.70
	5	3.58	17.03	0.59
	6	4.00	18.99	0.53

ADS: Adsorption
DES: Desorption

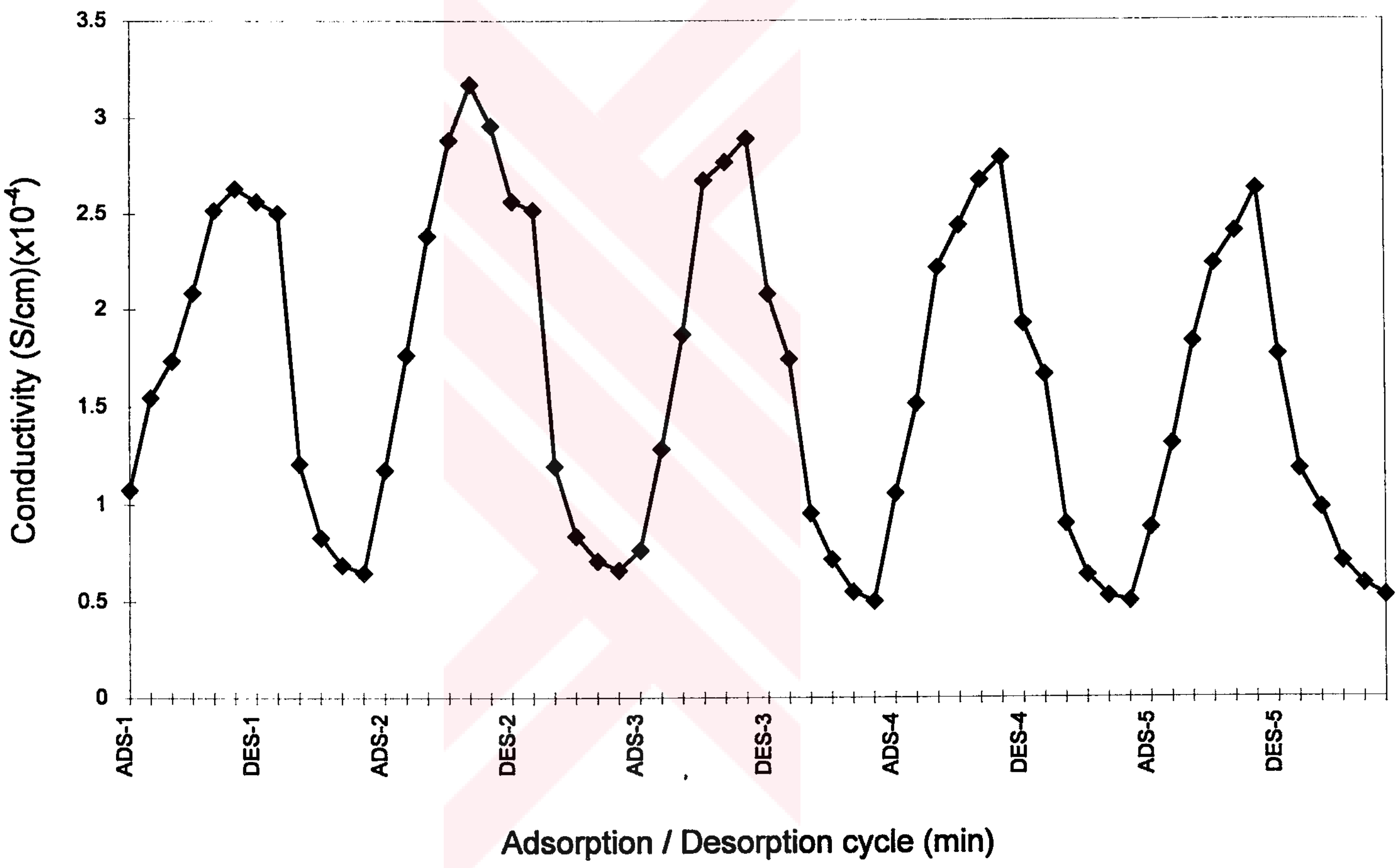


Figure 28. Sensitivity of heat treated PAN to moisture (sample I)

Table 22. Results of moisture sensitivity analysis of heat treated* PAN (sample J) (* 200°C, Air, $AlCl_3$ and 400°C, Air, $AlCl_3$)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^5$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^3$)	CONDUCTIVITY (S/cm) ($x10^{-4}$)
ADS-1	1	9.28	8.35	1.20
	2	4.45	4.01	2.50
	3	2.20	1.98	5.06
	4	1.49	1.34	7.45
	5	1.12	1.01	9.93
	6	1.10	0.99	10.14
DES-1	1	5.88	5.29	1.89
	2	9.87	8.88	1.13
	3	14.91	13.42	0.75
	4	17.69	15.92	0.63
	5	18.15	16.34	0.61
	6	19.98	17.98	0.56
ADS-2	1	6.05	5.45	1.84
	2	2.32	2.09	4.79
	3	1.49	1.34	7.48
	4	1.00	0.90	11.07
	5	0.98	0.88	11.36
	6	0.95	0.85	11.71
DES-2	1	1.63	1.47	6.81
	2	4.50	4.05	2.47
	3	6.16	5.54	1.80
	4	7.75	6.97	1.43
	5	8.66	7.80	1.28
	6	9.71	8.74	1.14
ADS-3	1	7.08	6.37	1.57
	2	3.31	2.98	3.35
	3	2.15	1.94	5:16
	4	1.65	1.49	6.73
	5	1.33	1.19	8.38
	6	1.17	1.06	9.47

ADS: Adsorption
DES: Desorption

Table 22. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^5$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^3$)	CONDUCTIVITY (S /cm) ($x10^{-4}$)
DES-3	1	2.68	2.41	4.15
	2	9.87	8.88	1.13
	3	14.91	13.42	0.75
	4	17.69	15.92	0.63
	5	18.15	16.34	0.61
	6	19.98	17.98	0.56
ADS-4	1	5.72	5.15	1.94
	2	2.78	2.50	3.99
	3	1.84	1.66	6.04
	4	1.50	1.35	7.43
	5	1.05	0.95	10.57
	6	0.98	0.88	11.31
DES-4	1	1.63	1.47	6.81
	2	4.50	4.05	2.47
	3	6.16	5.54	1.80
	4	7.75	6.97	1.43
	5	8.66	7.80	1.28
	6	9.71	8.74	1.14
ADS-5	1	8.70	7.83	1.28
	2	3.98	3.58	2.79
	3	2.56	2.31	4.34
	4	1.86	1.68	5.96
	5	1.55	1.40	7.16
	6	1.21	1.09	9.18
DES-5	1	2.68	2.41	4.15
	2	9.87	8.88	1.13
	3	14.91	13.42	0.75
	4	17.69	15.92	0.63
	5	18.15	16.34	0.61
	6	19.98	17.98	0.56

ADS: Adsorption
DES: Desorption

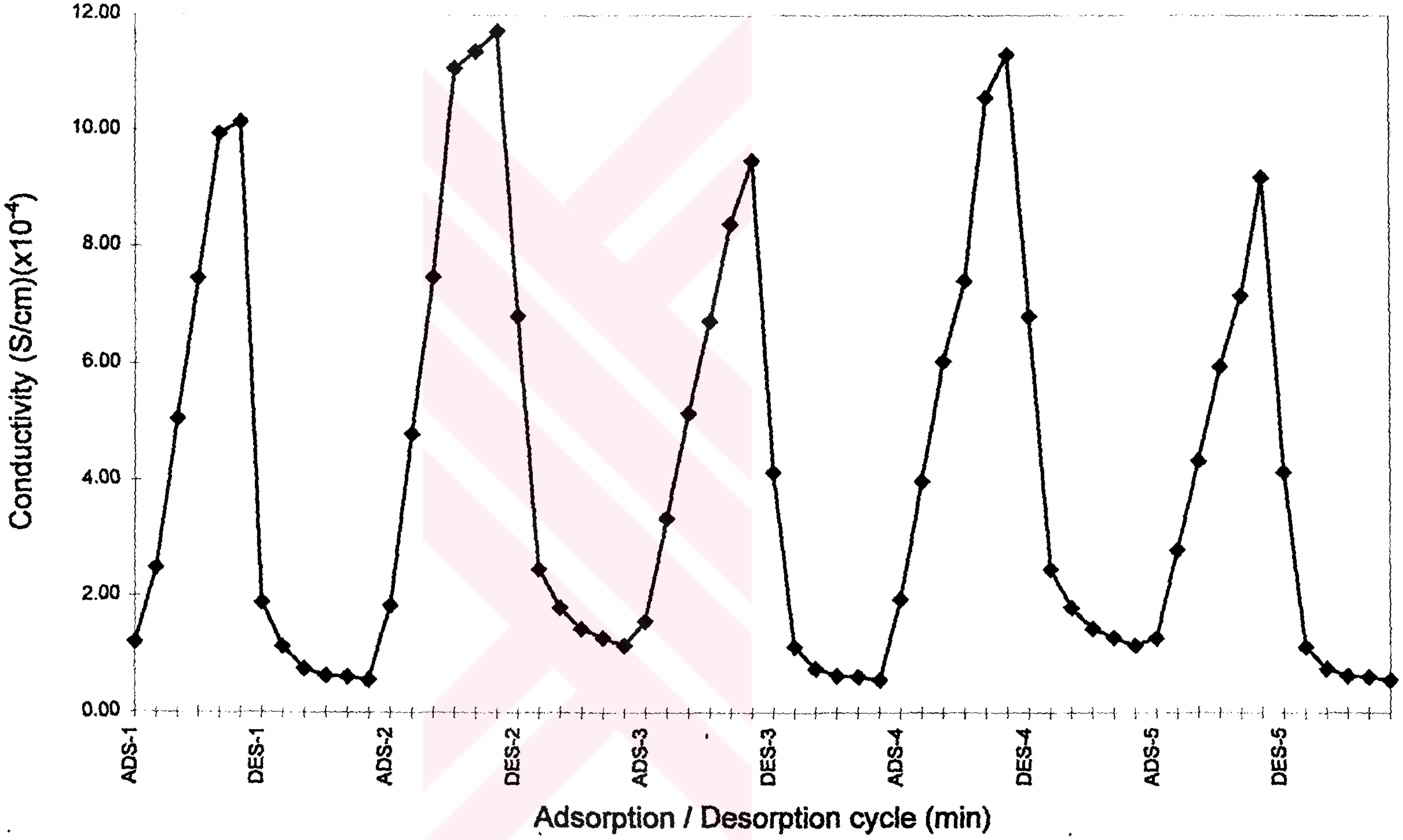


Figure 29. Sensitivity of heat treated PAN to moisture (sample J)

Table 23. Results of moisture sensitivity analysis of heat treated* PAN (sample K) (* 200°C, Vacuum, $AlCl_3$ and 400°C, Vacuum, $AlCl_3$

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) ($x10^5$)	SPECIFIC RESISTANCE (ohm.cm) ($x10^3$)	CONDUCTIVITY (S /cm) ($x10^{-4}$)
ADS-1	1	5.54	5.54	1.81
	2	2.89	2.89	3.46
	3	1.22	1.22	8.21
	4	1.02	1.02	9.78
	5	0.93	0.93	10.74
	6	0.88	0.88	11.42
DES-1	1	1.94	1.94	5.16
	2	4.10	4.10	2.44
	3	6.36	6.36	1.57
	4	9.17	9.17	1.09
	5	10.75	10.75	0.93
	6	12.99	12.99	0.77
ADS-2	1	5.38	5.38	1.86
	2	2.69	2.69	3.72
	3	2.04	2.04	4.91
	4	1.42	1.42	7.05
	5	1.12	1.12	8.95
	6	0.90	0.90	11.06
DES-2	1	2.89	2.89	3.46
	2	4.27	4.27	2.34
	3	6.00	6.00	1.67
	4	7.61	7.61	1.31
	5	9.75	9.75	1.03
	6	11.55	11.55	0.87
ADS-3	1	6.24	6.24	1.60
	2	3.47	3.47	2.89
	3	2.54	2.54	3.94
	4	1.45	1.45	6.89
	5	1.09	1.09	9.20
	6	0.85	0.85	11.83

ADS: Adsorption
DES: Desorption

Table 23. (cont.)

ADS. and DES. CYCLE	TIME (min)	RESISTANCE (Rs) (ohm) $(x10^5)$	SPECIFIC RESISTANCE (ohm.cm) $(x10^3)$	CONDUCTIVITY (S /cm) $(x10^{-4})$
DES-3	1	2.01	2.01	4.97
	2	3.43	3.43	2.92
	3	4.39	4.39	2.28
	4	6.00	6.00	1.67
	5	7.43	7.43	1.35
	6	8.91	8.91	1.12
ADS-4	1	4.87	4.87	2.05
	2	2.52	2.52	3.98
	3	1.95	1.95	5.13
	4	1.49	1.49	6.70
	5	1.19	1.19	8.37
	6	0.95	0.95	10.52
DES-4	1	2.89	2.89	3.46
	2	4.27	4.27	2.34
	3	6.00	6.00	1.67
	4	7.61	7.61	1.31
	5	9.75	9.75	1.03
	6	11.55	11.55	0.87

ADS: Adsorption
DES: Desorption

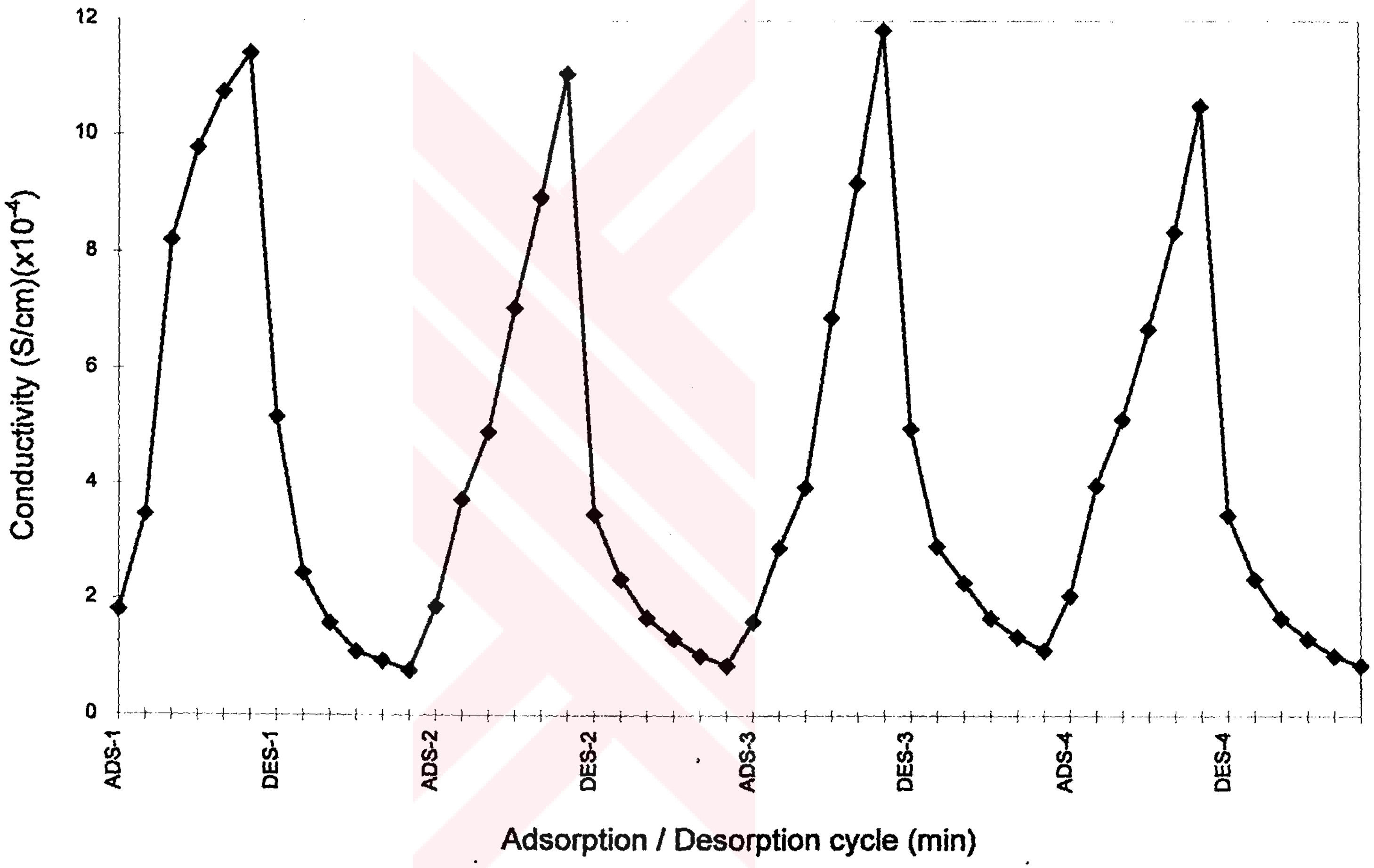


Figure 30. Sensitivity of heat treated PAN to moisture (sample K)

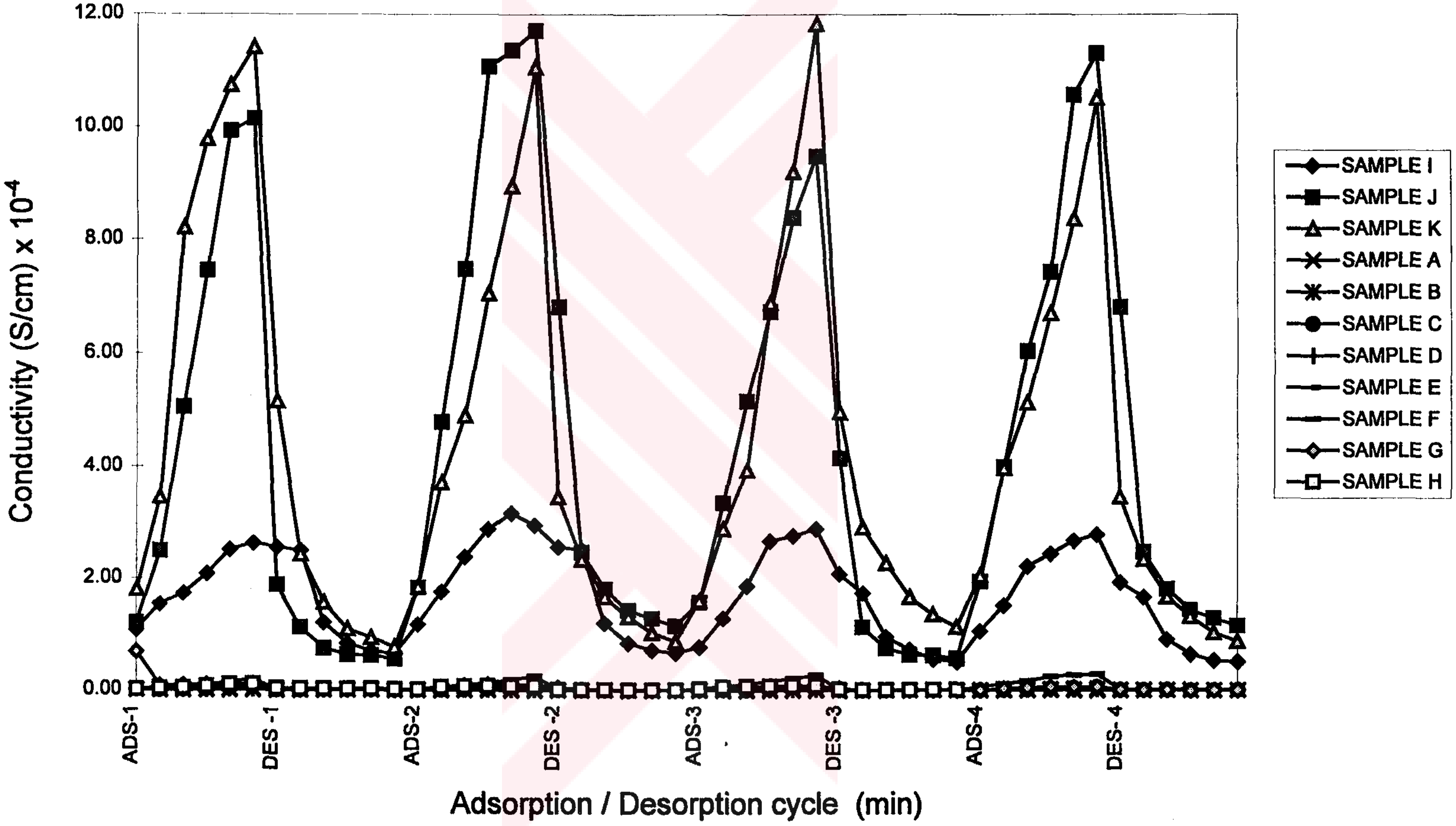


Figure 30. Comparison of moisture sensitivity of heat treated PAN

observed at high temperature treatments and in the presence of dopant. The resistance of all samples decreased very quickly during adsorption and a sharp resistance increase during desorption process was observed.

3.5. IR ANALYSES OF HEAT TREATED POLYACRYLONITRILES

The change of IR spectrum of heat treated polyacrylonitriles were given in Figure 32. One of the major variations observed was the decrease of intensity and the splitting of nitrile band (-C≡N) at 2240 cm^{-1} . This band totally disappears under high temperature heat treatment. The second major variation was the gradual decrease of methylene ($-CH_2$) band vibration at 2940 cm^{-1} and deformation at 1450 cm^{-1}. Similarly, nitrile band peak totally disappears upon further cyclization. Upon heat stabilization a broadening in 1600 - 1000 cm^{-1} region was observed. As nitrile absorption at 2240 cm^{-1} decreases conjugated -C=N absorption increases at 1670 and 1590 cm^{-1}. As coloration develops, increasing absorption was observed in the 1600 - 1500 cm^{-1} carbonyl stretching region. The incorporation of oxygen during heat treatment was assigned in literature (Figure 1) [14, 17].

3.6. THERMAL ANALYSIS OF POLYACRYLONITRILE

Thermal analysis of the catholyte (yellow) polymer and the commercial (white) polymer were carried out. DSC analysis indicated that both have no melting within the testing range. In other words a maximum heat flow reflecting the decomposition of catholyte was observed at around 270 °C, those for white polymer was around 290°C. A sharp decomposition peak of white polymer and a broad one for electrolytic one was observed. The difference in temperature was attributed to structural difference like cyclization and to the molecular weight difference (Figure 33 and Figure 34).

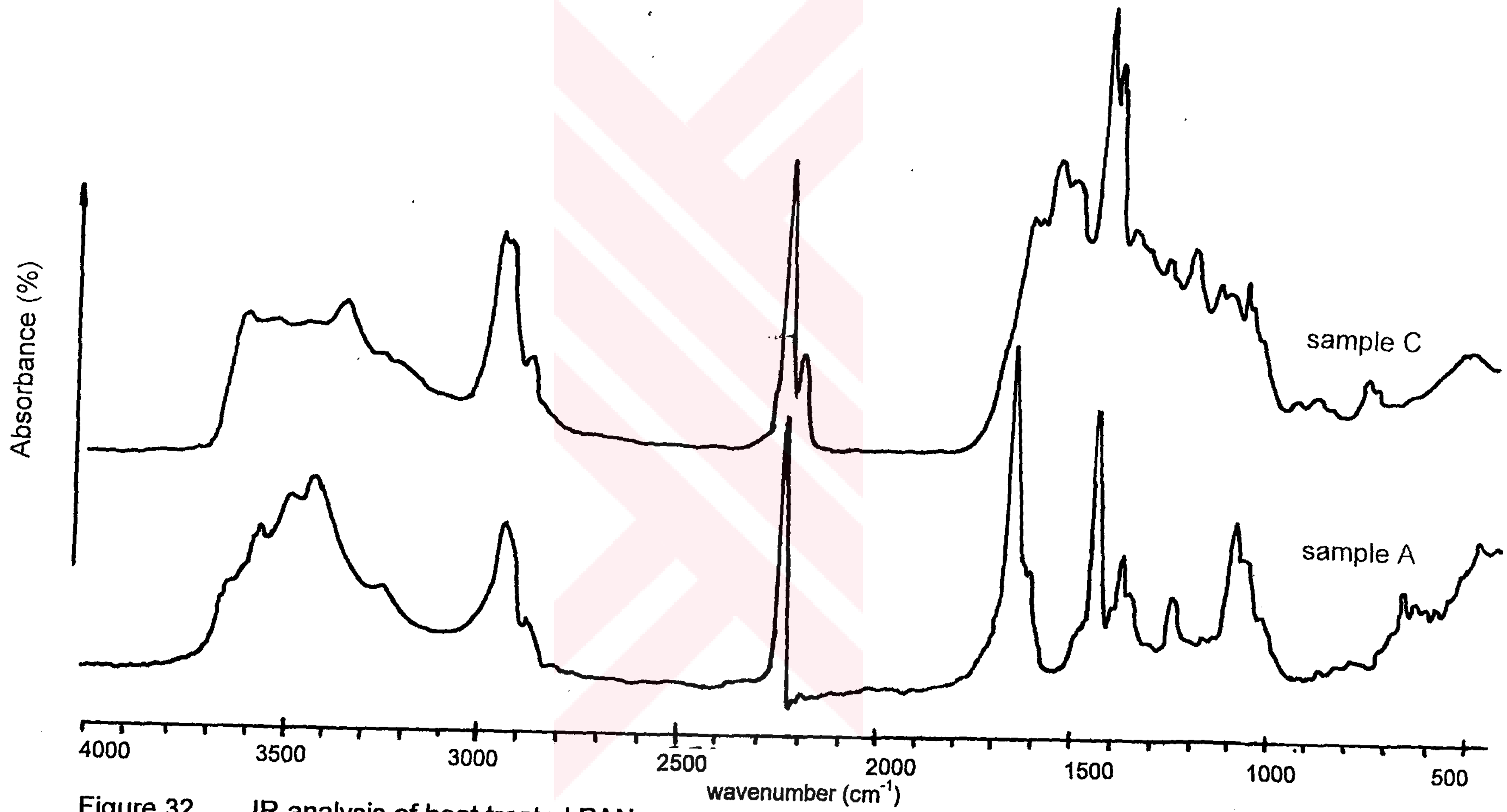


Figure 32. IR analysis of heat treated PAN

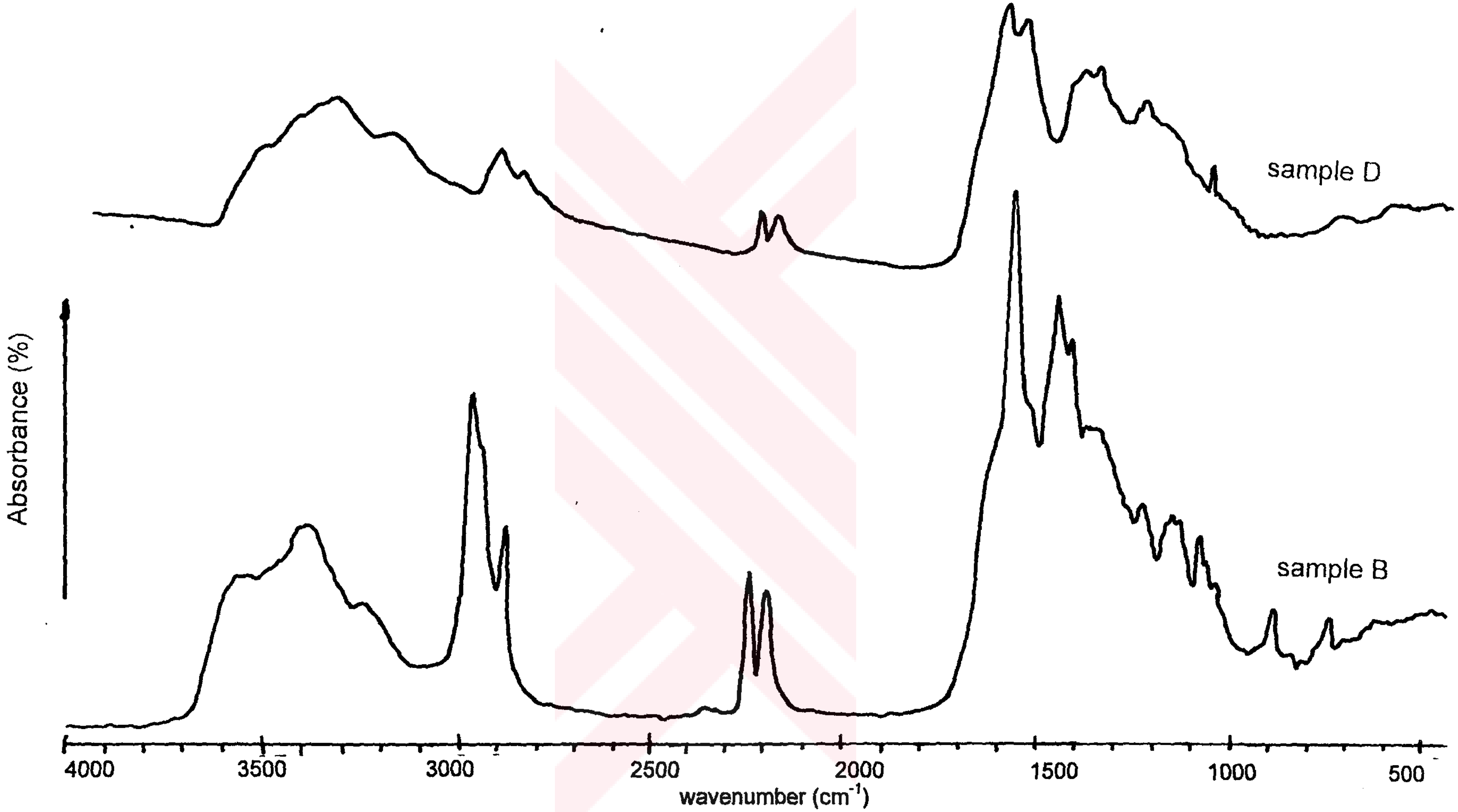


Figure 32. (cont.)

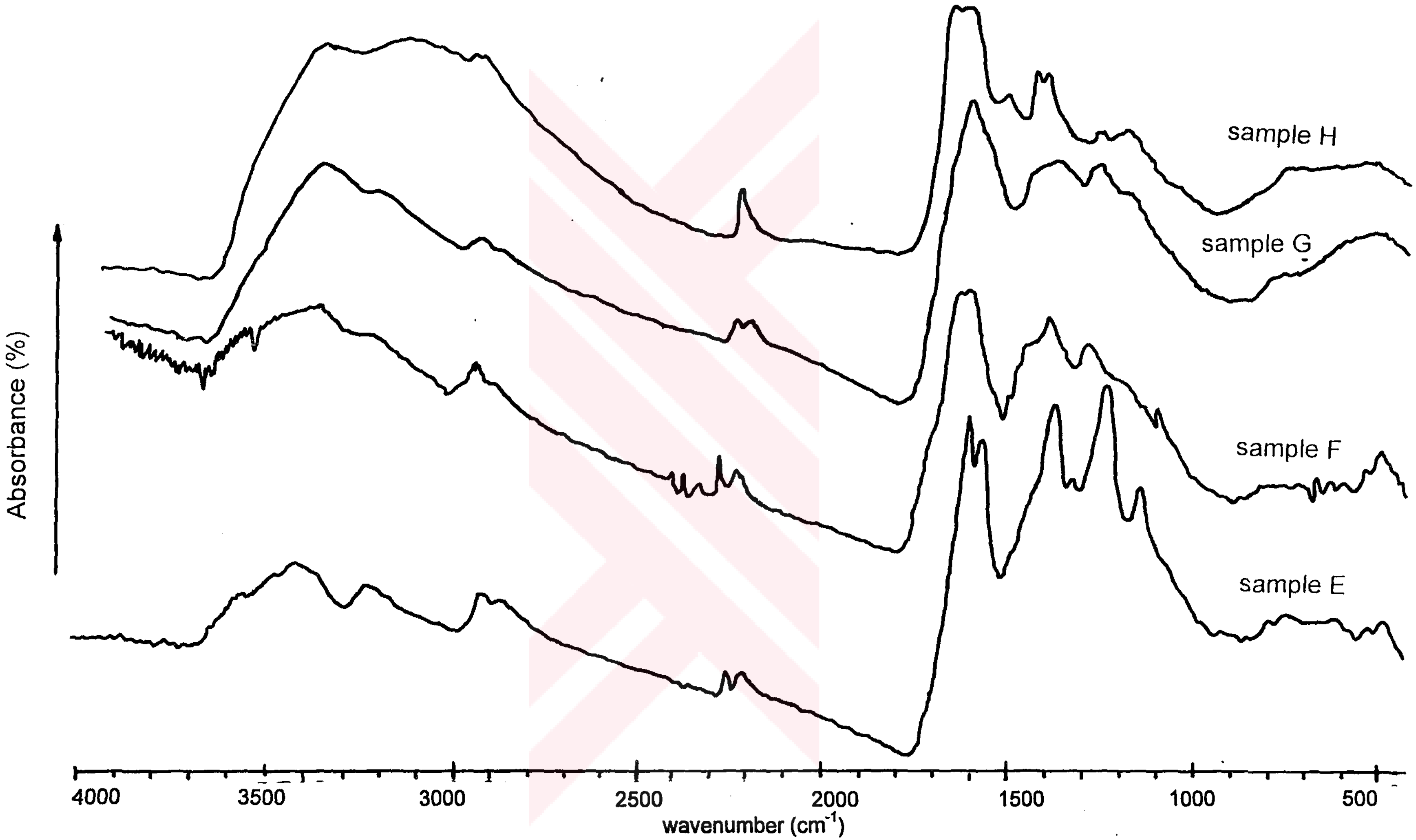


Figure 32. (cont.)

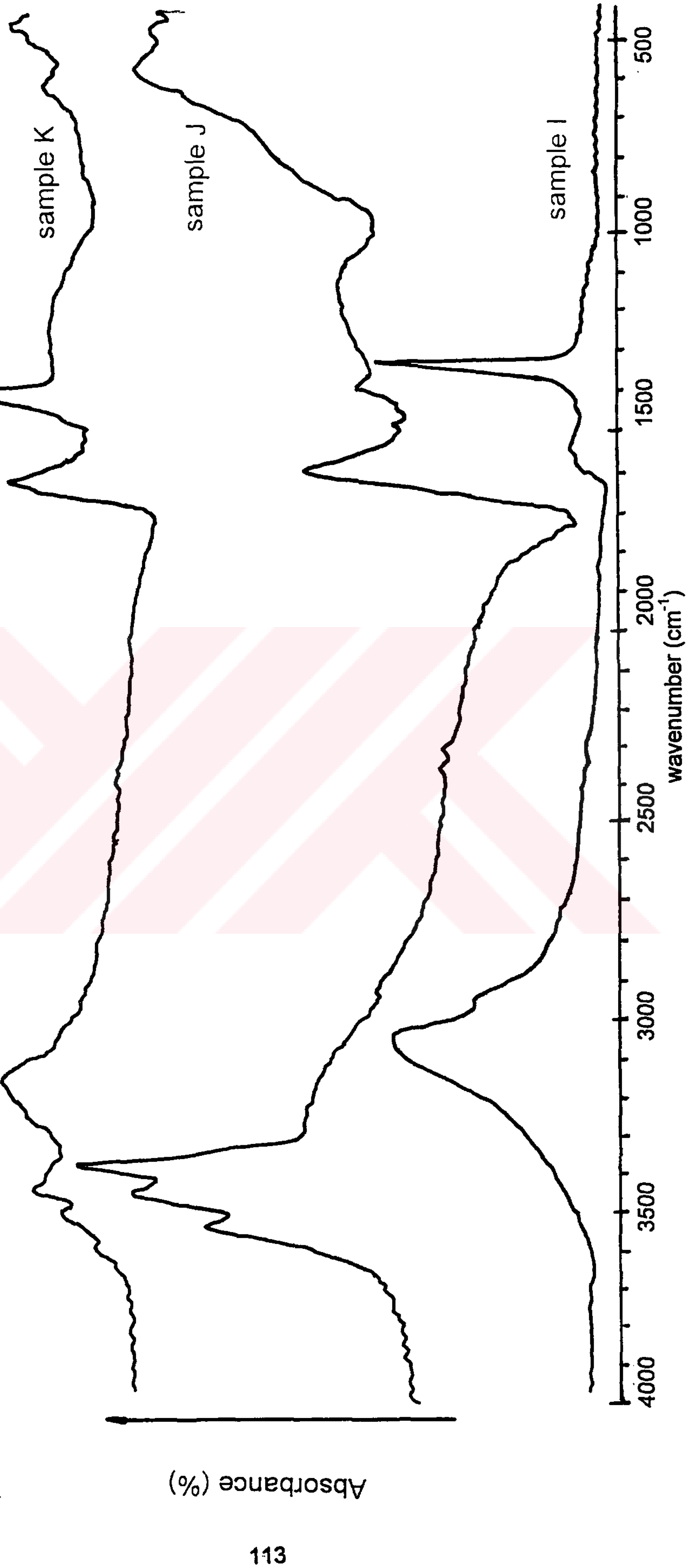


Figure 32. (cont.)

In the case of TGA analyses, the weight loss up to 600 °C was higher for the catholyte polymer compared to the white polymer. The total loss was approximately 51% in the former and 30.5 for the latter. This can be correlated to the heat treatment behavior and the molecular structure of polyacrylonitrile. The color change was apparently higher in the electrolytic polymer. This color change was the indication of nitrile cyclization. Above 600 °C an opposite behavior in weight loss was observed. That is the weight loss values were 46% for the electrolytic polymer, 62.7% for the commercial polymer (Figure 35, 36).

3.7 CYCLIC VOLTAMMETRY OF PYRROLE

The electrochemical behavior of PPy was determined by using acetonitrile - TBAFB system. The solvent - electrolyte couple was electroinert within ± 3.00 V vs Ag^o/Ag^+. The multistep cyclic voltammograms were performed with a potential scan from - 0.40 V to + 1.50 V. An oxidation peak for PPy film was observed at + 0.7 V on the anodic sweep and a corresponding reduction peak was observed at around + 0.20 V in cathodic sweep. The anodic peak was shifted to more positive potentials (+ 0.90 V) with repeated cyclings (Figure 37). The detailed analysis of electrochemical behavior of PPy film under different conditions was reported [55, 56].

3.8. CYCLIC VOLTAMMETRY OF THIOPHENE

The electrochemical behavior of thiophene was also determined by the same CV method. Multiscan cyclic voltammograms of PTh film in the potential range of - 0.50 V to + 2.00 V with Pt electrode was obtained (Figure 38). PTh film has an oxidation peak at + 1.25V on the anodic sweep and the corresponding reduction peak at + 1.00 V on the cathodic sweep. The electrochemical behavior of PTh was investigated in earlier reports [57].

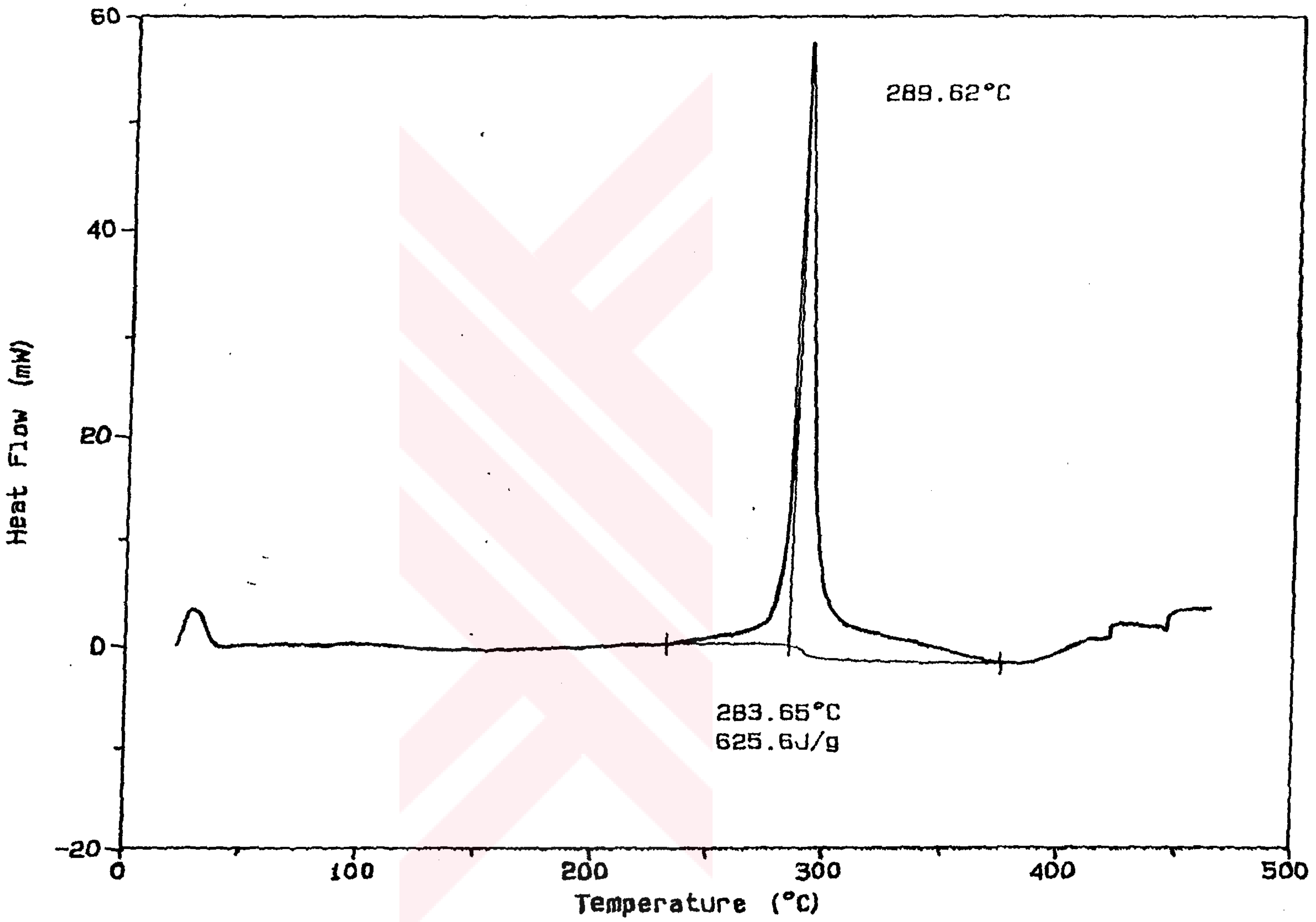


Figure 33. DSC spectrum of commercial PAN

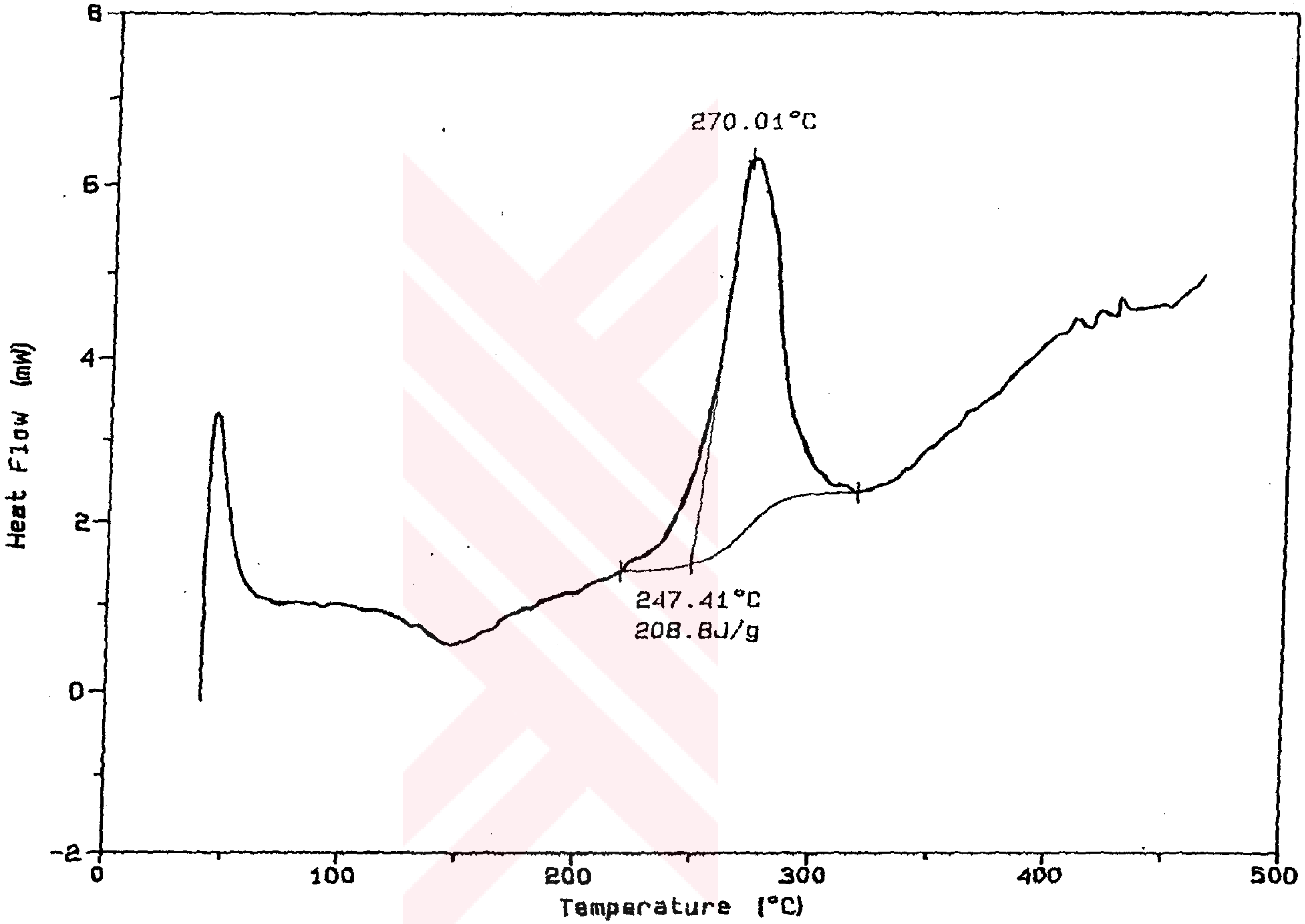


Figure 34. DSC spectrum of cathodic PAN

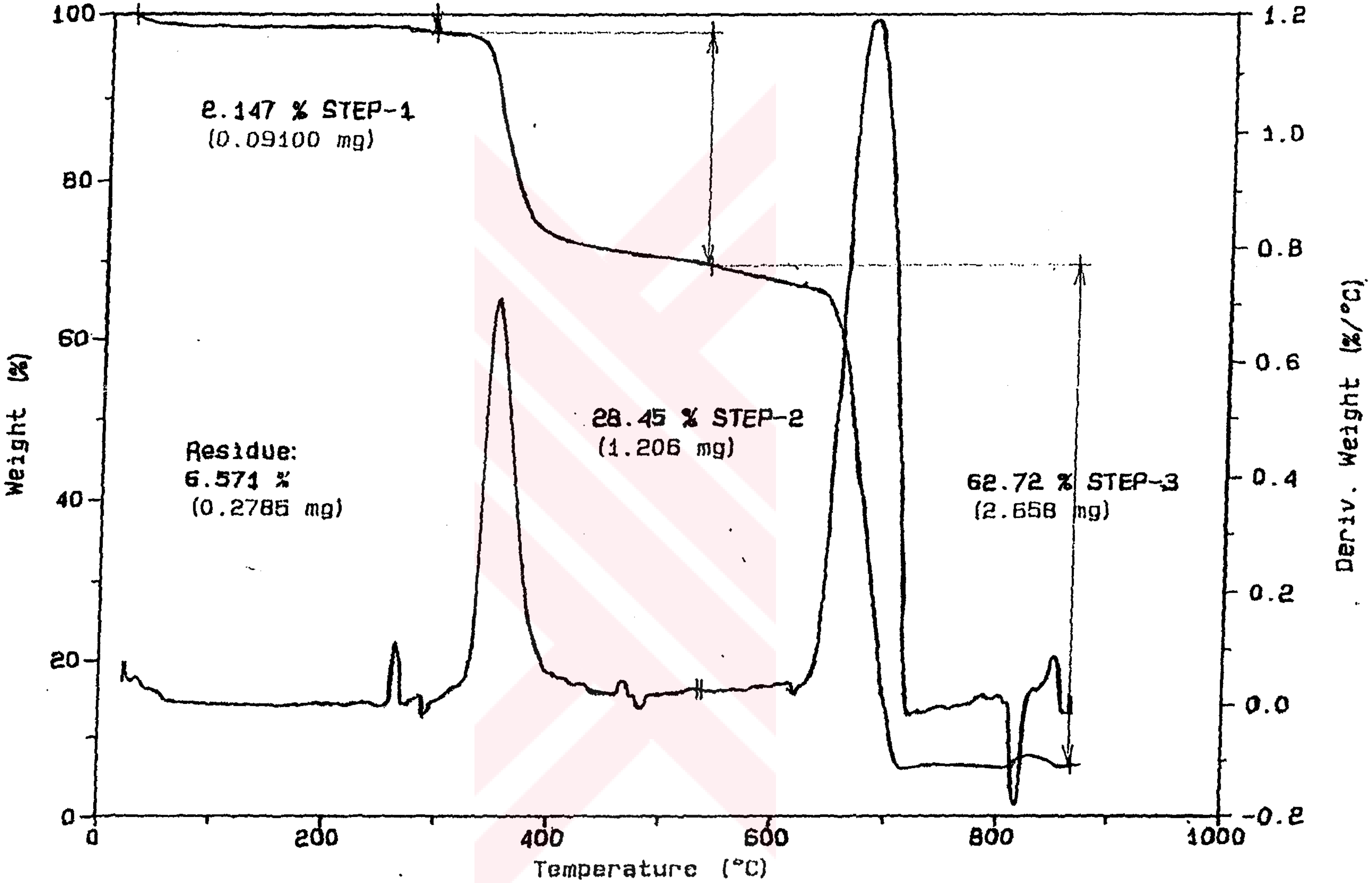


Figure 35. TGA spectrum of commercial PAN

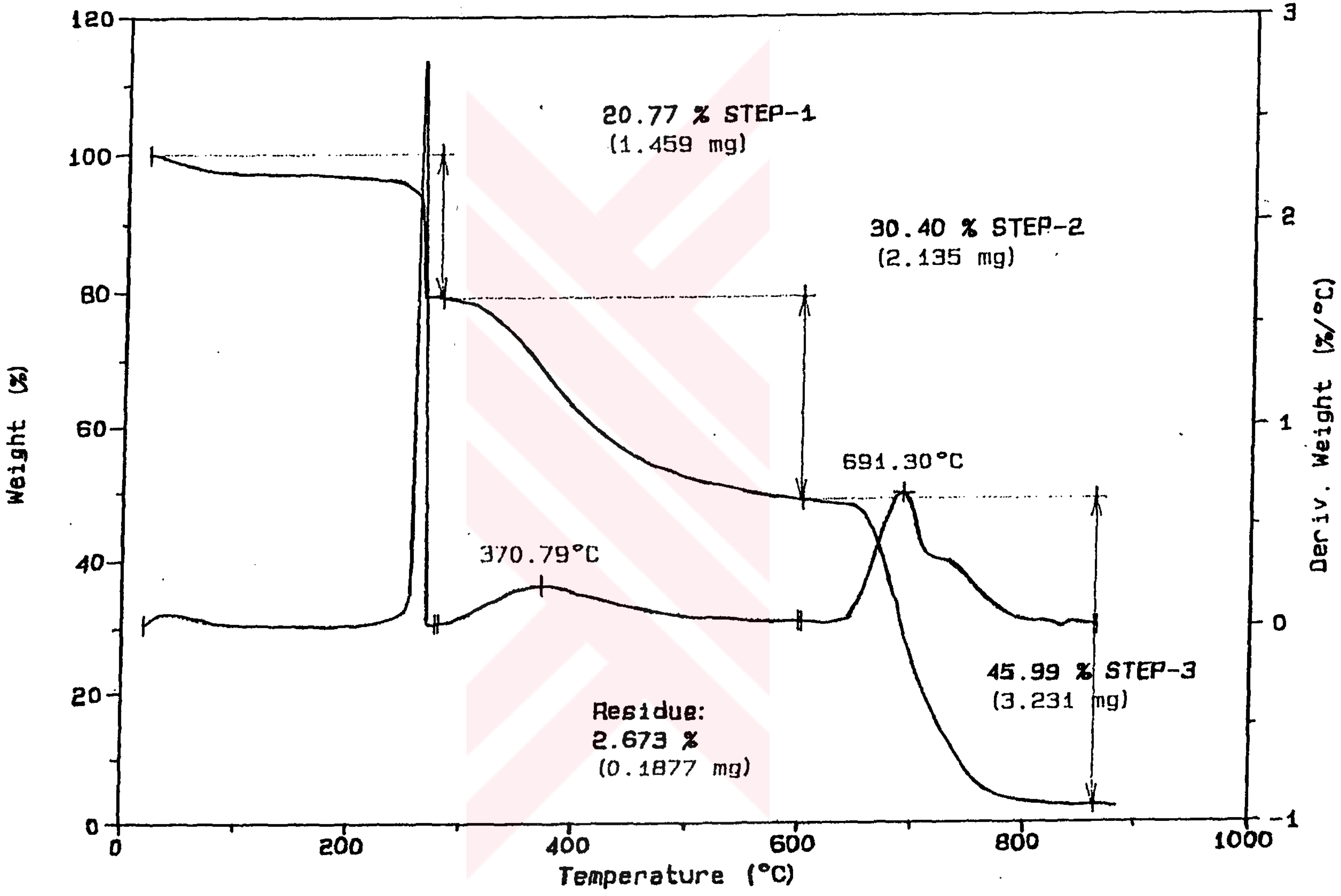


Figure 36. TGA spectrum of cathodic PAN

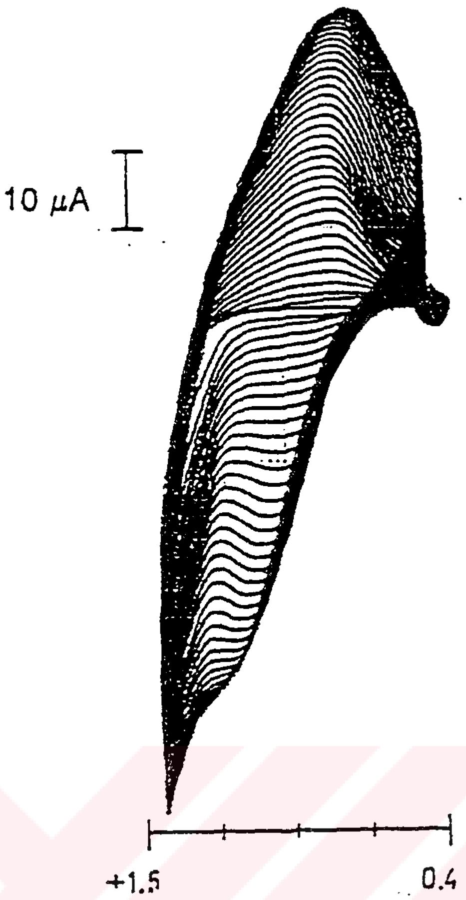


Figure 37. Multisweep cyclic voltammogram of pyrrole (10^{-3} M) in 0.1 M TBAFB- CH_3CN (voltage scan rate : 900 mV/sec).

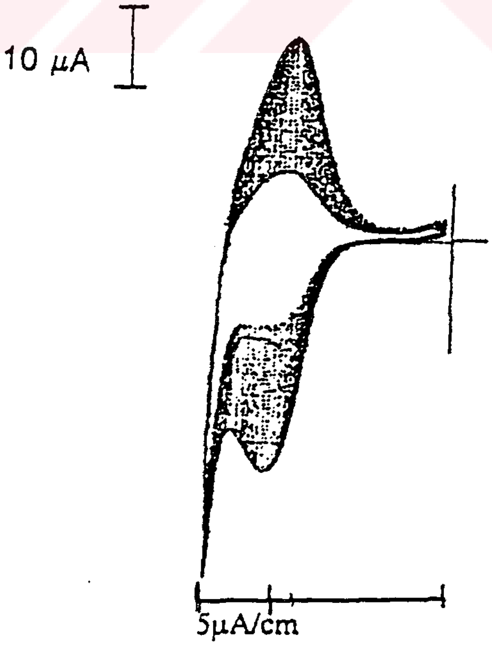


Figure 38. Multisweep cyclic voltammogram of thiophene (10^{-3} M) in 0.1 M TBAFB - CH_3CN (voltage scan rate : 900 mV/sec).

3.9. CONDUCTING POLYMER BLENDS

One of the major problems of conducting polymers is the difficulty in their processing due to their stiff structures. Regarding to undesired properties of conducting polymers, some investigations have been carried out [45, 56, 58, 59]. These investigations were concentrated on the preparation of semiconducting polymers in the form of blends of an insulating polymer with a conducting one. Using an insulating polymer as a host matrix and insertion of the conducting component works well in terms of physical properties of the resultant composite.

Electrochemical production of composites of polyacrylonitrile with polypyrrole and polythiophene was one of the aim of this work.

PAN - PPy and PAN - PTh composites were prepared by electrochemical polymerization of pyrrole or thiophene onto a PAN coated electrode. In order to overcome the resistance caused by insulating film higher potentials were applied. PAN - PPy composite was prepared at +1.6 V, whereas PAN -PTh composite was prepared at + 1.9 V. PAN film was dip coated from acetonitrile solution. The amounts of insulating and conducting polymer coatings were determined gravimetrically. The amount of PPy or PTh deposition were controlled by stopping the electrolysis at different time intervals.

The same type of experiments were planned for commercial white PAN. But we were unsuccesful to dissolve the polymer in acetonitrile, dichloroethane, DMF, chloroform, THF, acetone. However, the white polymer was soluable in dimethylsulfoxide (DMSO). Dip coating of electrode was tried but it was difficult to evaporate DMSO under atmospheric conditions. Evaporation was done under vacuum conditions, but unfortunately a uniform film could not be prepared instead, a highly wrinkled irregular film was produced. Since such type of films were not suitable for the polymerization of pyrrole and/or thiophene we could not synthesize blends with the commercial polymer.

Pure PPy and PTh films were prepared as free standing film in dichloromethane - TBAFB system.

3.9.1. CONDUCTING POLYMER BLENDS OF PYRROLE AND ACRYLONITRILE.

After dip coating the working (Pt) electrodes the synthesis of PPy was carried out at +1.50 V. Polyacrylonitrile coating on Pt anode has a yellow color. When the electrolysis was switched on, the monomer diffuses through the film towards electrode surface and form a polymeric film between polyacrylonitrile and the electrode surface. The color of PPy blend was bright black and it was rather difficult to peel off the electrode surface.

As explained previously, blends of PAN with PPy at different percentages of each component (Table 24) were prepared. In the blends, PPy content was ranged from 21% to 84.2 %. Pure PPy and PAN were used as the reference points (Table 24, Figure 39). The conductivity of pure PPy film was measured as $7.2x10^{-2}$ $S.cm^{-1}$ by means of four probe method. As the PPy was incorporated into the matrix the conductivity of blend increased (pure PAN conductivity 10^{-7} S/cm). For instance, incorporation of 21% PPy increased the conductivity to the order of 10^{-4} $S.cm^{-1}$, involvement of 37% PPy increased the conductivity to 10^{-3} $S.cm^{-1}$. Upto 60 % PPy contribution the conductivity increased but then almost a plateau was observed. At that point, i.e., 60% PPy a threshold conductivity was established. Thereon, the conductivity stayed about 10^{-2} $S.cm^{-1}$.

Table 24. The conductivities of pyrrole and acrylonitrile polymer composites

PPy Wt %	PAN Wt %	CONDUCTIVITY (S/cm)
0.00	100	2×10^{-7}
20.97	79.03	4×10^{-4}
37.14	62.86	3×10^{-3}
60.00	40.00	3×10^{-2}
67.51	32.47	4×10^{-2}
70.00	30.00	5×10^{-2}
84.19	15.81	6×10^{-2}
100	0.00	7×10^{-2}

PPy : polypyrrole
PAN : polyacrylonitrile

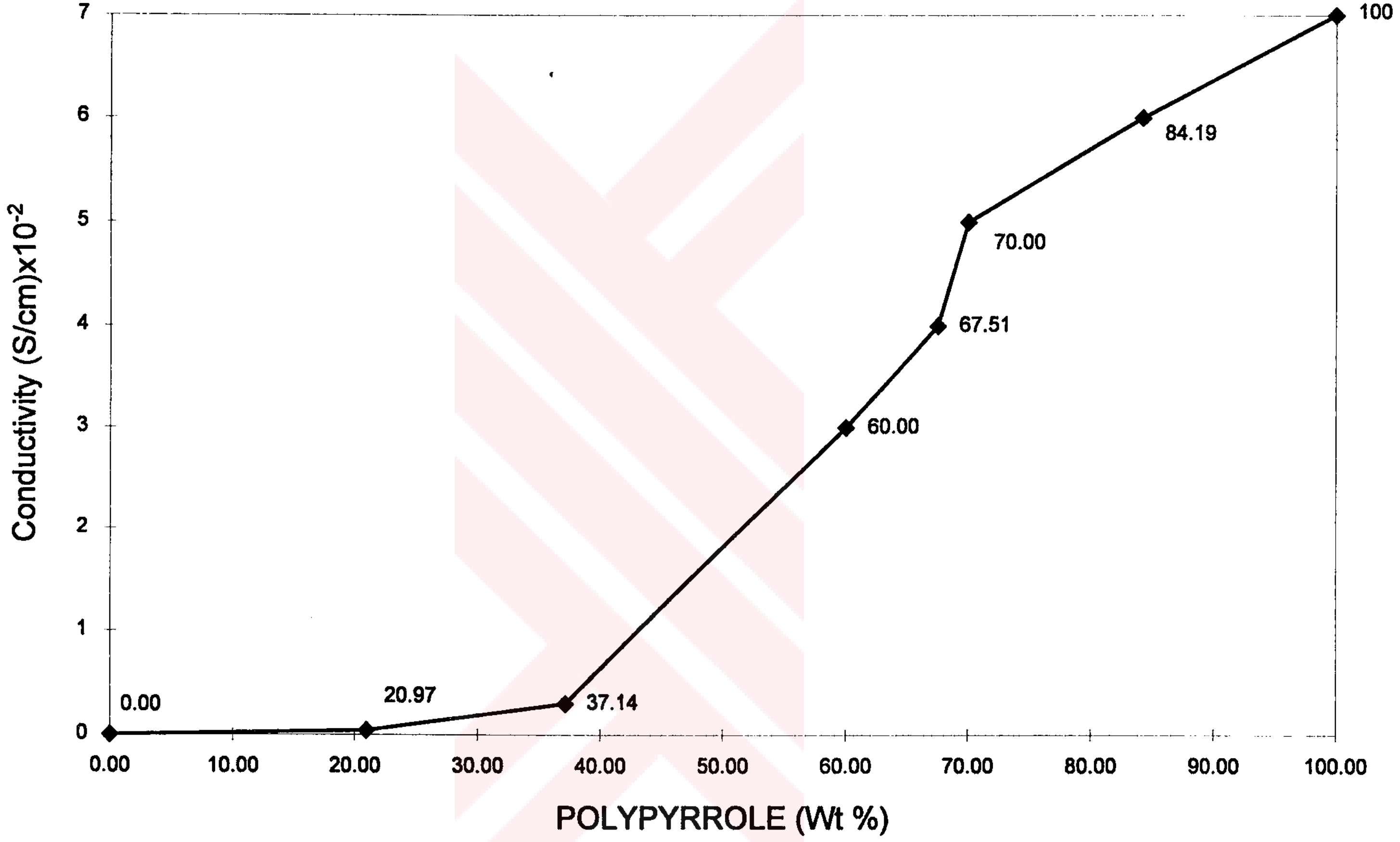


Figure 39. The conductivity of PPy-PAN composites

3.9.2. CONDUCTING POLYMER BLENDS OF THIOPHENE AND ACRYLONITRILE.

The synthesis of thiophene on a PAN precoated electrode was done at +1.9V vs Ag^{+}/Ag^{0} . Same as the pyrrole case, polymerization of thiophene takes place between polyacrylonitrile film and the electrode surface. The color of PTh blend has a greenish black color, less sticky and can be easily removed from the electrode surface as a free-standing film.

The blends were prepared by varying PTh and PAN contents. As a consequence of incorporation of PTh component in the blend, the conductivity was increased. In that case a threshold value was observed similar to the PPy-PAN case (Table 25, Figure 40). The conductivity of pure PTh electrode film was in the order of 10^{-2} $S.cm^{-1}$. Incorporation of 16% and 48.5% PTh increased the conductivity of the blends to 10^{-4} and 10^{-3} $S.cm^{-1}$, respectively. For higher percentages of PTh the conductivities in the order of 10^{-2} $S.cm^{-1}$ were observed. Same as the PPy blends, presence of almost 60% conducting component the conductivity did not change sharply. That is, it is possible to achieve a conductivity close to that of pure conducting polymer by incorporating almost 40 % insulating polymer in the blends.

3.9.3. OTHER EFFORTS TO OBTAIN CONDUCTING PPy - PAN AND PTh - PAN BLENDS

The preparation of conducting copolymers between acrylonitrile and pyrrole, acrylonitrile and thiophene were also investigated (Tables 5, 6). Although they do not have the same type of electrochemical behavior, i.e. acrylonitrile can be cathodically polymerized whereas the other two undergo

Table 25. The conductivities of thiophene and acrylonitrile polymer composites

PTh Wt %	PAN Wt %	CONDUCTIVITY (S/cm)
0.00	100	2×10^{-7}
16.22	83.78	3×10^{-4}
48.46	51.53	4×10^{-3}
58.30	41.50	2×10^{-2}
68.30	31.70	3×10^{-2}
81.60	18.40	5×10^{-2}
100	0.00	8×10^{-2}

PTh : polythiophene
PAN : polyacrylonitrile

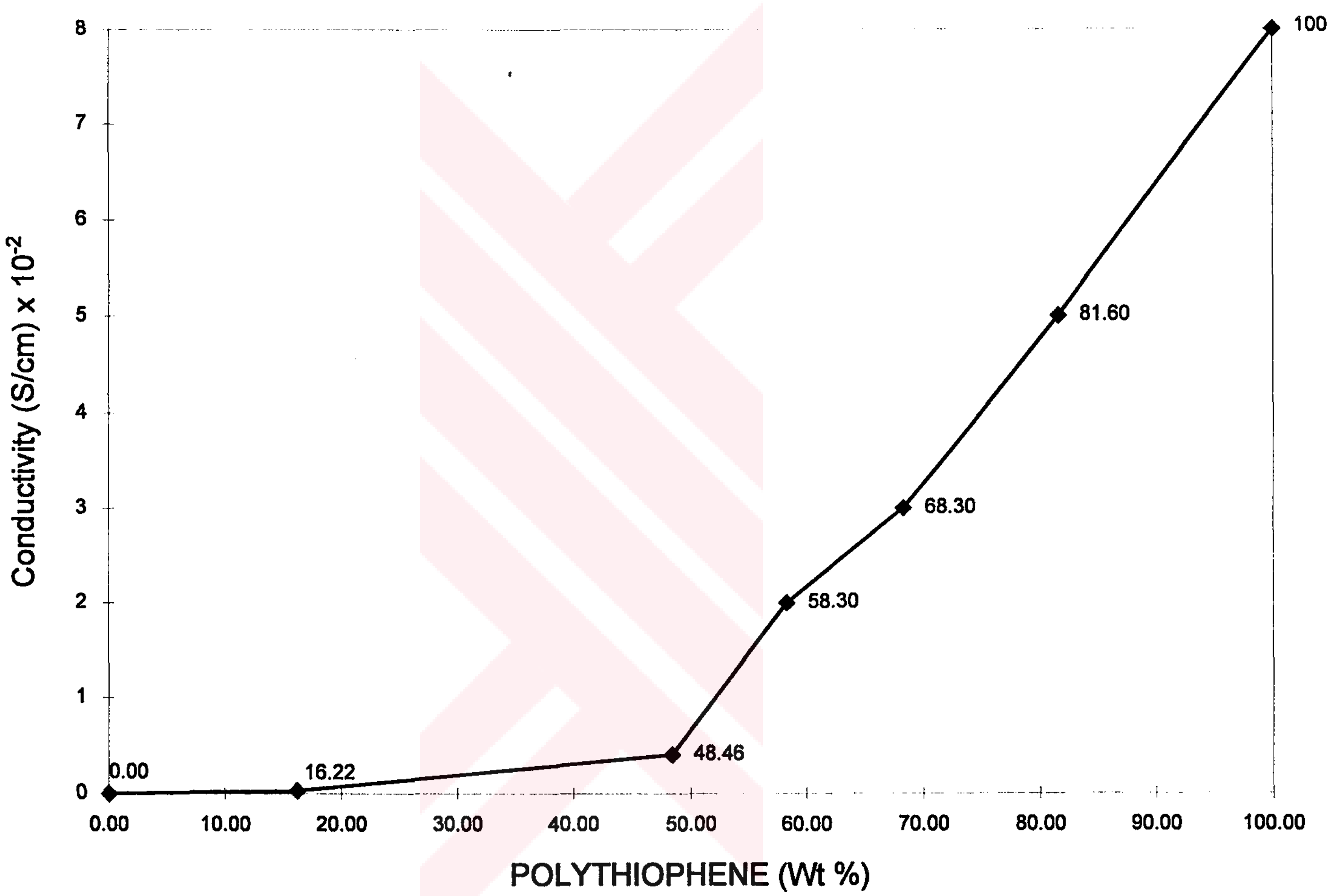


Figure 40. The conductivities of PTh-PAN composites

oxidative polymerization. If the potential of one monomer is chosen for the initiation of polymerization, involvement of the other in an indirect manner can be assumed. For that purpose, Py and AN were introduced into the electrolysis cell containing acetonitrile as the solvent and AN reduction potential (-2.6V vs Ag^+/Ag^o) was applied (sample R). The same procedure was applied to Th and AN for a conducting copolymer synthesis (sample Y). The surface of the cathode (working electrode) was not coated. Besides negligibly small amount of polyacrylonitrile was observed in the cathode compartment when the cell content was transferred into methanol. It was interesting to note that when acrylonitrile was homopolymerized in the same system in the absence of second component (Py, Th) considerably higher polymer yields ($\approx$40%) were obtained.

The conducting copolymer synthesis was also investigated in the reverse manner. Again Py - AN or Th - AN were introduced into the same electrolysis cell where the solvent was dichloromethane (samples S and Z). The applied polymerization potentials were +1.60 V vs Ag^+/Ag^o for Py-AN case and +1.90 V vs Ag^+/Ag^o for Th-AN copolymerization. The purpose of applying these potentials was to enhance the selective initiation of polymerization of the conducting component and indirect polymerization of the insulating component. Anodic films were obtained but as the homopolymers of pyrrole and thiophene. The incorporation of acrylonitrile was not accomplished.

Another effort was to synthesize graft copolymers of Py and AN, Th and AN. It was proposed that the possibility of having graft copolymers can be verified first by obtaining a conducting polymer film and later by electropolymerizing the insulating component on the previously obtained film. Therefore two different paths were followed after achieving the conducting film coating. Py and Th were separately polymerized on the surface of anode in DM at their own oxidation potentials. In the first path the coated electrodes were placed in a different cell separately. This cell contains AN monomer in acetonitrile solvent. As soon as the electrodes were placed into the second cell the potential (-2.6V vs Ag^{+}/Ag^{o}) was switched on. After one hour of electrolysis we could not obtained any grafted polyacrylonitrile (samples W and U). In the second path after conducting PPy and PTh electrode films were synthesized in separate cells, AN monomer was introduced into the cells and -2.6V vs Ag^{+}/Ag^{o} was applied (samples T and X). Still, we could not observed any grafting of polyacrylonitrile on the prepolymerized PPy and PTh.

It is necessary to emphasize that, in our earlier electrochemical polymerization studies, generally it was necessary to increase the polymerization potential due to formation of the insulating polymer films. Sometimes, we have applied ultrasonic vibration to overcome the resistance created by the film [54, 55, 56]. Now in this work, it was clearly observed that although the films (PPy or PTh) formed on the surface of the electrodes, their conductivity were sufficient to apply a desired potential for the polymerization of other monomer. At least,this was a solid evidence of the presence of conductive films which themselves behave as electrodes.

3.10. IR ANALYSIS OF PPy - PAN AND PTh - PAN FILMS

IR analysis of PPy-PAN and PTh-PAN blends were carried out as KBr pellets. However, since the conducting PPy and PTh components were free standing films that can not be pulverized, the uniform distrubution of the film in the KBr was rather difficult.

Pure cathodic PAN IR absorption peaks are 3000, 2240, 1700-1400 cm^{-1}, the incorporation of PPy or PTh affects the IR spectrum (Figure 41). For example as 20 % PPy is incorporated into the matrix the absorption peaks of

PAN at 3000 and 2240 cm $^{-1}$ are decreased considerably. The peaks in 1700 - 1400 cm $^{-1}$ region are broadened. 1600 - 1000 cm $^{-1}$ region contains pyrrole ring and 1080 cm $^{-1}$ tetraflouroborate anion vibrations. After reaching 60 % PPy in the PPy - PAN film, the spectrum did not change considerably. The main absorption C= C, C–H vibrations for pure PPy were observed in the 1700 - 1500 cm $^{-1}$ and 1200 - 1000 cm $^{-1}$ range.

IR spectra of PTh - PAN films are given in Figure 42. Since PTh films were rather more processable compared to PPy film for KBr pellet preparation better resolutions were obtained. Same as PPy - PAN films, incorporation of small amount PTh (16%) caused the sharp decrease in 3000 and 2240 cm $^{-1}$ peaks of PAN. After approximately 60 % and at higher percentages of PTh in the film, no appreciable change was observed. Same as PPy, the thiophene ring C= C, C–H vibrations within the 1700 - 1000 cm $^{-1}$ range and 1080 cm $^{-1}$ tetraflouroborate anion were clearly seen.

3.11. THERMAL ANALYSIS OF PPy - PAN AND PTh - PAN FILMS

3.11.1. DSC ANALYSIS OF PPy - PAN AND PTh - PAN FILMS

The DSC and TGA analyses of PPy, PPy-PAN film were performed. The same analyses were applied for PTh, PTh-PAN film. The thermograms of PAN were discussed in section 3.6.

In DSC analysis, pure PAN has an endothermic peak at 270°C (Figure 34). Under same conditions PPy has a decomposition above 300 °C (Figure 43.b). In DSC thermograms of PPy- PAN film, there exists two endothermic shoulders between 250 °C and 350 °C. The film has an extra endothermic peak

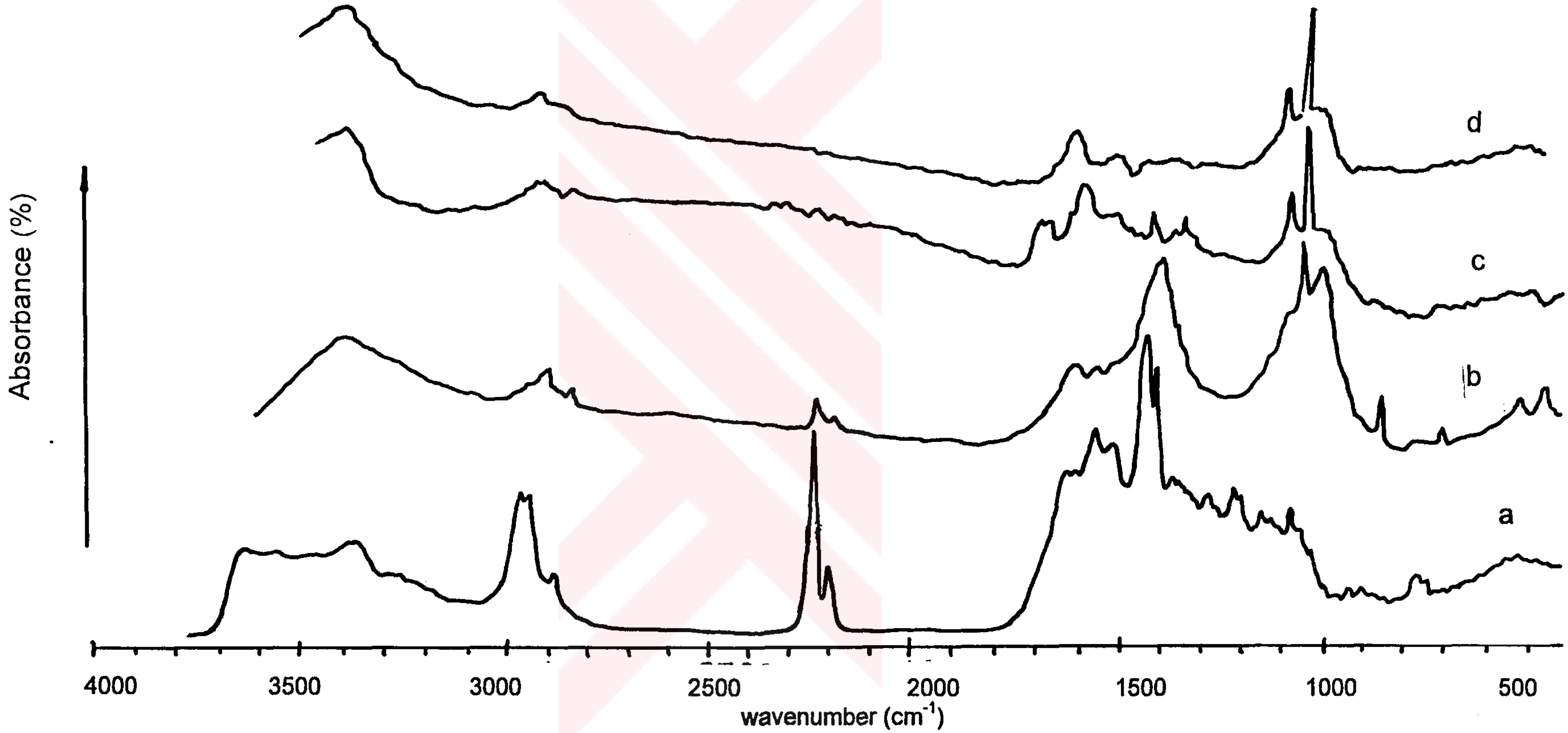


Figure 41. IR analysis of PPy-PAN films (a): 100 % PAN, (b): 79.03 %PAN - 20.97 % PPy, (c): 62.86 % PAN - 37.14 % PPy, (d): 40% PAN - 60 % PPy, (e): 32.47 % PAN - 67.51 % PPy, (f): 30 % PAN - 70 % PPy, (g): 15.81 % PAN - 84.19 % PPy, (h): 100 % PPy.

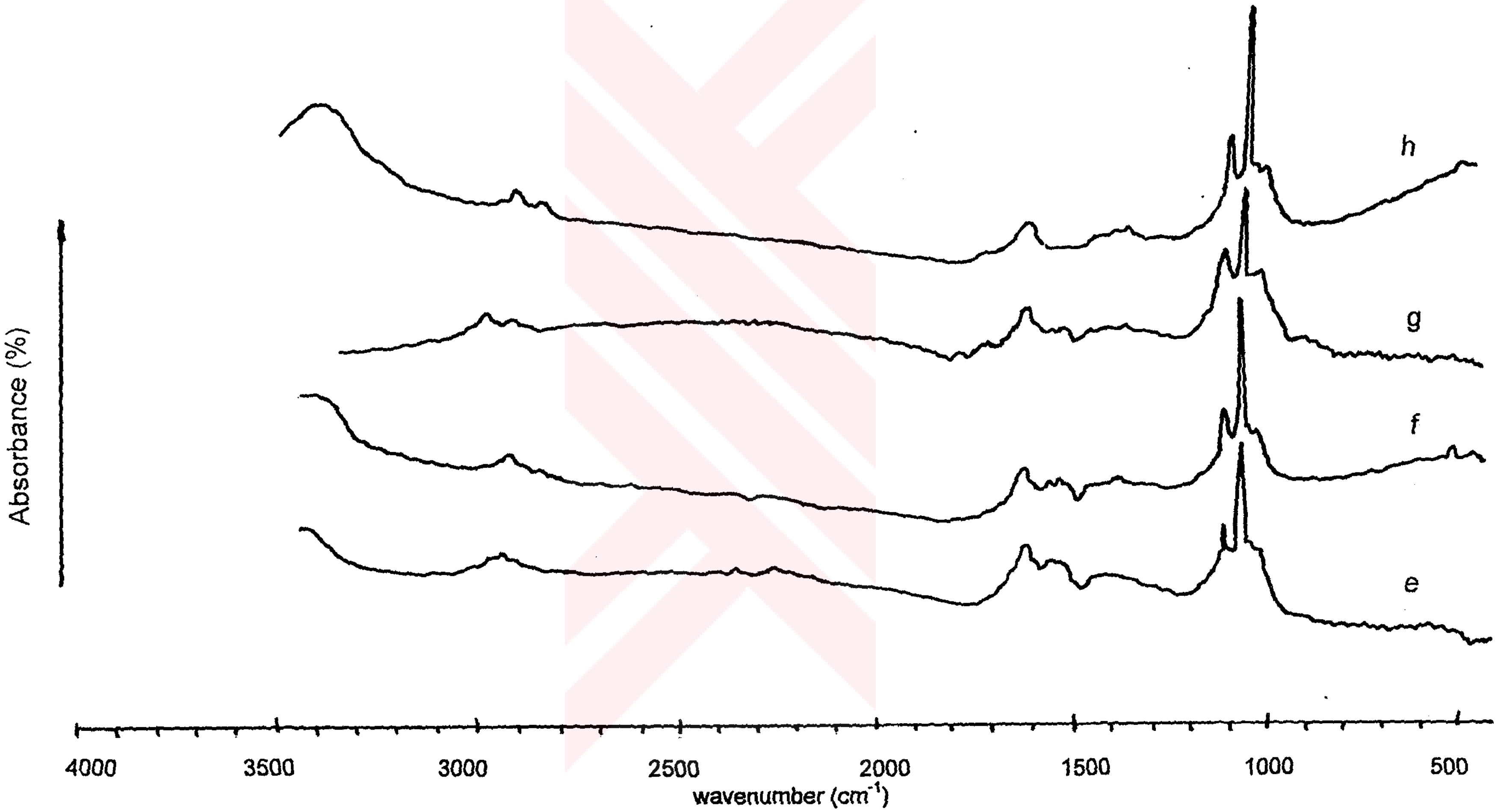


Figure 41. (cont)

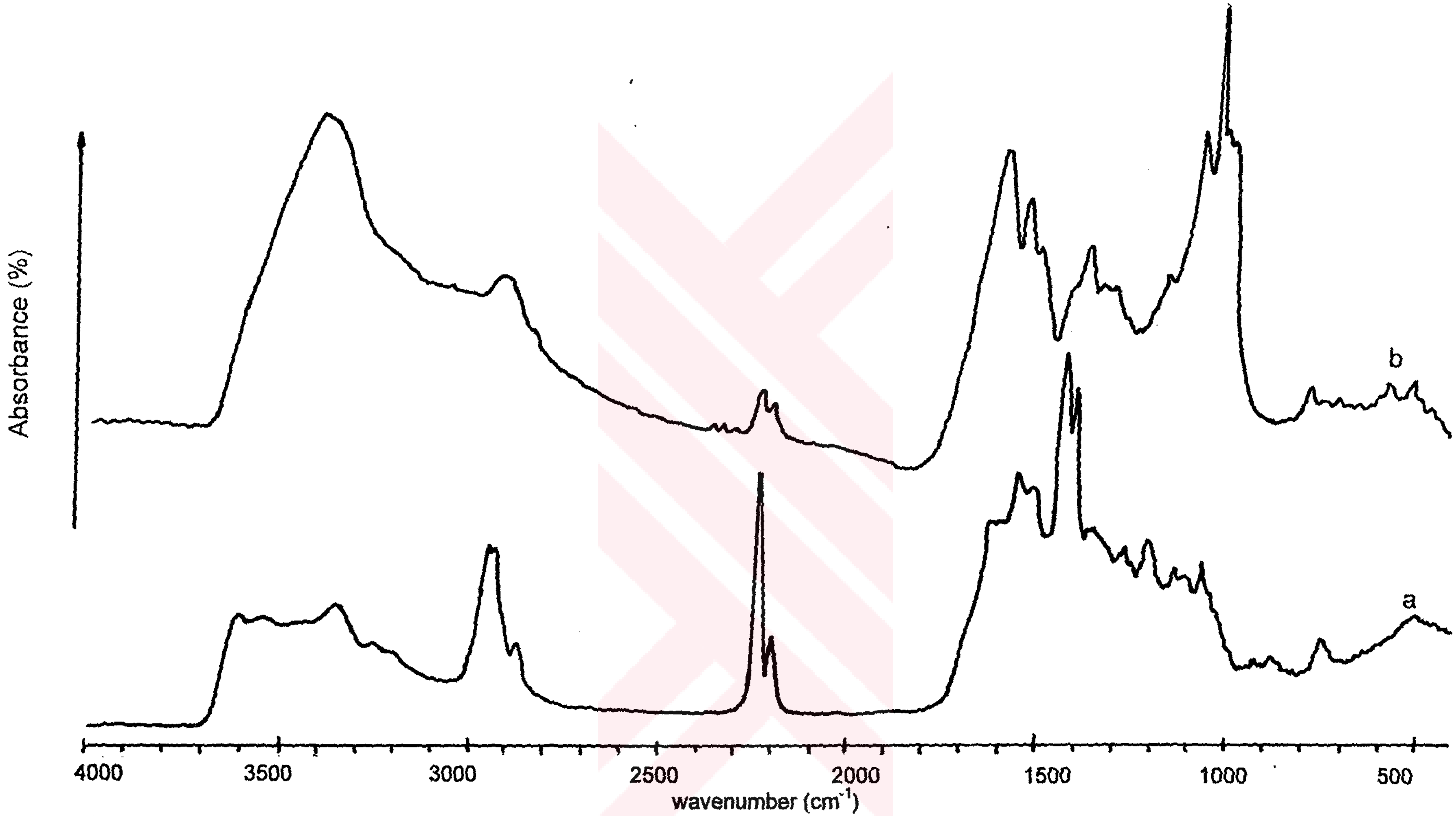


Figure 42. IR analysis of PTh-PAN films (a): 100 % PAN, (b): 83.78 %PAN - 16.22 % PTh, (c): 51.53 % PAN - 48.46 % PTh, (d): 41.5% PAN - 58.3 % PTh, (e): 31.7 % PAN - 68.3 % PTh, (f): 18.4 % PAN - 81.6 % PPy, (g): 100 %PTh..

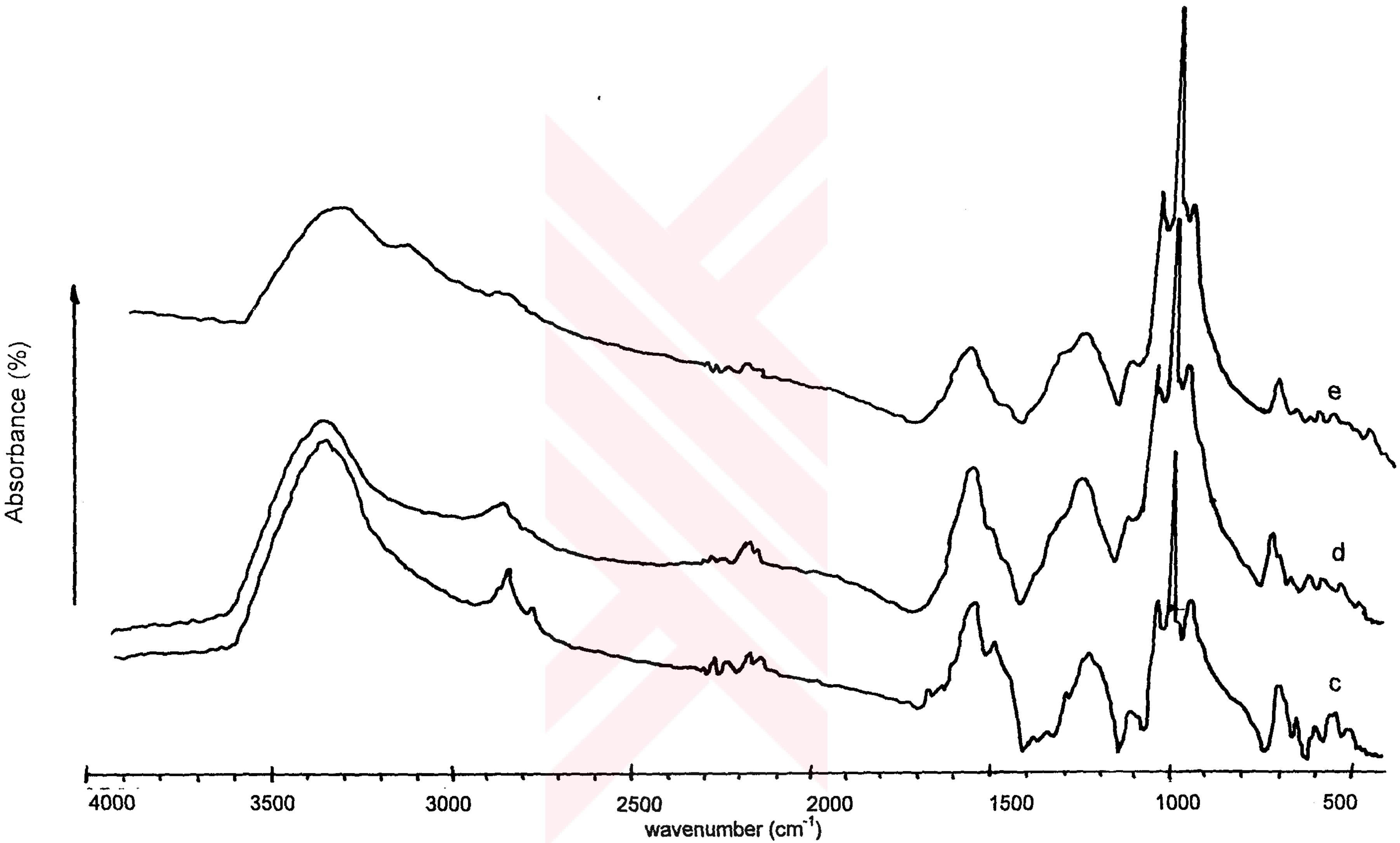


Figure 42. (cont.)

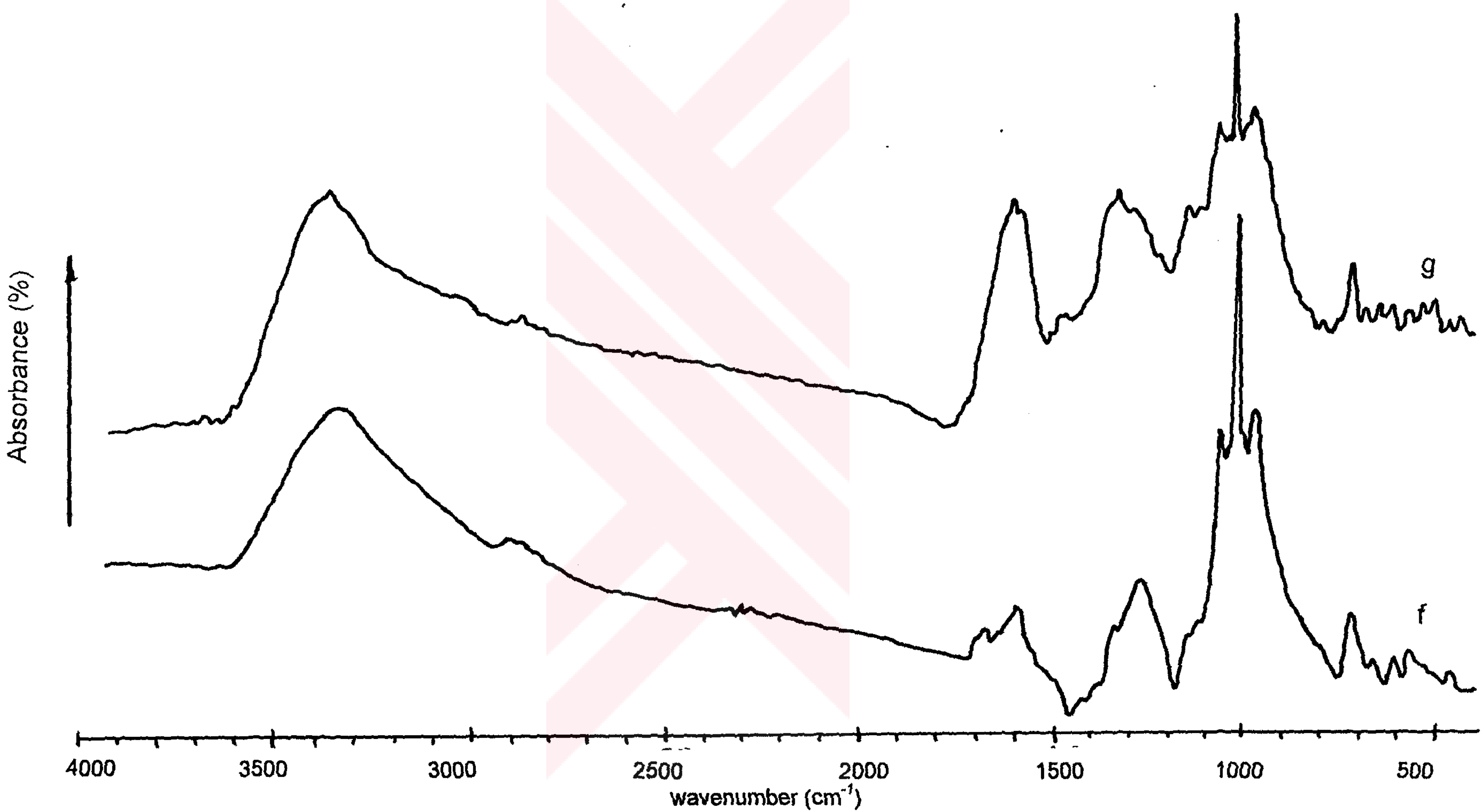


Figure 42. (cont.)

at 400 °C (Figure 43.c). Considering all thermograms the electrochemically prepared films were not simply physical mixtures of the homopolymers.

For thiophene studies the same investigations were carried out. PTh has a quite different DSC thermogram compared to PPy. PTh has several transitions between 270 °C and 380 °C (Figure 44.b). PAN has a decomposition peak at 270 °C. In the PTh - PAN film an exothermic broad peak was observed between 90 °C and 150 °C (Figure 44.c). Such a behavior was not observed in PTh or PAN homopolymers.The decomposition above 300 °C proceeded up to 400 °C. The difference in these thermograms was the solid evidence of production of different species other than physical mixture of the two homopolymers.

3.11.2. TGA ANALYSIS OF PPy - PAN AND PTh - PAN FILMS

The weight loss of polymers were followed by TGA analysis. TGA analyses of PPy electrolytic homopolymer film and PPy-PAN film were given in Figures 45, 46 respectively. Those for PTh electrolytic film and PTh-PAN film were given in Figures 47, 48 respectively. The thermogram for the cathodic PAN was already given in earlier sections (Figure 36).

All polymers have very similar type of weight loss behavior under gradual temperature increase. For instance, no matter what they are, all polymers (homopolymers or composite films) have mainly three weight loss steps. First weight loss was observed at around 250 °C where 20 % loss was determined. The second gradual weight loss was observed between 225 °C - 600 °C. Main and sharp loss was determined between 600 °C - 800 °C. The weight loss percentages observed on thermograms were summarized in Table 26.

Table 26. The weight loss percentages of polymers during TGA analysis

POLYMER	% WEIGHT LOSS			
	TEMPERATURE ($^{\circ}$C)			
	0 - 250	250 - 600	600 - 800	> 800 (RESIDUE)
PAN	20.77	30.40	45.99	2.67
PPy	16.87	15.38	55.43	12.40
PPy - PAN composite film	13.00	23.6 0	57.76	9.85
PTh	14.13	15.55	59.12	11.39
PTh - PAN composite film	15.88	20.06	53.22	10.78

3.12. SEM ANALYSIS OF PPy - PAN AND PTh - PAN FILMS

The SEM analysis reveals some morphological differences between the films. The solution side of pure PPy (Figure 49.a) and PTh (Figure 50.a) films show hemispheres producing cauliflower - like surfaces. The SEM pictures of electrode and solution sides of the electrolytic composites of PPy - PAN (Figure 49.b,c) and PTh - PAN (Figure 50.b,c) have different micrographs. The monomers diffuse through the host insulating polymer and an electron transfer occurs. The polymerization starts around the interface between the electrode surface and the polymer film. Referring to Niwa model [48, 55] the diffusion of monomer molecule through the insulating film and anion of the electrolyte result in different morphologies between the surfaces.

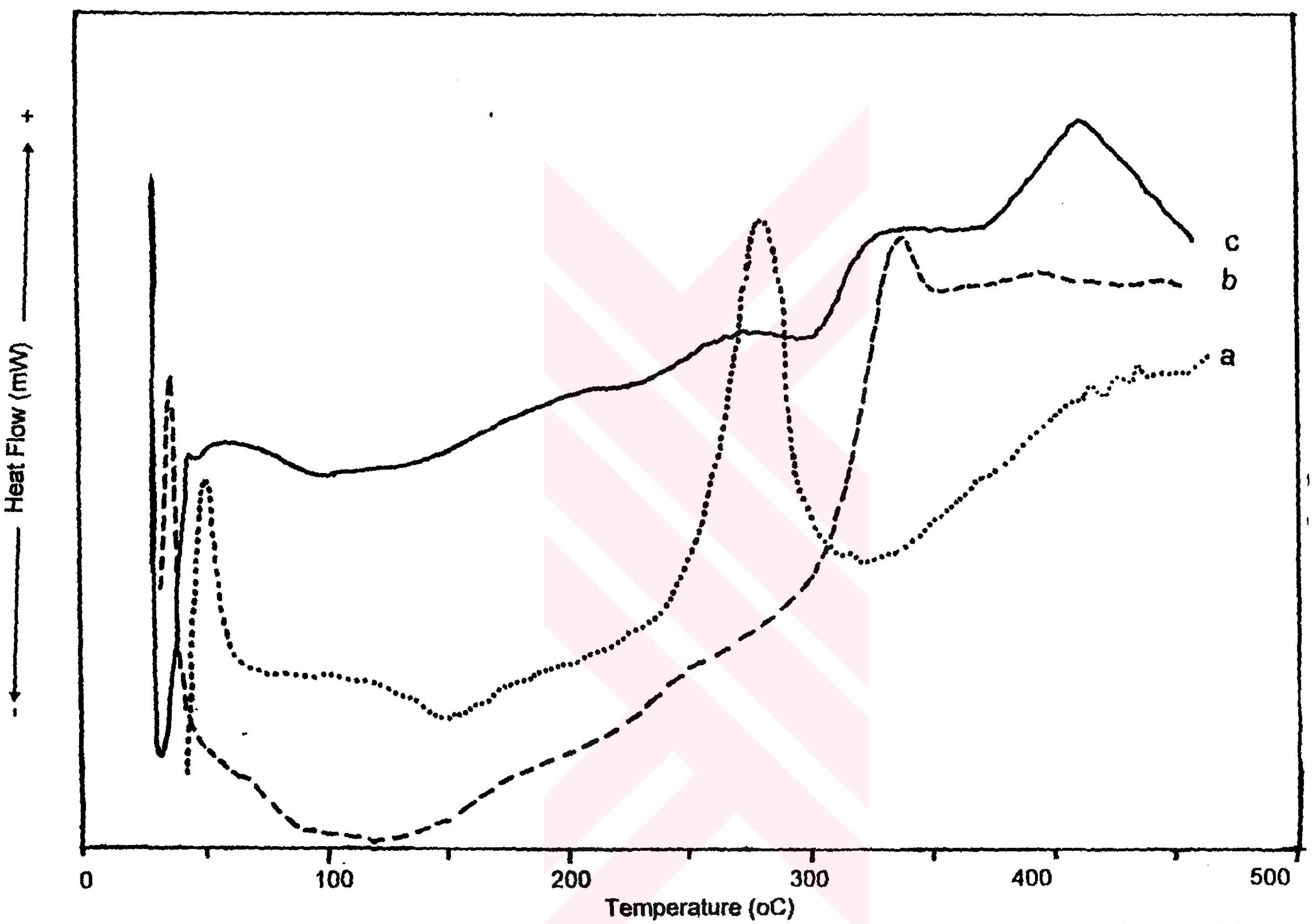


Figure 43. DSC thermogram of : (a) : Cathodic polyacrylonitrile, (b) : Polypyrrole, (c) : Electrolytic PPy - PAN composite film

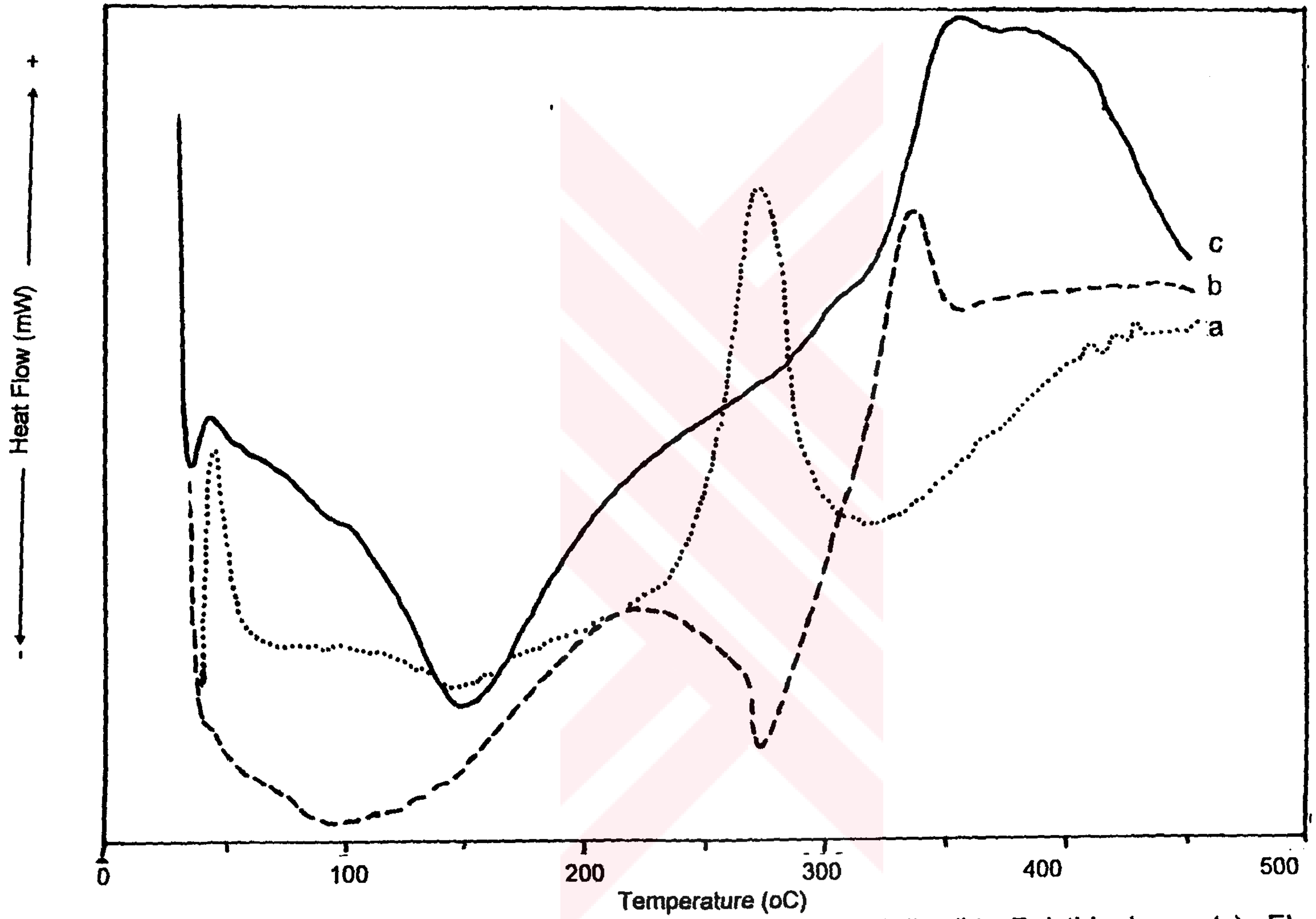


Figure 44. DSC thermogram of : (a) : Cathodic polyacrylonitrile, (b) : Polythiophene, (c) : Electrolytic PTh - PAN composite film

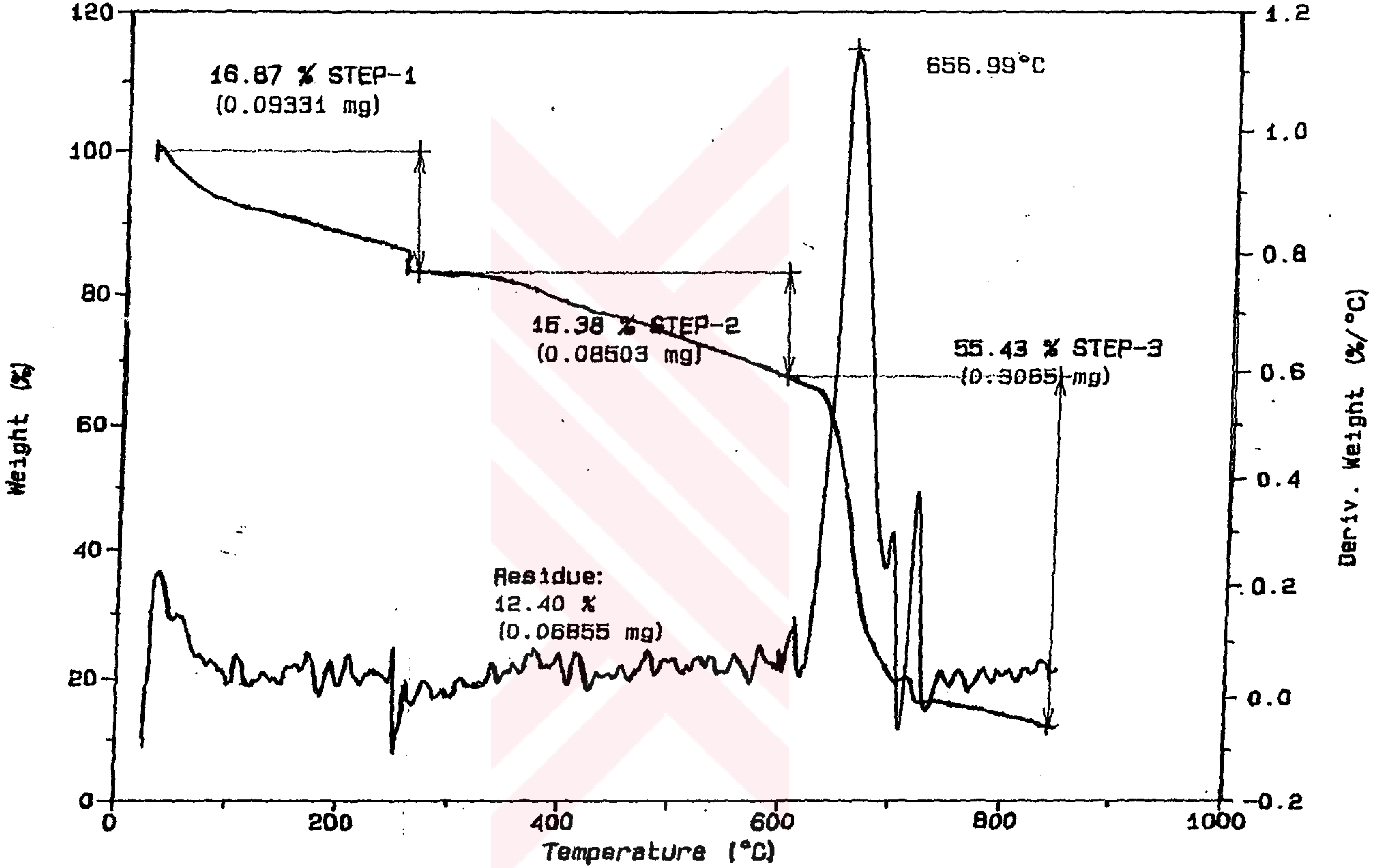


Figure 45. TGA thermogram of polypyrrole

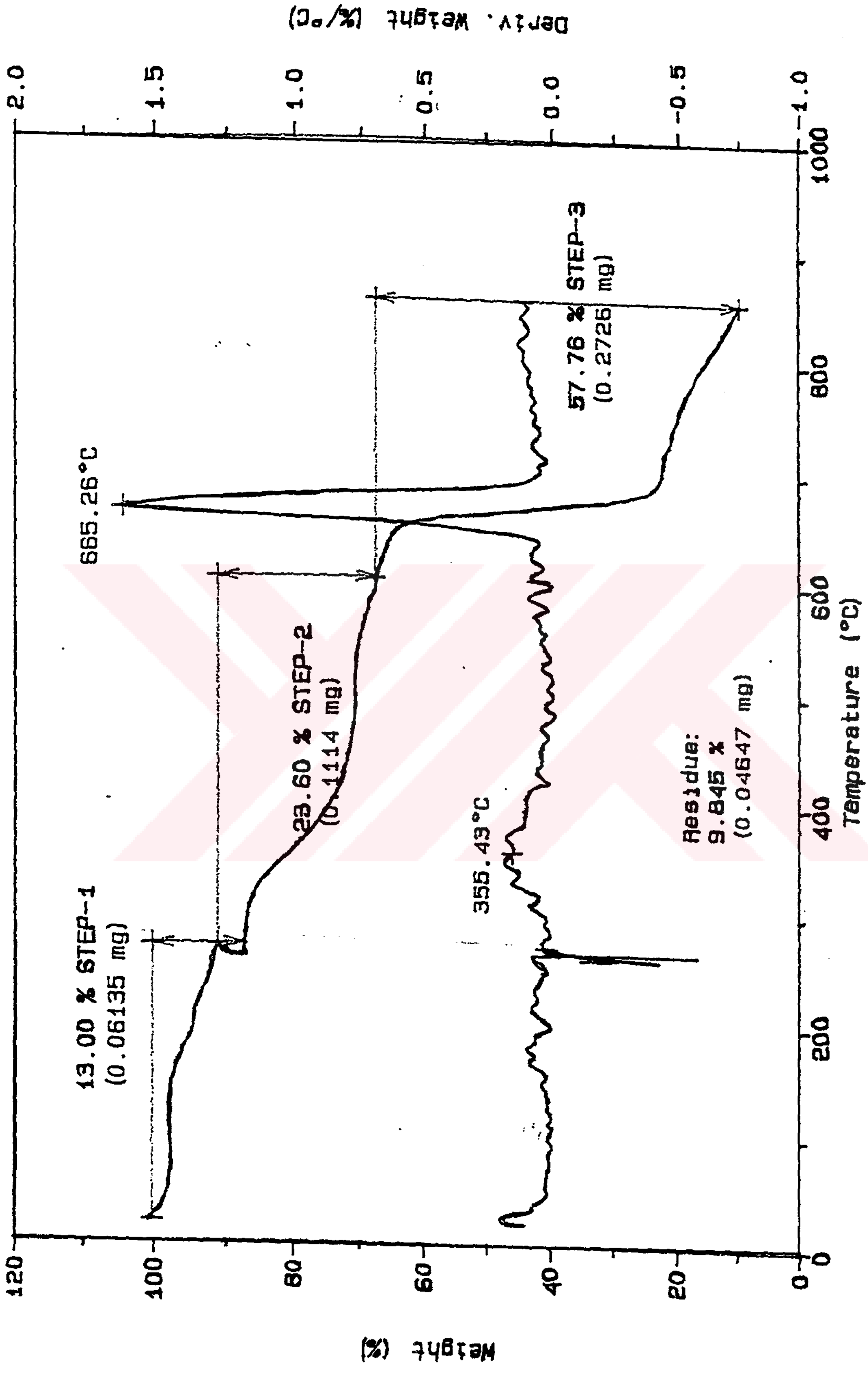


Figure 46. TGA thermogram of electrolytic PPy - PAN composite film

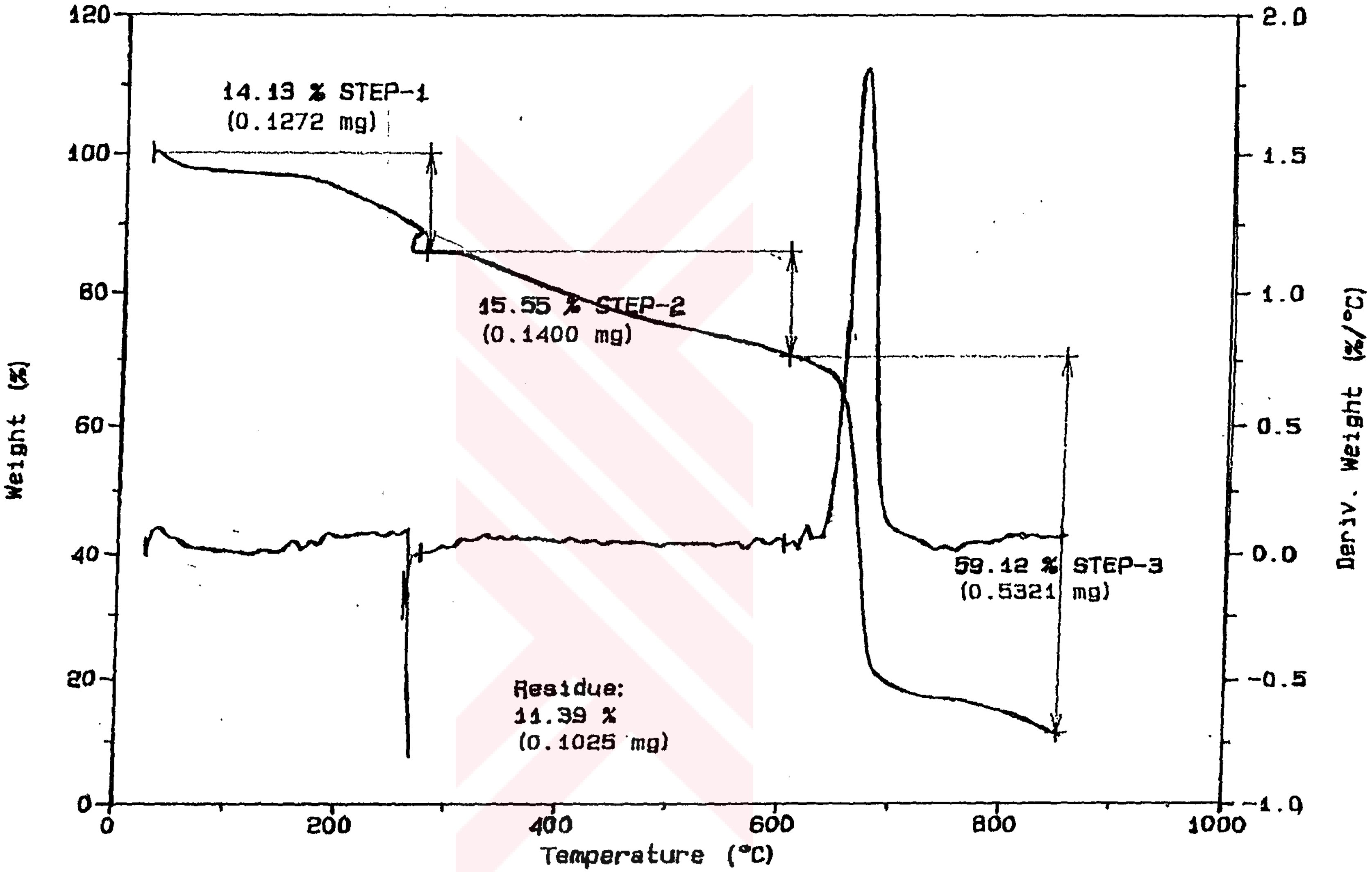


Figure 47. TGA thermogram of polythiophene

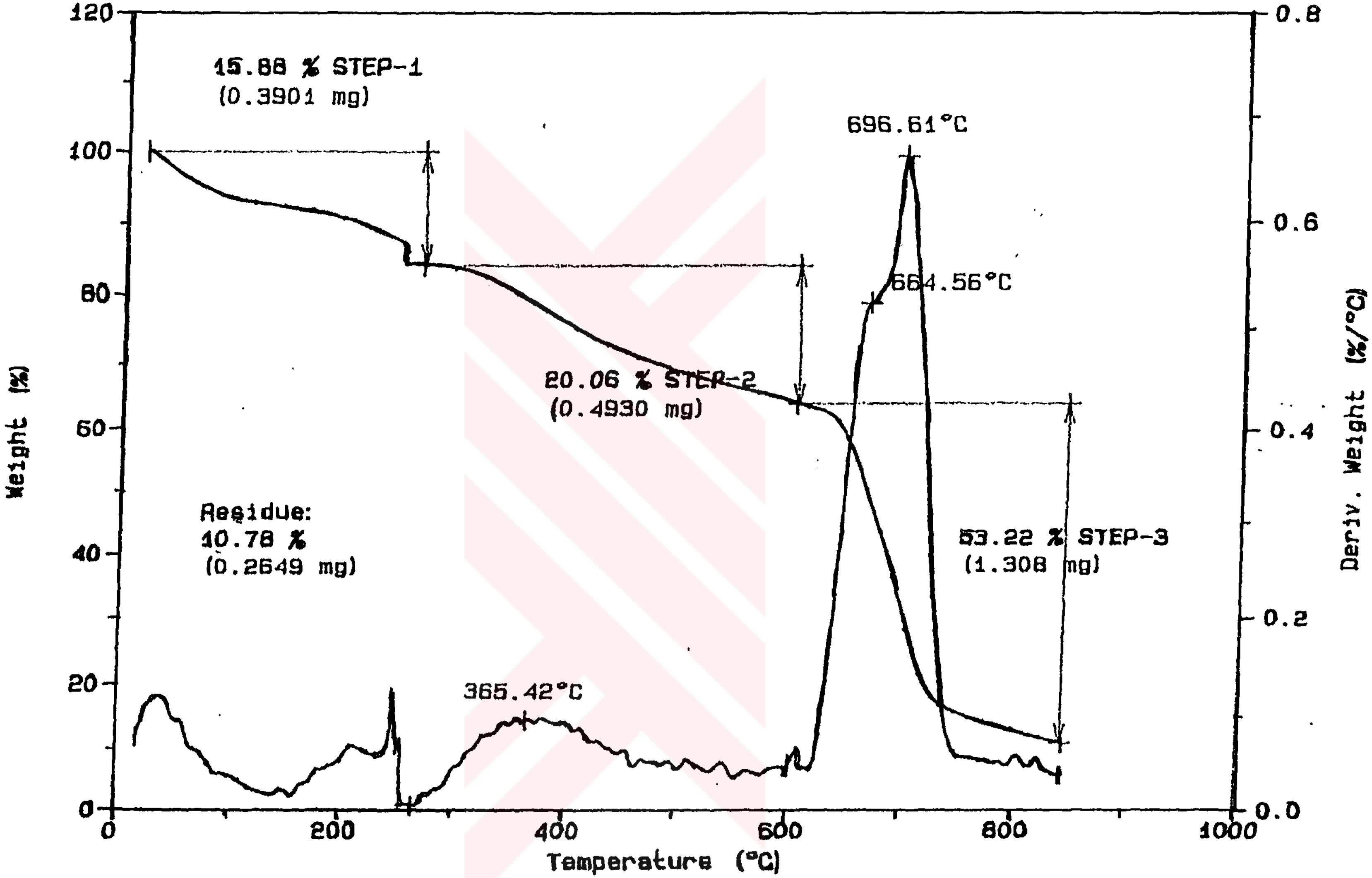


Figure 48. TGA thermogram of electrolytic PTh - PAN composite film

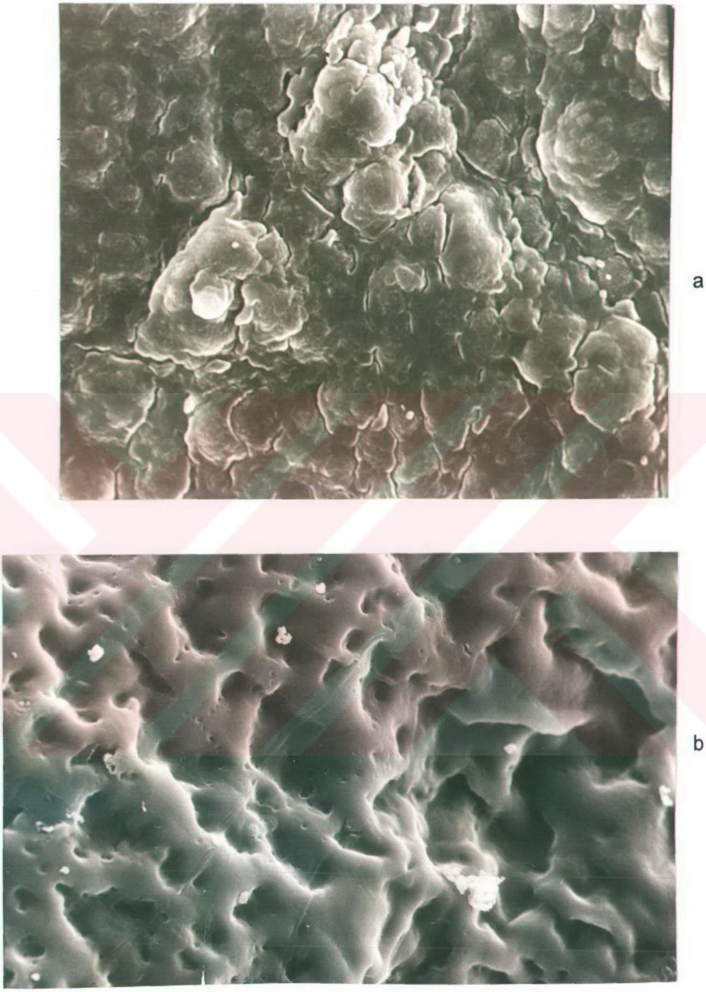


Figure 49. SEM pictures of (a) : Ppy solution side, (b): Ppy - PAN film electrode side, (c): Ppy - PAN film solution side

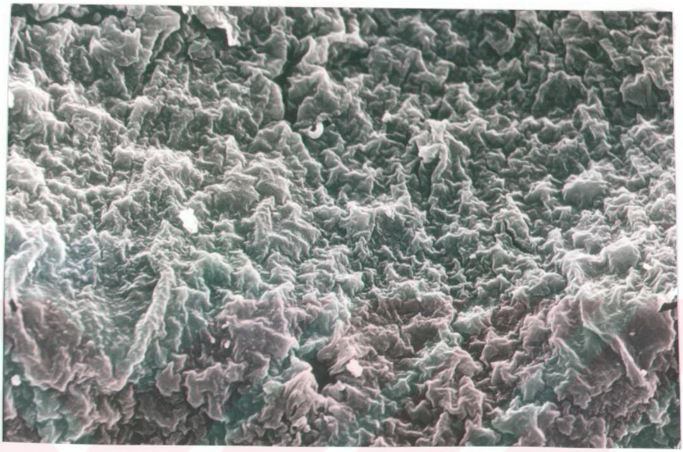
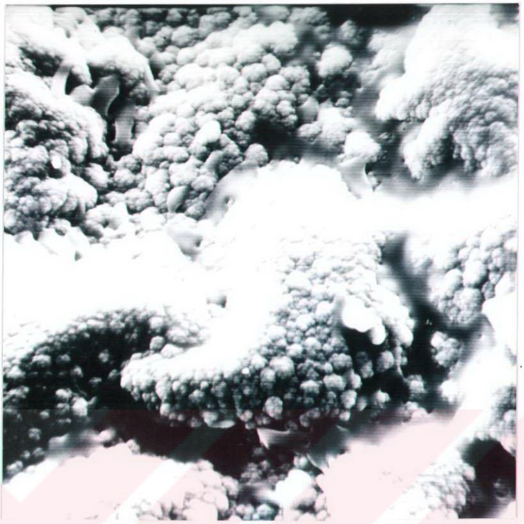


Figure 49. (cont.)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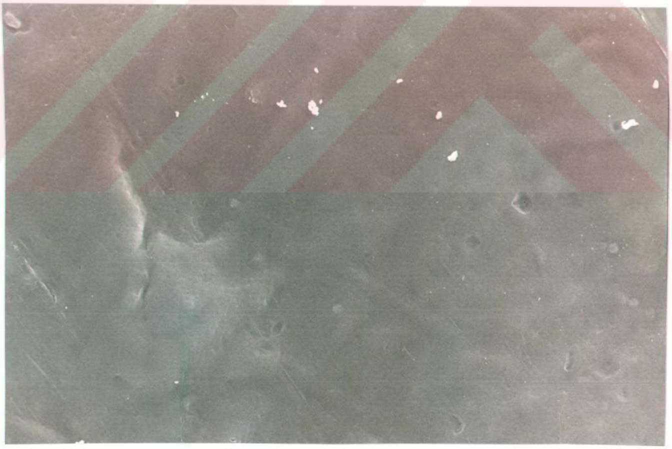
b

Figure 50. SEM pictures of (a) : PTh solution side, (b): PTh - PAN film electrode side, (c): Pth - PAN film solution side

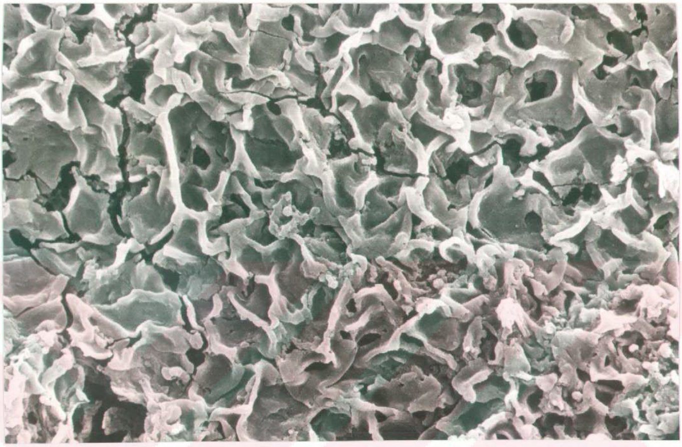

Figure 50. (cont.)

CHAPTER 4

CONCLUSION

In this work the studies performed to obtain conducting polymers were handled in three groups. The use of polyacrylonitrile as an insulating polymer was demonstrated. The first group experiments were organized to obtain this insulating polymer by electrochemical techniques. In the second group, the improvement of conducting ability of the electrochemically obtained polyacrylonitrile was considered. A series of heat treatment experiments were carried out. The last group analysis were directed to the preparation of composites using polyacrylonitrile as the insulating host polymer using either polypyrrole or polytiophene as the conducting component.

Polyacrylonitrile polymer was obtained by anionic electrochemical polymerization of the monomer at its own reduction peak potential by constant potential electrolysis. The voltammetric behavior of the monomer was determined by cyclic voltammetry prior to electrolysis. Since the applied polymerization potential was the monomer's reduction potential and within the solvent - electrolyte discharge range, the polymerization proceeded selectively through the monomer. The kinetics of polymerization in cathode and anode compartment at different temperatures was investigated. The results was the direct proportionality of monomer conversion and yield with the polymerization temperature. Viscosity measurements indicated that low molecular weight polymers were obtained. The electrochemical product was yellow colored. The coloration was attributed to the intermolecular cyclization which was also proven by the splitting of 2240 cm^{-1} peak.

In order to improve the conductivity of electrolysis polyacrylonitriles a series of heat treatment analysis were applied. The parameters during the heat treatment analysis were the temperature, the environment (vacuum and air) and the dopant. It was thought that the positive effect of temperature on the cyclization will increase the conjugation resulting an improved conductivity. Additionally, the dopant will also affect the conductivity in a positive manner. The heat treatments were made with yellow cathodic polyacrylonitrile and commercial polyacrylonitrile. The conductivity measurements of all heat treatment products were made after each set of condition. The conductivity of commercial polyacrylonitrile was around 10^{-8} S/cm, whereas yellow cathodic polymer and the cathodic film (as prepared on the cathode surface) conductivity were around 10^{-7} S/cm. The conductivity difference between linear and yellow polymer can be attributed to the cyclization in the molecular structure through $-C{\equiv}N$ functional groups. The conductivity of heat treated polymers increases in the presence of doping agent, and also at higher temperatures. The maximum achieved conductivity of heat treated polymer was around 10^{-5} S/cm. During this heat treatment evaluation of NH_3, HCN, N_2, H_2 led a ladder polymer at further steps yielding a network polymer structure. It was observed that, as the heat treatment temperature or time increases the color of polymer turns to black because of the carbonization reaction. As a consequence, the complete loss of $-C{\equiv}N$ peak and appearance of $-CH{=}N$ and $-C{=}C-$ peaks in the range of 1605 - 1645 cm^{-1} were observed in the IR spectra.

The sensitivity of heat treated polymers toward water vapor was analyzed by exposing the samples to water vapor. Upon exposure of the heat treated polymer to water vapor, the conductivity increases. As soon as the polymer removed from water vapor a sudden decrease in conductivity was observed.

Subsequent repetition of these adsorption desorption steps indicated that polymers have a reproducible and reversible sensitivity toward water vapor.

In the third group studies, the preparation of composite polymer films were aimed. Therefore the composites of insulating polyacrylonitrile with conductive polypyrrole and polythiophene were prepared at different percentages. The conductivities of these films were determined by four probe technique. The conductivity of both PPy - PAN and PTh - PAN composites increase as the percentage of the conducting component increases. In both cases the conductivity increased from 10^{-7} S/cm to 10^{-2} S/cm and a threshold value was established almost at 60 % of the conducting component in the composite. The characterization of the composites were made by FTIR, DSC, TGA and SEM analyses. DSC thermograms of conducting polymer - polyacrylonitrile composites revealed that the electrolytically obtained films were not simple mixture of the polymers. The morphology of the composite films were different and dependent on the type of monomer.

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VITA

Berrin Yurttaş Yılmaz was born in Fatsa, Ordu on February 1, 1961. She has received her B. S. and M. S. degrees from the Chemistry Department of METU in June 1983 and in June 1985, respectively. The project investigated during the master program was 'The electroinitiated polymerization of isoprene and effects of ultrasonic convection on the electroinitiated copolymerization'. She has four papers published in international journals. She has been working in KORDSA A. Ş. / İZMİT as research engineer since 1988.

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