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TABLE OF CONTENTS

LIST OF ABBREVIATIONS

AN : Acrylonitrile
CAN : Cerium Ammonium Nitrate
CV : Cylic Voltammeter
FT-IR : Fourier Transform InfraRed
NVCz : N-vinyl carbazole
Pt : Platinium
SEM : Scanning Electron Microscope
St : Styrene
TEAP : Tetra Ethyl Ammonium Percholarate
UV : Ultra-Violet Visible

LIST OF TABLES

1. OBJECTIVES

A great deal of attention has been given to Poly(N-VinylCarbazole) PNVCz over years because of it's unusual electrical and photoelectrical properties. It has been suggested for a number of applications, photo active devices, sensors and electrochoromic devices. The common usage of PNVCz material has been restricted due to the poor processibility and the lack of stability .

Our group has profoundly studied copolymerization of carbazole and it's derivates with acrylamide. Result show that there is improvement in the mechanical properties of copolymer with the introduction of acrylamide in to the structure.

Electrochemically modified Poly(Carbazole-Acrylamide) Platium electrode was checked for it's electrochemical behaviour to dopamine.

Oxidative polymerization of NVCz is studied with CAN. Due to it's clean stoichoimetry and strong oxidizing power of Ce(IV) has been used recently in the polymerization of vinyl monomers,pyrole in acetonitrile and in the polymer matrix.

On the other side to improve the surface properties of carbon fibers electrochemical polymerization of electro-active monomers, such as pyrole, 3-methylthiophene and aniline ,onto several carbon fibers have been studied, in a certain detail.

In this study it was aimed to to copolymerize N-Vinylcarbazole with Styrene and Acrylonitrile so that this can offer some improvements in the mechanical properties and processibility. Secondly these polymers were coated on Ptlatinium and carbon fiber electrode by electrochemically which is checked for dopamine behaviour some improvement is achieved when compared with the bare electrode.

2. INTRODUCTION

2.1 Polymerization of NVCz

NVCz is a strongyl basic monomer which undergoes facile cationic polymerization with conventional cationic initiators such as protonic acids, Lewis acids and carbocations(1,2). Since many of these catalyts also functions as electron acceptors towards electron-donor monomers such as NVCz , both addition and electron transfer modes of initiation have to be considered. Because of high reactivity of NVCz it is extremenyl diffucult to differentiate between these two initiation processes.

2.1.1 Oxidative Polymerization of NVCz

The oxidative polymerization of NVCz in nonaqueous systems, using metal ion oxidant .i.e., Cerium (IV), has not been studied systematically.Wang(3) presented the first report on the polymerization of NVCz initiated by oxidizing nitrates in methanol. According to him ceric ammonium nitrate ,ferric nitrate and cupric nitrate are capable of polymerizing NVCz in methanol solution and also of polymerizing compeletely the mixture of NVCz and Styrene [4-5] Such metal salts could accept electrons leading to oxidation NVCz during which radical ion might be formed as an intermediate. The polymerization of NVCz in ethylene dichloride, acetone,benzene and dioxane with cupric nitrate, ferric nitrate,ceric ammonium nitrate catalyst was studied. In all of these mentioned cases polymerization seemed to be cationic type and yields are around %20-%50 for ceric ammonium nitrate.in 2 hours. (6).

Oxidative polymerization of NVCz is studied with CAN (7). Due to it's clean stoichoimetry and strong oxidizing power of Ce(IV) has been used recently in the polymerization of vinyl monomers (7,8,9),pyrole in acetonitrile[10] and in the polymer matrix.Polyvinyl carbazole in solution can show high electrical conductivies when suitable ratio of oxidant/monomer is selected (8) The results indicated that the

reaction proceeds by a different route depending on the CAN concentration. If CAN concentration is 5 times lower than the monomer concentration a colerless polymer is formed indicating polymerization proceeds through the vinyl groups. When the concentration ratio is higher than this value polymerization proceeds from benzene rings forming green dark polymers.

Sarac et al (11) indicated that in the Ceric salts initiated vinyl polymerization, both ceric anions and primary free radicals participate in the initiation process while termination occurs exclusively by interaction of propagating chain radicals and ceric ions or mutual combination of growing chain.

2.1.2 Free- Radical Polymerization

Free-radical polymerizations carried out in dispersion and suspension. Like many free-radical polymerizations, that of NVCz is inhibited by oxygen. Perhaps more important is the effect of certain impurities (anthracene, phenanthrene and sulfur) inherent in carbazole derived from coal-tar sources.

Bevington and Dyball have carried out end group studies on PVCz prepared by polymerization at 60 ^{0}C in benzene using either AIBN or BPO as initiator [12]. AIBN gave polymers having an average of *1.35* initiator fragments per molecule. BPO gave polymers of unexpectedly low molecular weight, having close to two initiator fragments per molecule at concentrations of monomer greater than 0.08 mol dm^{3}. That a competitive process is operative, in which simple free-radical polymerization may also be occurring to a small extent, is indicated by the presence of a small amount of high molecular weight polymer.

NVCz is readily polymerized by free radical initiators such as azo compunds and peroxides and other free radical producing systems. The monomer also can be polymerized in bulk(13,14), thermally or in the presence of free radical initiators, in suspension(15,16) and emulsion(17).

Convential free radical polymerization of NVCz is achieved with azobisisobutyronitrile(16). Although thermal bulk polymerization of NVCz gives rather irreproducible results and often colored product especially with impure

monomers,(7,18) the addition of di-t-butylperoxide and particulary AIBN improves the reproducibility, appearance, and molecular weight of the polymer.

2.1.3 Cationic Polymerization

In its free-radical polymerization, NVCz is typical of many other vinyl monomers (methylvinyl ether, N-vinylpyrrolidone, etc.). However, unlike other electron rich monomers, NVCz can be polymerized cationically even by the weakest initiators. Indeed, it has been polymerized with protonic acid [19]. Even the generally accepted concept that basic solvents preclude cationic polymerization can not be applied to NVCz.

Boweyer et al. [20] have studied the cationic polymerization of NVCz by tropylium hexacholoroantimonate and tropylium perchlorate. Polymerization initiated by both catalysts showed identical features. Molecular weights of PVCz from the perchlorate initiation were slightly lower than those from the hexachloroantimonate catalysis and did not show the same temperature variation. From both catalysts, however, the molecular weight data showed clear evidence of a transfer reaction characteristic of homogeneous cationic systems [21].

Ledwith and Sherrington [22] have also reported the only example of a propagating dication by reaction of NVCz with the stable cation-radical tris-(pbromophenyl) aminium hexacholoroantimonate. Although this system with the propagating dication is extremely interesting and important, a question remains as to why relatively large amunts of catalyst must be used and why a molecular weight of ~10.000 can be achieved. Ledwith [23] has suggested that this may be caused by competitive cyclodimerization.

There are numerous other reports of the cationic polymerization of NVCz, utilizing a variety of acidic reagents [24]. Among the most recent studies are those by Pielichowski [25] who described the polymerization of NVCz initiated by hydrogen halides, HF, HCI, HBr and HI .(26)

There are number of reported examples of cationic polymerization of NVCz under conditions that eare excepted to show typical free radical behavior. Apparently the

nucleophilic radical formed from the donor NVCz monomer can be oxidized to the corresponding cation by appropriate electron acceptor species, e.g.,

The electron releasing carbazole group attached to the C- centered radical favors electron transfer by stabilizing the product carbocation and hence lowering the oxidation potential of the free radical.

Thus, polymerization of NVCz initiated with cupric salts is cationic, whereas the polymerization of 4-vinylpyridine proceeds by a free radical mechanism(21).the most convincing evidence for the cationic propagation of NVCz is the copolymerization with sytrene which differs markedly from the true radical copolymerization.

2.1.4 Photocationic Polymerization

Silver(43) ($AgClO_4$, $AgBF_4$) and gold(27) [$(n\text{-}C_4H_9)_4N\ AuCl_4$] salts have been used to phtoinitiate the cationic polmerization of NVCz. The mechanisö is still unresolved. Participation of the metyal salts in electron transfer oxidsation and as a source for the stabilizing counter ion gas been proposed. An alternative mechanism invokes photodecomposition of the metal salt to produce an acidic initiating species, e.g., hydrogen halide.(27).

2.1.5. Ziegler-Natta Polymerization

Early reports(28,29) that NVCz can be polymerized by conventional heterogeneous Z/N catalyst systems to produce stereoregular, crystalline polymer have been questioned. The high reactivity of NVCz to cationic poılymerization suggest that this process dominates the reaction and that the coordinated Z/N type mechanism is not involved (30). Polymers isolated from free radical, cationic and Z/N systems are essentially atactic (certainly not highly stereoregular) and amorphous.

2.1.6 Anionic Polymerization

Attempts to polymerize NVCz with conventional anionic initiators, e.g., Na metal – S^-, n-BuLi were unsuccessful(31). The monomer radical anion, $NVCz^{-\cdot}$, is produced by electron transfer initiation. This species is stable only at low temperatures and

has been spectroscopically (ESR; UV-VIS) characterized. It does not dimerize nor initiate the polymerization of NVCz but can initiate polymerization of other monomers, e.g. styrene. At elevated temperatures $NVCz^{-\cdot}$ decomposes via C-N bond cleavage to produce carbazole and ethylene.

Mulvaney (32) has shown that NVCz can be polymerized with lthium di-n-buthyl cuprate, R_2CuLi, and proposed a coordinated anionic mechanism. The Cu species complexes with the growing carbanion chain and the incoming monomer unit, reducing the π electron density of the monomer and making it more susceptible to nucleophilic attack. If this mechanism is substantiated it represent the only known example of the anionic polymerization of NVCz.

2.1.7 Charge Transfer Polymerization

Polymerization reactions involving electron donor-acceptor interactions (charge transfer interactions) have been of considerable interest since Labes et al(33) and Ellinger(34) independently reported in 1963 that donor monomers such as NVCz could be spontaneously polymerized in the presence of electron acceptor molecules.

The original scheme proposed for the polymerization of NVCz induced by electron acceptors such as chroranil, TCNE, halogens, maleic anhydride, acrylonitrile and fumaronitrile, involved formation of an electron donor-acceptor or charge transfer complex (CTC) followed by electron transfer to produce an initiating species.

Labes(33) proposed the monomer radical cation, $NVCz^{\cdot+}$, formed by one electron oxidation, as the initiating species. Ellinger(34,35) favored a mesomeric polarization mechanism involving partial electron transfer.

These two publications triggered an explosion of activity in the area and several excellent review articles have since appeared(36,37,38)

2.1.8 Photoinduced Charge Transfer Polymerization

It was shown that NVCz is readily polymerized with strong electron acceptors in polar solvents. With weak electron acceptors, however, thermal activation is required to induce polymerization, and in most instances no reaction occurs in the

dark at ambient temperatures. Such systems can be polymerized readily by photoactivation. The excited states of charge transfer complexes can arise either by direct excitation of the ground state comlex, $[DA] \rightarrow [D^{+}A^{-}]^{*}$ or by ndiffusion controlled collision between locally excited donor (or acceptor) and ground state acceptor(or donor).

2.1.9 Electrochemical Polymerization

Breintenbach(39) reported the anodic (cationic) polymerization of NVCz in nitrobenzene $Et_4N^{+}ClO_4^{-}$ as supporting electrolyte. Unfortunately this particular system (perhlorate salts in the presence of traces of water) is highly susceptible to nonelectrolytic cationic polymerization(40), casting some doubt on the results. Smith et al.(41,42) investigated the electroinitiated reaction of NVCz in acetone in the presence of $ZnBr_2$ with Pt electrodes. Depending on the current density employed, either polymer or cyclodimer can be produced in high yield(43). Although the exact nature of the electrode process is not known, it is proposed that NVCz-$ZnBr_2$ complex undergoes electrolytic reaction to form $NVCz^{\cdot +}$, the initiating species for the polymerization and cyclodimerization. The mechanism is equivalent to that proposed for the chemical and photochemical reactions.

It should be noted that up till 1982 the electrochemical polymerization of NVCz has only been undertaken for preparative purposes [44-45], and that only products obtained in solution have attracted attention. Ambrose and Nelson [46], who are the first to have studied the mechanism involved in the electrochemical oxidation of a certain number of carbazoles, reported a complex behaviour for NVCz which they did not attempt to elucidate.

Electrochemical polymerization of NVCz is different from that of pyrrole (Py), thiophene etc. [47,48]. In comparison with the rather simple molecules of these five membered heterocycles, NVCz represents a more developed π-electron system with more mesomeric forms of the cation radical and with polymerization centres on both the benzene ring and the vinyl group [49]. It should be emphasized that PVCz is polymerized not only through carbazole units but also through vinylene groups. Consequently polymers with different structure and composition can be prepared by electrochemically [50].

Furthermore, it is possible to regulate the extent of polymerization through carbazole units and vinylene groups. It was found previously that the main role in this process is played by water present in acetonitrile solution of the monomer.

The electrochemical oxidation of NVCz is a complex process which depending on experimental conditions, involves several reaction pathways.

When NVCz is subjected to controlled-potential electrolysis, since oxidation of the solvent or of the supporting electrolyte salt is hindered, it seems likely that the first step in the electrochemical oxidation of NVCz involves a monoelectron transfer which yields the cation radical $(NVCz)^{\bullet+}$.

Several authors have reported that polypyrrole, polythiophene and Poly (N-vinylcarbazole) films obtained in solutions containing added water are uniform and adherent , although they exhibit lower conductivity than films prepared in dry acetonitrile [49, 51-54]. The substantial differences in polymer resistance have been ascribed to structural transformations during polymerization. The modification of the conducting and mechanical properties of the film may also result from changes in chain length, and there is evidence that shorter chains are produced in the presence of water [51]. During redox cycling of the polymers, ion and solvent exchange occur and nucleophilic solvents such as H_20 can react with the cation radical cations or dications produced during oxidation leading to degradation of the polymer [49, 55-56].

The redox behaviour of PVCz films depends strongly on the water content of the acetonitrile solution. In dry acetonitrile, the redox process is relatively fast and reversible. In a mixture containing 10% H_20 + 90% CH_3CN , irreversible changes of the polymer occur during oxidation, and these are attributed to nucleophilic reaction of water molecules with the radical cations of PVCz. In a solution containing 90% H_20 + 10% CH_3CN, oxidation of the polymer is inhibited, probably because of a strong contraction of the polymer film in contact with the aqueous phase.

2.1.10 Solid Polymerization

The solid state polymerization of a monomner, it can be achieved topochemically, is an interesting approach for producing stereoregular, crstalline and high molecular

weight polymer. There have been several publications describing the solid state polymerization of NVCz in the crystalline state initiated by high energy radiation(57-60), cationic catalyst (61), halogen vapors(62,63) and redox systems(64). Both free radical and cationic mechanism have proposed, primarily on the basic kinetic and polymer molecular weight analysis.

2.2 Physical Proporties

2.2.1 Mechanical properties

PNVCz is glassy polymer with unusual high thermal stability for a vinyl polymer. The glass transition temperature of >200 ^{0}C is the highest among known vinyl polymers. This excellent thermal stability is, however, offset by the extreme brittleness of the material. Values of 0.3 to 1,1% for the elongation ratio of PNVCz(65-66) clearly demonstrate its mechanical limitations, particularly since these represent static strains, and cyclic or fatigue limits are likely to be considerably lower. Since most glassy polymers fail because of cracking/fracture, there have been many attempts to improve the mechanical and processing characteristics by orientation, copolymerization and plasticization. Most of the reported plasticizers serve to reduce viscosity and permit processing at lower temperatures. Improvements in the mechanical properties by orientation have also been claimed, and both unaxial(66) and biaxial(67-69) orientations have been achieved.

2.2.2 Glass Transition Temperature

Glass transition temperatures of PNVCz raning from 150 to 248 have been reported(70-72). The highest reported value of T_g of 248 ^{0}C was for PNVCz prepared ny cationic polymerization(72). This polymer is claimed to be somewhat more isotactic than polymers prepared free radically, the high T_g value was attributed to isotactixity. Recent measurements(65,73), however, indicate that the high T_g of Such polymers are reduced to more typical values following vitrification from melt, causing doubts on the stereoregularity explanation.

2.3 Electrical Proporties

2.3.1 Dielectric Properties

PNVCz is an extremenyl attractive material for dielctric applications because the dielectric constant ($\in^{'}$) and the loss factor ($\in^{''}$) are remarkably constant over a wide temperture and frequency range. Also, the bulk and surface resistivity values are high, $>10^{14}$ ohm cm.

2.3.2 Photoconductivity

The discovery of photoconductivity in PNVCz (74) stimulated the development of photoelectrically active organic materials which ultimately resulted in commercial applications. PNVCz is an efficient insulator in the dark. However, it supports passage of positive charge carriers, holes, which can be produced by exposure to uv radiation or injected from certain types of electrodes, towards a negatively charged carriers can be shifted into the visible and near infrared range of wavelenghts by approriate,sensitizers.

The capability of both producing and transporting charge carriers in an electric field through a particular substance is a precondition of photoconductivity. Since PNVCz absorbs only uv radiation it can function as a true photoconductor only in the uv region of the spectrum. In the visible region another component is needed to accompolish carrier generation, either alone or in conjunction with PNVCz

Hoegl et al(71,74) idendified a number of compounds such as electron acceptors or dyes that render PNVCz photosensitive in the visible range. Follwing this discover, an avalanche of scientific papers appeared in the literature dealing with various aspects of photoconductivity in the PNVCz and related materials. PNVCz is now the best understood organic photoconductor, and studies of this polymer have led to a much better understanding of the fundamental principles of photoconductivity in amorphous organic systems.

2.3.3 Conductivity

PNVCz can be useful either as an insulator or photoconductor, depending on the circumstances. The polymer has also shown promise as interesting p-type semiconductor. The possibility of introducing unpaired electrons exists in PNVCz, and stable cation radicals can be produced by oxidation, for example using tris-(p-bromophenyl)ammoniumyl hexachloroantimonate) (75). The conductivity at 293 K(σ_{293}) depends on the mole fraction of carbazole groups converted to cation radicals (χ)

Films of the polymer exhibit some loss of conductivity over an extended period of the time, especially samples with high degree of χ. On the other hand, a sample with $\chi=0.6565.10^{-3}$ was stable for at least 6 months.

These partially oxidized PNVCz samples absorb in the visible and also exhibit photoconductivity(76).

2.4. Degradation and Stability of N-Carbazole Derivatives

Although there is a very wide spectrum of conductive materials with extremely different behaviour, we can still identify certain fundamental processes involved in the degradation and stability behaviour of conductive polymers.

Since PVCz is a vinyl derivative with a high Tg, requires high processing temperatures (> 230 ^{0}C),and sees enviroments in photoelectric applications such as UV light, oxygen and corona discharge, the molecule is expected to degrade. Very little work has been done in the past on the thermal and radiative degradation, oxidation and ozonization of PVCz.

Decomposition of polymers can occur via a direct or indirect process. Direct decomposition occurs when chromophores or irregular bonds are contained in the main chain (77). Indirect decomposition includes energy-transfer processes and radical reactions following absorption by impurities. Whether by direct or indirect decomposition, the formation of a free radical can lead to one or more reactions [77]. The first step is associated with the initiation reaction and is influenced by the

presence of radical initiators, oxidation products and sensitizers. The second step is associated with propagation and is influenced by the presence and diffusion of oxygen. The third step is causes of branching and crosslinking in the polymer.

Oxidation of pendant group is also possible. In vinyl polymers it is initiated by an attack on the tertiary hydrogen and, in some cases, by an attack directly on the pendant group [78]. Generally, the aromatic groups oxidized to form quinones, which can then undergo further reactions to form alcohols (79].

Thermal, oxidative and enviromental degradation tests have been performed on several commercial and fractionated PVCz materials as a function of ambience, temperature and time [80]. Low molecular weight samples were the most resistive to degradation in air and argon at 180, 280 and 330^0C. High molecular weight PVCz performed better than an "as receieved "commercial material which contained approximately 5% impurities. The impurities evidently initiate and help propagate degradative reactions leading to a discolored cross-linked matrix. The differences observed in air and argon are due to the presence of oxygen which, according to the suggested reactions, increases the propagation reaction and leads to branching and crosslinking.

There are quite studies about thermal properties of modified or copolymers of PVCz. Polymerization way also effect thermal characteristic. For insantance, thermogravimetric analysis reveals that PVCz prepared with $FeClO_3$:NVCz mole ratio of 9:1 exhibits higher stability than that obtained with a ratio of 6:1. The temperatures for initial 20%, 40% and 60% for these two polymers are respectively, 230, 190; 310, 280; 420, 370 and 460, 420 ^{0}C. In either case, the polymers undergo 95% decomposition at >550 ^{0}C. The higher stability of the 9:1 PVCz is evidently due to a higher molecular weight than the 6:1. The FeC 103 initiated PVCz, on the other hand, exhibits a somewhat higher initial decomposition temperature, about 260 ^{0}C, but beyond 20% decomposition becomes progressively less stable (40% at 350 ^{0}C and 50% at 390 ^{0}C) than the suspension-polymerized PVCz. The trend is again consistent with the lower molecular weight for this polymer. Differential thermal analysis reveals a sharp exotherm around 450 ^{0}C, signifying oxidative degration of the polymer network [81].

Copolymers of methyl and ethyl methacrylate with NVCz were synthesized by free radical bulk polymerization using benzoyl peroxide as an initiator. It has been found that with an increase of NVCz content in the copolymers, their thermal stability increases [82].

The thermal degradation of phosphorylated PVCz also was studied by thermogravimetry. The onset degradation temperature decraeses with respect to that of unmodified PVCz indicating a lower thermal stability for the phosphorylated sample [83].

Hydrogen halides were studied to understand effecting this group of thermal properties of PVCz. It was found that the polyvinylcarbazole-hydrogen halide molecular complexes undergo thermal decomposition with release of hydrogen halides in the temperature range of 80-180 ^{0}C. Thermal stability of PVCz, after removal of hydrogen halides, is higher by approx. 10 ^{0}C in comparison with PVCz itself. This can be explained by a more streoregular structure of PVCz obtained upon polymerization in the presence of hydrogen halides.

Feric Chloride-initiated polymerization of pyrrole in the presence of N-Vinylcarbazole was studied. The initial decomposition temperature ,is Ppy (210 ^{0}C) < P(Py-NVCz) (225 ^{0}C) < PVCz (225 ^{0}C) has been found. The DSC scan for Ppy is similar but the peaks are less sharp. It is obvious from the DSC scan the major structural degredation occurs in the range 250-520 ^{0}C in these systems.[84] .

2.5.Copolymers of Carbazole

Conductive polymer composites and copolymers of Py and NVCz was investigated as well [85] Both insulating and conducting polymers of NVCz are utilized in the electroinitated polyrization of Py. These study showed that, a sufficient homogeneity of the films can also be achieved by blending/grafting a conducting with a nonconducting polymer which has an electroactive group.

Although some studies have been conducted on the copolymerization of AAm with vinyl monomers, there is not much studies about copolymer of AAm with conjugated polymers [86 In spite of many studies about conductive polymer blends and

composites are prepared by combining an insulating polymer with an intrinsically conductive polymer. Polyaniide/polypyrrole composite film was obtained by the electrode coating method [87)The polyamide film was obtained in situ by coating a stainless steel electrode with a polyamic acid film followed by imidization with pyridine and acetic anhydride. The coated electrode was submitted to a constant current in a Py/$LiCIO_4$ solution in acetonitrile. Combination of polypyrrole with this polyamide was shown to increase markedly its thermal and enviromental stability

Table 2.5 Copolymerization involving N-vinylcarbazoIe

Comonomers	**Copolymerization Process**
NVCz/p-nitrostyrene	(a)Photoirradiation (b)Thermal/AIBN
3-Vinyl-N-ethylcarbazole/styrene	Free-Radical
3-Vinyl-N-methylcarbazole/styrene	Free-Radical
3-Methyl-NVCz/styrene	Free-radical
NVCz/ N-vinylphthalimide	Free-radical
NVCz /vinylferrocene	Free-radical
NVCz / 4-vinylpyridine	Free-radical
NVCz/5-nitroacenapthene	Free-radical
NVCz / m-nitrostyrene	Free-radical
NVCz./styrene	Free-radical
NVCz / N-vinylpyrrolidone	Cationic
NVCz/ N-propenylcarbazole	Cationic
NVCz / 1 -vinylnaphthalane	Free-radical

It is now widely accepted that most of the useful and scientifically important properties of PNVCz are associated with the pendant carbazole groups. Practical utilization of PNVCz is, however, hampered by its poor mechanical properties resulting from extreme stiffness of the chain. Several attempts have therefore been made to prepare other carbazole containing polymers with improved properties in which more freedom of rotation is imparted to the pendant groups. These polymers were obtained either by copolymerization of NVCz with other monomers or by

sythesis and polymerization and polymerization of other carbazole containing monomers.

2.5.1 Random Copolymers

NVCz has been copolymerized with a variety of co-monomers. In most instances the objective of this work was to maintain the desired electronic characteristics of PNVCz and improve the mechanical properties by insertion of suitable comonomers into the chain. Although thermal and mechanical behavior could be improved by copolymerization, the conductivity was substantially impaired(88). This was demonstrated in the case of copolymers with styrene, vinylacetate and N-vinyl pyrrolidone. The electrophotographic gain was found to decrease with increasing content of comonomer units such as n-octadecyl, n-dodecyl, n-decyl and cyclohexyl methacrylate in the terpolymers with NVCz and styrene(89). On the other hand the introduction of electron acceptor comonomers containing 3,5-dinitrobenzyl, chloranil,etc., groups resulted in copolymers which exhibited photo conductivity in the visible range of wave lenghts copolymerization with butyl acrylate, disisobuthyl maletate, vinyl-2-ethylenehexanoate, acrylophenone, vinyl alcohol and acryloyl cholride have been reported(90).

Most of the NVCz copolymers were prepared by free radical copolymerization. However, under certain conditions, and particulary in the presence of electron acceptor species, free radically initiated copolymerization may be accompanied by cationic homopolymerization of NVCz. In these cases, the product may be a mixture of copolymer and cationically polymerized PNVCz.

2.5.2 Block and Graft Copolymers

Since NVCz does not polymerize anionically, conventional anionic techniques cannot be used to prepare controlled block and graft copolymers. Stannet et al (91) have synthesized block copolymers of NVCz with ethyl vinyl ether (EVE) and isobuthyl ether (IBVE) using a sequential carbenium ion polymerization technique. At high ratios of initiator (e.g., Ph_3C^+ , $SbCl^-_6$) to monomer and low ratios of solvent to monomer, termination and chain transfer reactions are suppressed to the point where a pseudo-living system prevails. Under such conditions high yields of low molecular weight PEVE-b_PNVCz and PIBVE-b-PNVCz were produced. Cationic

graft copolymerization of NVCz on to poly(vinylchloride) via carbenium ion centers formed by reaction of Lewis acid ($AlCl_3$, $TiCl_3$, $SbCl_5$, etc.) with a halogen on the polymer has also been reported(92). Grafting efficiencies (percent NVCz grafted of total NVCz polymerized) of up to 44.5 % and ratios of grafted NVCz to the PVC as high as were achieved. Block copolymers with wide composition and molecular weight distributions are formed in the solid state, radiochemical copolymerization of NVCz-acenaphthalene(93)

Stolka(94) has synthesized multiblock, $-(AB)_n-$ copolymers of NVCz with alkyl methacrylates, e.g.lauryl, dodecyl, using a two step free radical polymerization procedure initiated by sequential initiators such as di-[1,3-dimethyl-3-(t-buthyl-peroxy)buthyl] peroxydicarbonate. Under conditions where the polymer precipicates from the reaction medium, high molecular weight, multiblock products containing 50-90% NVCz and essentially free of homopolymers can be obtained.

2.5.3 Alternating Copolymers

NVCz exhibits an unusual tendency to form 1:1 alternating copolymers with several electron accepting monomers such as diethyl fumarate(95-99), fumaronitrile (95,97-100), acrylic acid (101), 4-phenyl-1,2,4-triazoline-3,5-dione(102), diethylazodicarboxylate (103), dimethyl-1-cyano-1,2-ethylenedicarboxylate (104) and trimethylethylene tricarboxylate(103). Alternating polymerizations can be initiated by free radical initiators or by the action of light.

2.5.4 Other Carbazole-Containing Polymers

The number of published papers dealing with carbazole polymers other than those based on NVCz is limited. The sythesis of the monomers can be difficult, and the polymerization does not always lead to high molecular weight product.

Photoconductivity and the properties of charge transfer complexes with strong electronic acceptors are the main fields of interest with these polymers. None of these materials exhibits photoelectronic properties comparable to those of PNVCz or PNVCz:TNF(1:1) and materials have yet to find commercial application.

2.6. Applications

The major utilization of PNVCz based materials has been as an organic photoconductor in electrophotography. Several other possible applications have been reported in the literature which have yet to be exploited commercially.

2.6.1 Image Storage Systems

The concept of using the persistent conductive state of organic photoconductors has been widely discussed but never realized. Formation of an electrostatic duplication master in a PNVCz:TNF:leuco dye film has been recently described(104). Kumada et al(105). have created long lived latent images in dual layer ferroelectric (FE)-PNVCz:TNF structures which can be developed using liquid toner systems. Problems of sensitivity, image stability, quality and erasure have to be overcome before this approach to image retention/utilization becomes practical.

2.6.2 Photothermoplastic Imaging

Direct optical relief recording on thermoplastic organic photoconductor layers has been demonstrated(106,107), and the technology has been considered for display devices, ''add-on-image'' microfiche and ''instant'' microfilm. A single layer device has recently been described (108,109) which is based on copolymers of NVCz with acrylates, methacrylates or styrenes. In these single layer systems optimization of the thermoplastic properties generally comes at expense of photoelectronic properties, and devices with adequate spectral response and sensitivity have yet to be constructed. Their application in electron beam recording has also been used in devices suitable for holographic recording, image intensification and optical buffer storage(110,111).

2.6.3 Photovoltaic Devices

The development of low cost, readily fabricated, large area photovoltaic cells for solar energy conversion is highly desirable, and organic polymeric systems based on PNVCz have been examined. An estimate of the phtovoltaic conversion effiency for the PNVCz:TNF (1:1) systems has been made(112). In the films of thickness > 1μm , space charge limited conductance limits the effiency. In thinner films, <1μm, the

efficiency will be determined by the photogeneration process, and it may be possible to achieve efficiences in the 10^{-2} to %1 range. At the 1% conversion efficiency level, cost and fabrication advantages could make organic systems competetive with the higher effiency (10-15%) but very expensive in organic solar cells.

The poly[γ-(β-(N-carbazolyl)ethyl)-L-glutamate]-TNF complex has displayed a rectification effect, similar to that in semiconductors. The p-n junction was accomplished by immersing a layer of the polymer in a 2,4,7-trinitrofluorenone solution using a solvent which is poor solvent for the polymer. The TNF molecules diffuse into the polymer, forming a p-n junctionat the diffision boundaries, leaving the TNF-free region p-type and the surface TNF-rich region n-type. The device also exhibit photovoltaic behavior(113).

2.6.4 Non-Convential Imaging Systems

A non-silver photo-graphic process utilizing the polymerization of NVCz was described by Yamada, garland and Bruck(114). NVCz and CBr_4 are dispersed together in micron diameter particles in a gelatin matrix, and imagewise exposure to visible light initiates the polymerization with quantum amplification to a colorles PNVCz product. After ex posure, the film is subjected to amore intense white light treatment and heat, causing the unreacted NVCz to undergo a color forming reaction. The color density developed in any small area is inversely proportional to the degree of polymerization initiated in the initial exposure. The process is adry one with no added chemicals and produces a direct positive image. A photoinduced electron transfer mechanism involving the monomer cation radical, $NVCz^{\cdot+}$, has ben postulated. At the light intensities of the imaging step the polymerization reaction is favored. In the development process coupling and carbazole group substitution reactions leading to colored products predominate.

Hasegawa et al(115) have described a light sensitive paper based on the above NVK:CBr_4 emulsion, which can be used to produce copies from a CRT printer and as a high speed facsimile receiver sheet.

A photoimaging system based on PNVCz has been described by Smets(116). The components of the system are PNVCz,CBr_4 and a dye precursor, di-β-

naphthospiropyran (DNSP). PNVCz serves both as a reactant in the image formation chemistry nand as a binder. The mechanism involves photoproduction of acid (HBr) from PNVCz:CBr_4 charge transfer complex followed by the reaction of the acid with the DNSP to produce a blue pyrylium dye latent image.

The pyrylium dye salt forms a complex with CBr_4 which is activated with light of 500-700 nm to produce more HBr. This optical development process establishes a chain reaction to produce more dye and an accumulation of dye at the sites of primary irridation. The image is fixed by heating to remove the CBr_4 activator from the film.

2.6.5 Polymer Modified Electrodes

Electroactive polymers can be divided into three broad classes: electronically conducting polymers, such as PPy in which conduction is associated with motion of charge carriers along the chains; redox polymers, such as poly (vinylferrocene) in which conduction is associated with cross-exchange reactions between discrete redox sites; and polymer electolytes, such as nafion, in which conduction is associated with ion motions within the film.

Films of these polymers can be deposited on the electrode surface by a variety of methods, including electropolymerization and dip or drop, coating from solutions of the performed polymer. The former technique has two advantages:Deposition can be controlled by adjusting the electrode potential, and the process is localized at the electrode surface. This has led many groups to study electropolymerised films as method for immobilizing enzymes and other biological components. However to use this technique, the polymer must be soluble in the electrolyte solution ultimately used for electrochemical studies.

Modified electrodes are used for detecting and measuring the concentration of various chemical species in liquid or gas phase. An ideal chemical sensor should exhibit high sensivity, selectivity, high operation speed, reversibilty and stability under operating conditions. Morever, it should not be sensitive to temperature changes of various kind.

For over ten years extensive investigations of various metals, oxides, inorganic semiconductors, solid electrolytes, carbon- and silicon like materials have ~y been carried out and changes in the electrochemical potential, electrical, optical, magnetic, thermic and other properties taking place in these materials as a result of their interaction with particular gases have been studied [94].

Electronically conducting polymers with conjugated it bands, e.g. polyacetylene, polyparaphenylene, polypyrrole, polythiophene, polyaniline,polycarbazole are likely to show properties meeting the requirements mentioned above, because their conductivity depends on the electronic structure which can undergo changes under the influence of a chemical species adsorbed on the surface of the polymer layer. These changes may result e.g. from redox or acid-base interactions between polymer and the chemical species.

For instance, polyacetylene may be used for determining the concentration of nitrate ions in acid solutions because, as the result of the process involving the intercalation oxidation. The conductivity of this polymer changes which is probably due to disturbances occurring in the band structure of n electrons [117].

Interestingly with our studies, polycarbazole has been investigated earlier [118,119, 120] for its catalytic activity. It was not known at the time whether this polymer would be selective enough for the oxidation of biologically active molecules. And then it is established that this electrodeis selective some biological active molecules. For this purpose, it was used to determine dopamine [121-122].

3.EXPERIMENTAL

3.1.Materials

CAN(Aldrich), NVCz(Aldrich), Styrene(Aldrich), Acrylonitrile(Fluka),tetraethyl ammoniumperchlorate(TEAP)(fluka)(Merck), Dichloromethane(Merck),acetonitrile (Carlo Erba) DMF (Merck) were all highest reagent grade chemicals were used as obtained.

3.2 Spectrometers

Fourier Transform InfraRed (FT-IR) spectra were obtained by Mattson 1000 spectrometer. Spectrums were measured between 4000-400 cm^{-1} wave numbers with KBr disks, quantatively prepared by 1/150 (sample/KBr) ratio Carbon fibers are high strength (HS) carbon fibers C320.000A (CA)(Sigri Carbon, Meitingen, Germany) containing 320 000 single filaments in a roving.Grafted carbon fibers are analysed by Fourier Transform InfrarRed reflectance Spectrorometer (Perkin elmer with an ATR atachement of spectrum one Universal ATR-with diamond and ZnSe).

A Shimadzu 160 A, that have deuterium and tungsten light sources which allow to measurements between 200-1100 nm. UV-Visible Recording spectrophotometer with 10 mm quartz cells for reference and sample solutions were used absorption measurements.

Cyclic voltametric (CV) measurements were performed by convential three-electrode system was used for electrochemical oxidation. The anode Pt or C-fiber and cathode was a Pt wire and the reference electrode is Ag wire and the ferrocene couple has a redox potential, E=0.35 V, vs this reference electrode. The electrochemical measurements were carried out using WENKING POS 73 potensiostat connected with a Kipp and Zonen X-Y recorder.

3.3 Conductivity Analysis

The electrical conductivity measurements were performed on Keithley 617 solid-state electrometer connected to a four-probe head with gold tips.

3.4 Scanning Electron Microscope

Samples were analyzed by scanning electron microscopy (SEM) using a Hitachi S-2700 scanning electron microscope (Nissei Sangyo GmbH, Rathingen, germany) ,which was connected to an energy dispersive X-ray micro analyzer (EDX) (Kevex type delta V,Foster City,CA,USA). The excitation energy was 10 keV at a beam current of 0.5 nA.

3.5 Polymerization Procedure

The polymerization was carried out in a pyrex vessel (100 ml) at 25 ^{o}C. The calculated quantity of CAN was dissolved in a known minimum volume of acetonitrile and the solution and the solution added to the desired amount of monomer solution in CAN. The mixture was stirred continuously during the polymerization process (20 min). A white powder formed almost instantaneously and in the reaction time. After filtration unreacted monomer is washed away with acetonitrile and solid was dried in a reduced vacuum

4. RESULTS AND DISCUSSION

4.1 Polymerization Yield

Yields of the polymers were calculated according to the following formula % Yield= [the amount of obtained polymer/ the amount of monomer (NVCz)]x100

4.1.1 Effect of Styrene

Table 4.1.1 Effect of styrene to yield

[NVCz]	[St]	[CAN]	%yield
0.2	-	$2.5.10^{-4}$	72
0.2	0.05	$2.5.10^{-4}$	80
0.2	0.1	$2.5.10^{-4}$	75
0.2	0.2	$2.5.10^{-4}$	67
0.2	1.0	$2.5.10^{-4}$	61

Effect of styrene was examined range between 0.05 and 1.0 M. As it can be seen from the table4.1.1 the yield of copolymerization increase at 0.05 M styrene concentration when compared with the homopolymerization of NVCz. By increasing concentration of styrene the yield starts to decrease slightly.

4.1.2 Effect of Acrylonitrile

Effect of was examined range between 0.05 and 1.0 M. As it can be seen from the table the yield of copolymerization increase at 0.05 M styrene concentration when compared with the homopolymerization of NVCz. By increasing concentration of styrene the yield starts to decrease slightly.

Table4.2.2 Effect of acrylonitrile to yield

[NVCz]	**[AN]**	**[CAN]**	**%yield**
0.2	-	$2.5.10^{-4}$	72
0.2	0.05	$2.5.10^{-4}$	75
0.2	0.1	$2.5.10^{-4}$	71
0.2	0.2	$2.5.10^{-4}$	63
0.2	1.0	$2.5.10^{-4}$	55

4.2 Conductivity Analysis

4.2.1. Conductivity Results For Electrochemical Oxidation

Table 4.2.1 Conductivity values for PNVCz,P[NVCz-co-St], P[NVCz-co-AN] after electrochemical oxidation which is prepared at different $[St]_0/[NVCz]_0$ or $[AN]_0/[NVCz]_0$ monomer ratios.

Ratio of $([St]_0/[NVCz]_0$ or $[AN]_0/[NVCz]_0)$	**Conductivity (S/cm^{-1})**
PNVCz	6.10^{-4} S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=0.5$	$4.5.10^{-4}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=1$	$3.2.10^{-4}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=2$	2.10^{-4} S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=5$	5.10^{-5} S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=0.5$	$3.1.10^{-4}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=1$	$1.8.10^{-4}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=2$	7.10^{-5} S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=5$	2.10^{-5} S/cm^{-1}

0.0040g/4 ml of homopolymer of PNVCz, P[NVCz-co-St], P[NVCz-co-AN] copolymers were dissolved in CH_2Cl_2 and 0.05 M TEAP is used as supporting electrode,and anode and cathode electrodes were stainless steel. A constant potential is applied a green dark polymer was coated on anode for all polymers.Obtained polymers were skin off from the electrode (free standing film) for conductivity measurements. Fig 4.2.1. shows conductivity , $[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ ratio relationship for electrochemical oxidation. It can be seen that with

increasing amount of St or AN in the copolymers conductivity decrease which is due to decreasing conjugation. Also oxidized homo polymer of PNVCz has conductivity of 6.10^{-4} S/cm which is higher than the copolymers. All these results are similar to current density results which is obtained from Cyclic voltammetry the current density is higher for the homopolymer of PNVCz and decrease in the case of P[NVCz-co-St] and P[NVCz-co-AN] so both obtained results from conductivity and the cyclic voltammetry supporting each other and also indicating the introduction of vinyl monomer in structure.

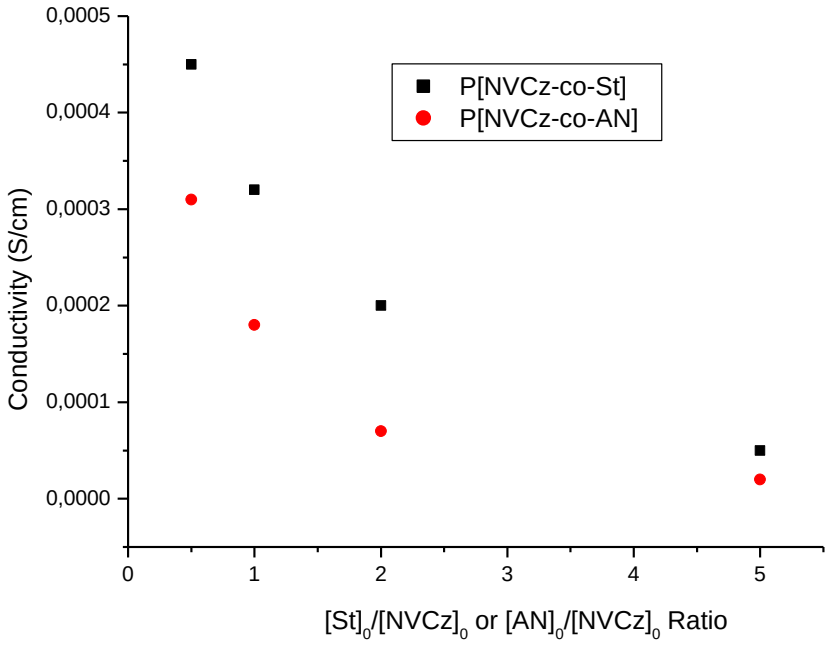

Figure4.2.1 Conductivity-$[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ Graph for electrochemical oxidation

4.2.2 Conductivity Results For Chemical Oxidation

For chemical oxidation, previously obtained polymers (0.01g/10 ml) dissolved in DMF and 0.01 M of CAN was added to solution until the dark green polymers were obtained.Obtained polymers were preapered as pellet and used for conductivity measurements. Fig 4.2.2 shows conductivity , $[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ ratio relationship for chemical oxidation. It can be seen that with increasing amount of St or AN in the copolymers conductivity decrease which is due to decreasing conjugation. Also oxidized homo polymer of PNVCz has conductivity of 10^{-5} S/cm^{-1} which is higher than the copolymers. All these results are similar to current density

results which is obtained from Cyclic voltammetry the current density is higher for the homopolymer of PNVCz and decrease in the case of P[NVCz-co-St] and P[NVCz-co-AN] so both obtained results from conductivity and the cyclic voltammetry supporting each other and also indicating the introduction of vinyl monomer in structure. Chemical and electrochemical oxidation of the polymers are achieved for characterization and also for obtaining electronically conductive polymers also electrochemical oxidation of the polymers leads the coating of stainless steel and this copolymer modified electrodes can be used for biosensor applications a similar method is used for the coating of the stainless steel by NVCz acrylamide copolymers by our group and electrochemical response of the copolymer modified electrode to dopamine was successfull(20)

Table 4.2.2: Conductivity values for PNVCz,P[NVCz-co-St], P[NVCz-co-AN] after chemical oxidation which is prepared at different $[St]_0/[NVCz]_0$ or $[AN]_0/[NVCz]_0$ monomer ratios.

Ratio of $([St_0]/[NVCz]_0$ or $[AN]_0/[NVCz]_0)$	**Conductivity (S/cm^{-1})**
PNVCz	$\mathbf{10^{-5}}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=0.5$	$\mathbf{8.10^{-6}}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=1$	$\mathbf{4.9.10^{-6}}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=2$	$\mathbf{1.2.10^{-6}}$ S/cm^{-1}
P[NVCz-co-St] $([St]_0/[NVCz]_0)=5$	$\mathbf{10^{-7}}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=0.5$	$\mathbf{7.10^{-6}}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=1$	$\mathbf{3.10^{-6}}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=2$	$\mathbf{8.10^{-7}}$ S/cm^{-1}
P[NVCz-co-AN] $([AN]_0/[NVCz]_0)=5$	$\mathbf{6.10^{-7}}$ S/cm^{-1}

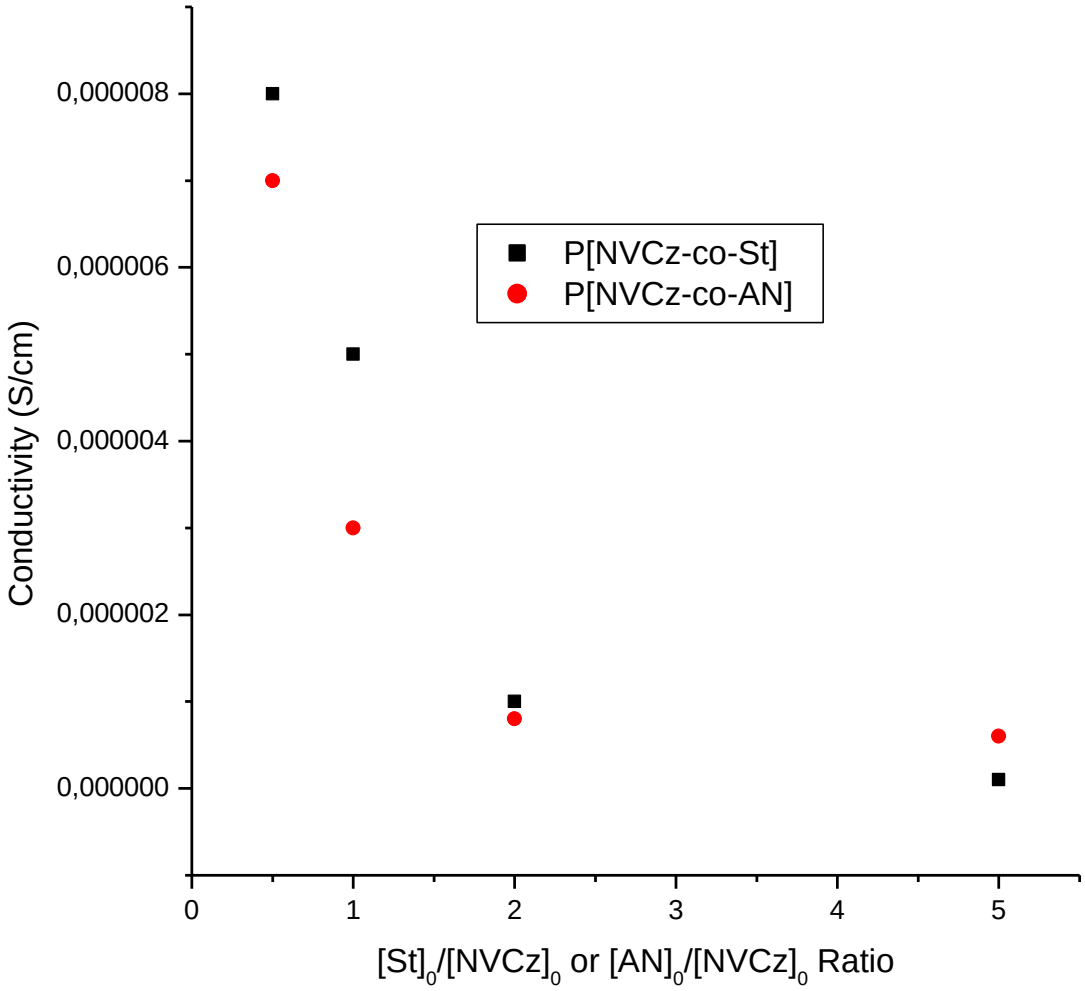

Figure 4.2.2: Conductivity- $[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ Graph for chemical oxidation

4.3 Cyclovoltametric Results

4.3.1 Cyclovoltametric Results On Pt

0.0040g homopolymer of PNVCz and P[NVCz-co-St], P[NVCz-co-AN] copolymers were dissolved in 4 ml of CH_2Cl_2 and 0.05 M TEAP is used as supporting electrode. Anode and cathode electrodes were Pt wire. All polymers were oxidized again by using a single potential scan at 20 mV s^{-1}. Figure (4.3.1-4.1.3) shows the the cyclic voltammograms corressponding to the potentiodynamic electrooxidation(and electrochemical coating) of PNVCz,P[NVCz-co-St],P[NVCz-co-AN] respectively.

Application of potential between 0-1.3 V vs Ag induces the development of a redox system corresponding to the doping/undoping process of the growing film. The

current density values were extracted from CVs during the doping and undoping process of the polymeric film.

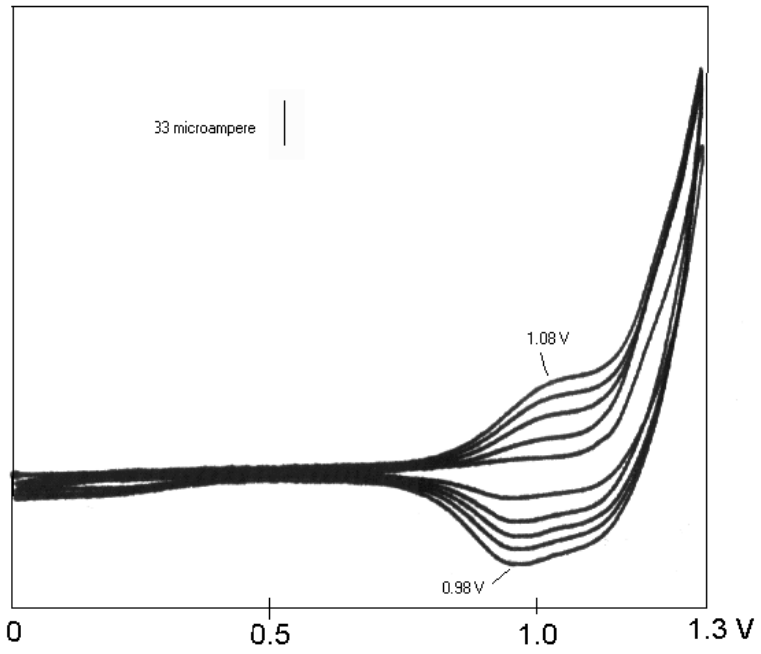

Figure4.3.1 Electrochemical oxidation of PNVCz in 0.05 M TEAP supporting electrolyte by CV on Pt between 0-1.3 V at 20 mV s^{-1} first5 cycle

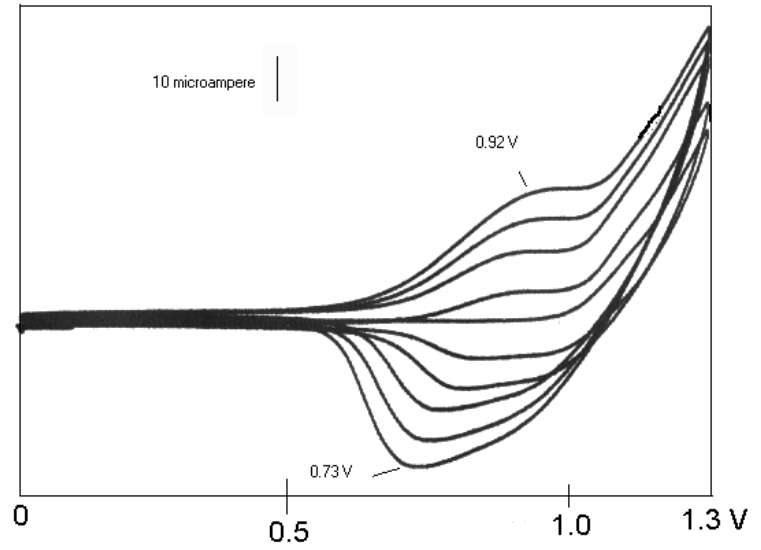

Figure4.3.2 Electrochemical oxidation of P[NVCz-co-St] in 0.05 M TEAP supporting electrolyte by CV on Pt between 0-1.3 V at 20 mV s^{-1} first 5 cycle

Figure 4.3.4 and figure4.3.5 shows the relationship between the scan number and current density and scan rate current density of homo and copolymers it can be seen that current density of copolymers are lower than the homopolymer of PNVCz which

is due to decreasing conjugation also the current density of P[NVCz-co- St] is higher than the P[NVCz-co-AN] copolymer this is because of conjugation of the aromatic benzene ring present in the styrene.

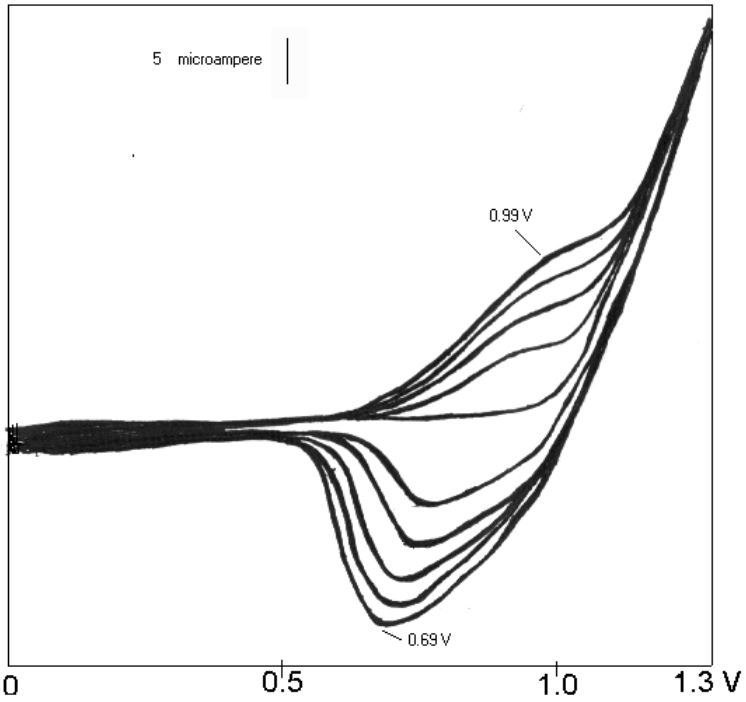

Figure4.3.3 Electrochemical oxidation of P[NVCz-co-AN] in 0.05 M TEAP supporting electrolyte by CV on Pt between 0-1.3 V at 20 mV s^{-1} first 5 cycle

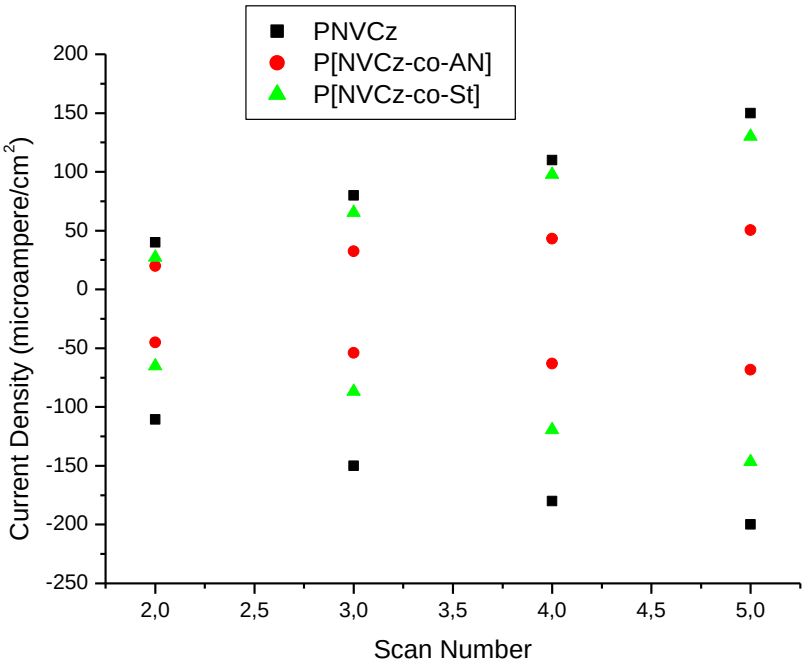

Figure 4.3.4 Current Density Graph -Scan Number (between 0-1.3 V at 20 mV s^{-1} scan rate on Pt electrode)

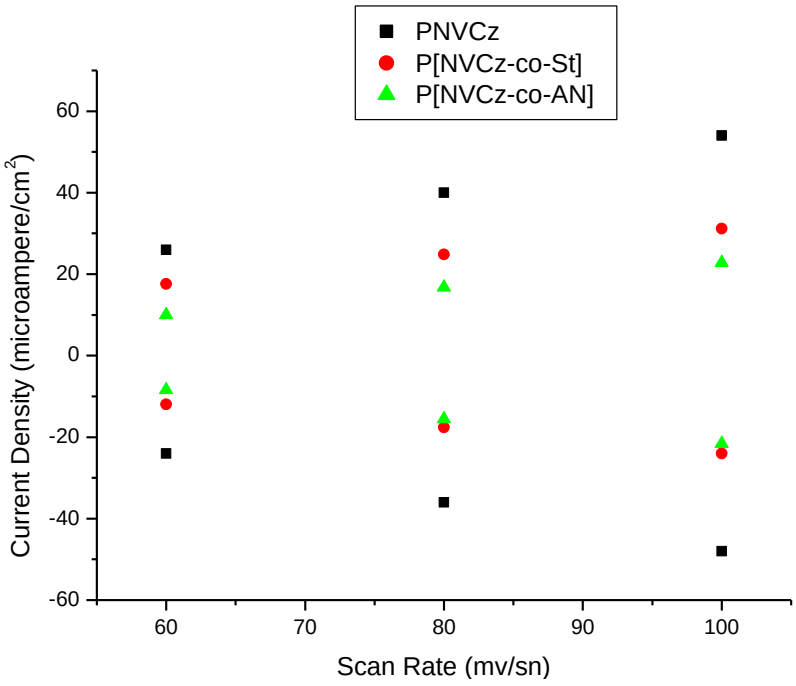

Figure 4.3.5: Current Density Graph -Scan Rate (between 0-1.2 V and 60-100 mV s^{-1} scan rate on Pt electrode)

4.3.2 Cyclovoltametric Results on C-Fiber

0.0040g homopolymer of PNVCz and P[NVCz-co-St], P[NVCz-co-AN] copolymers were dissolved in 4 ml of CH_2Cl_2 and 0.05 M TEAP is used as supporting electrode. Anode was carbon fiber electrode and cathode was Pt wire. All polymers were oxidized again by using a single potential scan at 20 mV s^{-1}.Figure(4.3.6-4.3.8) shows the the cyclic voltammograms corressponding to the potentiodynamic electrooxidation(and electrochemical coating) of PNVCz,P[NVCz-co-St],P[NVCz-co-AN] respectively. Application of potential between 0-1.3 V vs Ag induces the development of a redox system corresponding to the doping/undoping process of the growing film. The current density values were extracted from CVs during the doping and undoping process of the polymeric film.

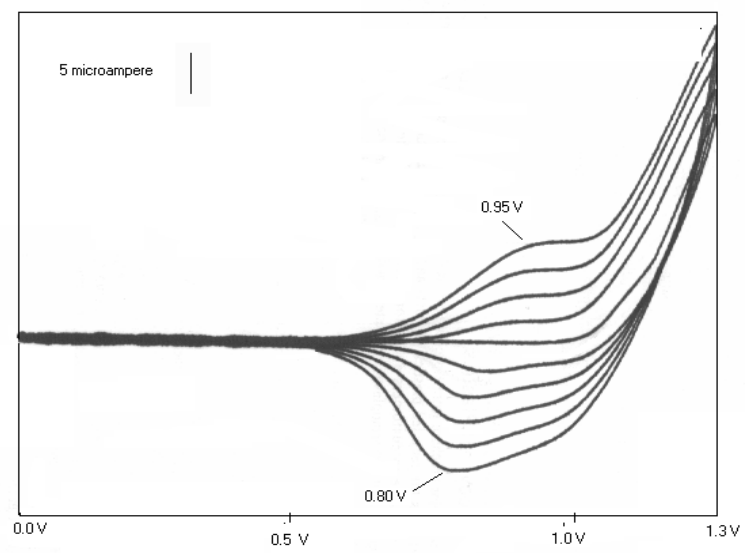

Figure4.3.6 Electrochemical oxidation of PNVCz in 0.05 M TEAP supporting electrolyte by CV on carbon fiber between 0-1.3 V at 20 mV s^{-1} first 5 cycle

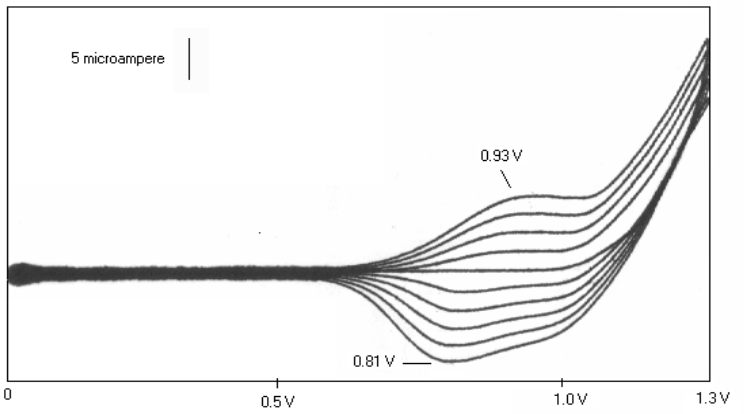

Figure4.3.7 Electrochemical oxidation of P[NVCz-co-St] in 0.05 M TEAP supporting electrolyte by CV on carbon fiber between 0-1.3 V at 20 mV s^{-1} first 5 cycle

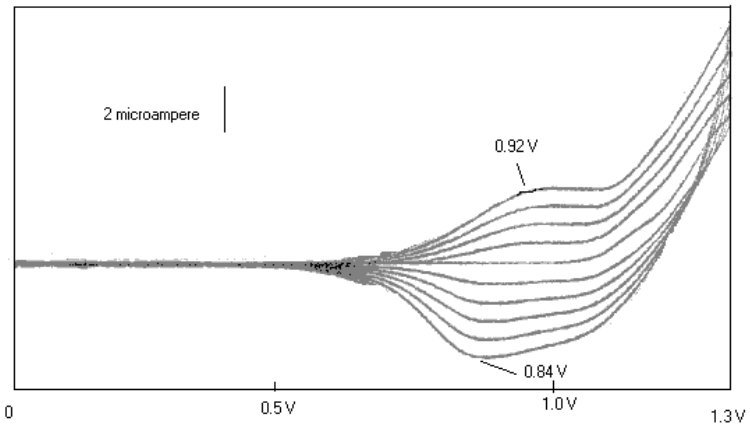

Figure4.3.8 Electrochemical oxidation of P[NVCz-co-AN] in 0.05 M TEAP supporting electrolyte by CV on carbon fiber between 0-1.3 V at 20 mV s^{-1} first 5 cycle

Figure 4.3.9 and 4.3.10. shows the relationship between the scan number and scan rate and current density of homo and copolymers it can be seen that current density of copolymers are lower than the homopolymer of PNVCz which is due to decrasing conjugation also the current density of P[NVCz-co-St] is higher than the P[NVCz-co-AN] copolymer this is because of conjugation of the aromatic benzene ring present in the styrene. AppendixB(1-3) shows CV of the PNVCz,P[NVCz-co-St], P[NVCz-co-AN] in monomer free solution .

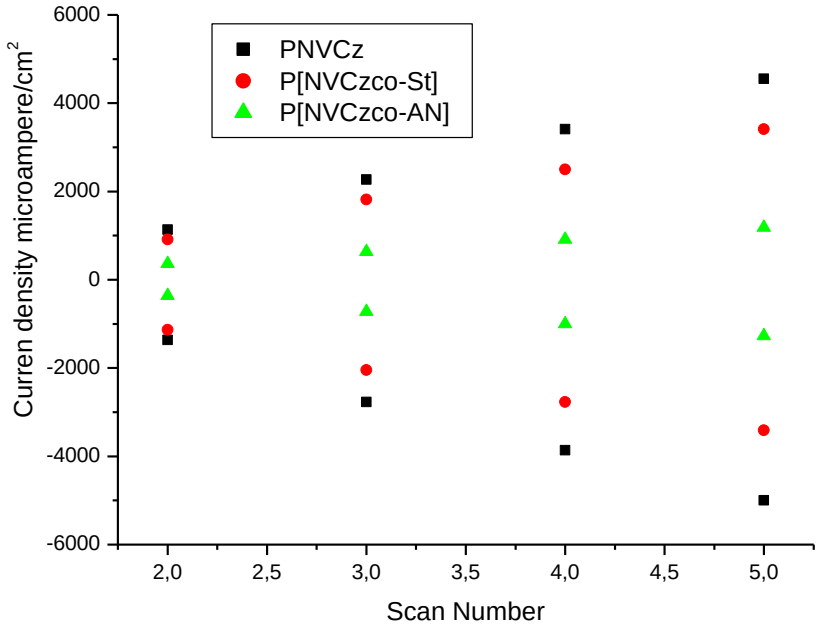

Figure 4.3.9: Current Density Graph- Scan Number Graph (between 0-1.3 V at 20 mV s^{-1} scan rate on carbon fiber)

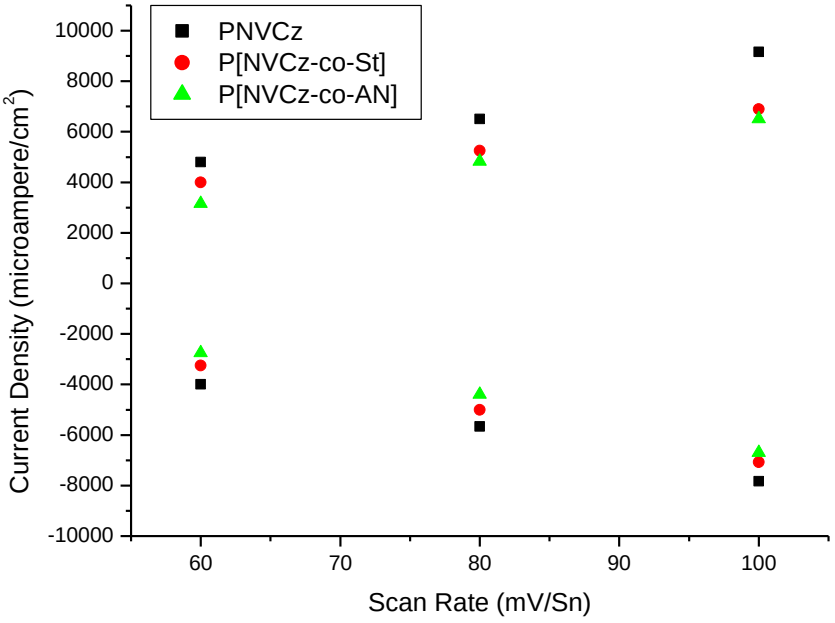

Figure4.3.10: Current Density Graph -Scan Rate (between 0-1.2 V and 60-100 mV s^{-1} on carbon fiber)

4.4 UV-Visible Results

In order to probe the electronic structure of the obtained polymers are oxidized from 0.0040 g/4 ml solution and 0.05 MCH_2Cl_2 as electrolyte by using ITO coated glassy electrode as working , Pt as a counter, Ag wire as a reference electrode.Polymer films were coated on ITO by potentiostatically at 1.3 V for 90 sn. After the film rinsed with the monomer free electrolyte and 1.0 V applied for 1 min for all polymers then UV-Visible results are taken. UV spectra of doped and undoped PNVCz is given on figure 4.4.1. Table(4.4) shows the UV-Visible spectra of PNVCz, P[NVCz-co-St], P[NVCz-co-AN] the maximum absoption peak at 715, 400,323 nm have been understood to arise from the bonding level to antibonding state of a polaron, a polaronBonding level to to antibonding state of polaron, a polaron bonding level to the Π^* conduction band and a valance bond to conduction band respectively. Also it can seen that absorbance of copolymer peaks decrease when compared with the homopolymer of PNVCz this due to more thicker films form in the case of PNVCz when compared with the copolymers because the the conductivity of PNVCz is higher the more thicker films formed for PNVCz and absorbance is higher as result of this. Figure (4.4.2-4.4.3) shows the $[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ ratio versus current densities obtained from CV and the absorbance obtained from the UV it can be seen that both the current density and absorbance obtained decrease with increasing ratio of $[St]_0/[NVCz]_0$ and $[AN]_0/[NVCz]_0$ so results obtained from UV and the CV corresponds with each other also it fits with the solid state conductivity data's .

Table 4.4 Absorbance of polymers at 323,400,715 nm coated on ITO by applying 1.3 V constant potential

	323 nm	**400 nm**	**715 nm**
PNVCz	1.25	1.0	0.65
P[NVCz-co-St] ($[St]_0/[NVCz]_0$=1)	0.95	0.60	0.48
P[NVCz-co-St] ([St]o/$[NVCz]_0$=5)	0.8	0.34	0.28
P[NVCz-co-AN] ($[AN]_0/[NVCz]_0$=1)	1.10	0.72	0.30
P[NVCz-co-AN]($[AN]_0/[NVCz]_0$=5)	0.93	0.40	0.18

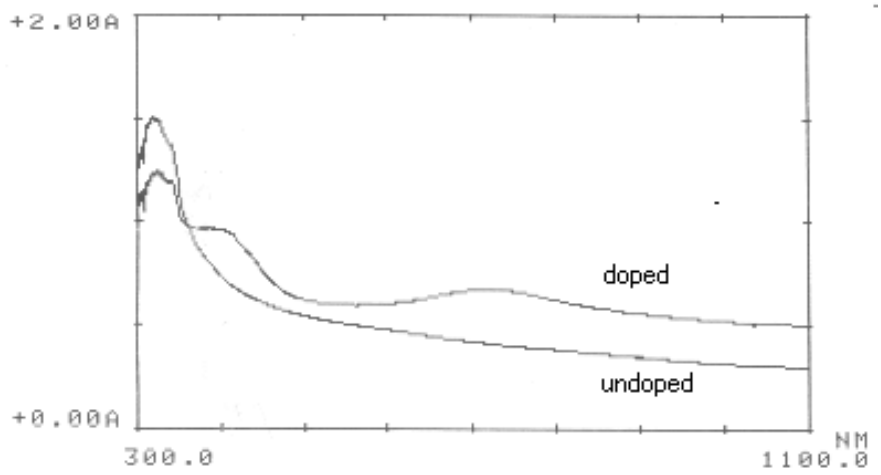

Figure 4.4.1. UV spectra of doped and undoped PNVCz coated on ITO by applying 1.3 V constant Potential

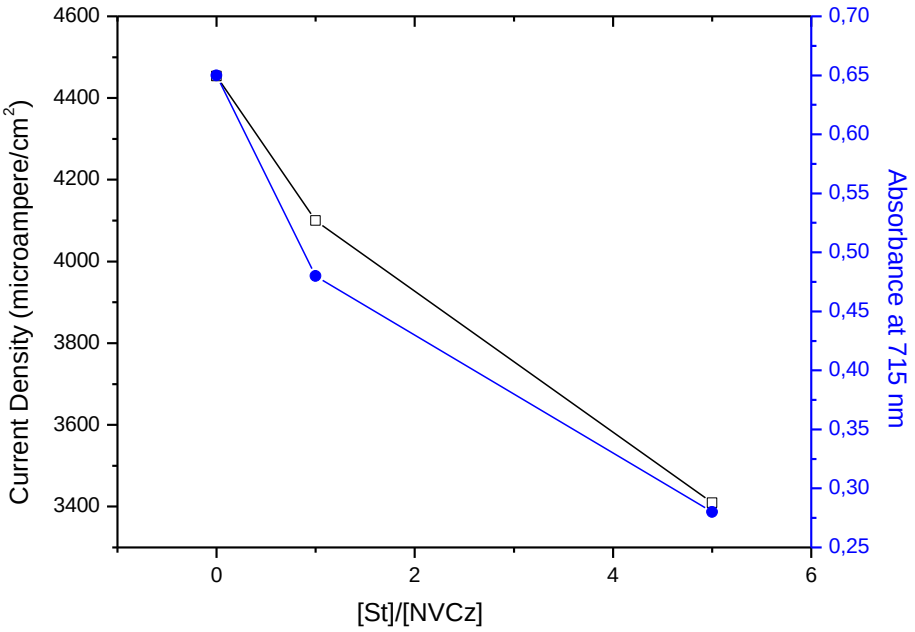

Figure4.4.2 Current Density,Absorbance - $[St]_0/[NVCz]_0$ ratio Graph (current density results obtained from CV at 5. cycle and Absorbance values obtained from UV results of polymer coated ITO)

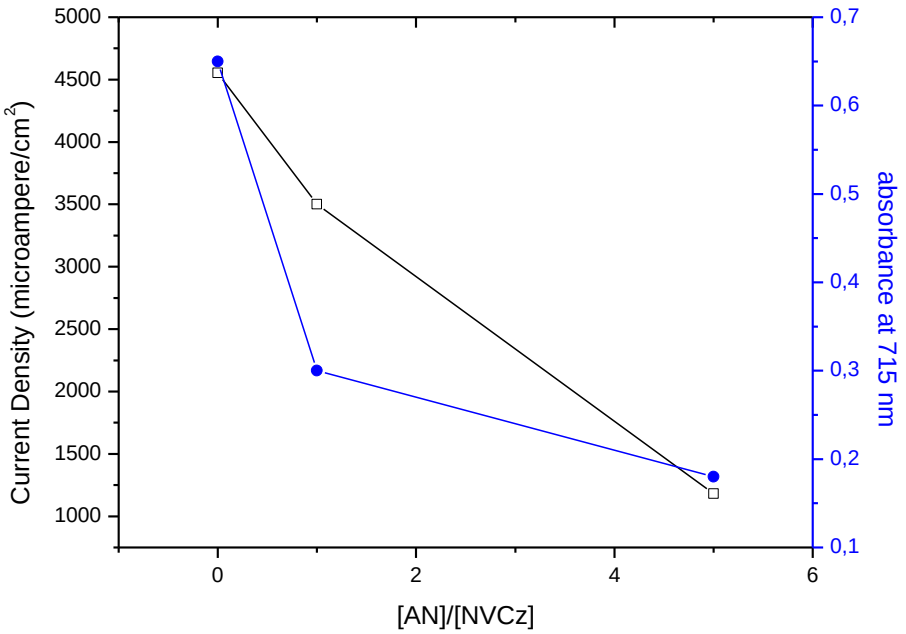

Figure 4.4.3 Current Density,Absorbance- $[AN]_0/[NVCz]_0$ ratio Graph (current density results obtained from CV at 5. cycle and Absorbance values obtained from UV results of polymer coated ITO)

4.5 Surface Morphology

The SEM micrographs show that the coatings exhibit linear and homogenous growth on whole fiber. Also the morphology of the grafted polymer change with cycle number at high cycle numbers the polymer growth starts to show a nucleation growth on certain sites. Figure(4.5.1-4.5.3) shows the SEM of PNVCz, P[NVCz-co-St], P[NVCz-co-AN] coated with 3 cycle respectively. It can be seen that copolymers show more homogenous and linear growth compared with the homopolymer of PNVCz. Little nucleation sides appear on the morphology of P[NVCz-co-St] when compared with the PNVCz also there is almost no nucleation sides in the structure of P[NVCz-co-AN]. Figure 4.5.4 shows the graph of thickness of electrografted carbon fiber and current densities obtained from CV and absorbance values obtained from polymer coated ITO. It can be seen that there is a decrease in the thickness with the decrease in the current density and absorbance these results also support the solid state conductivity results.

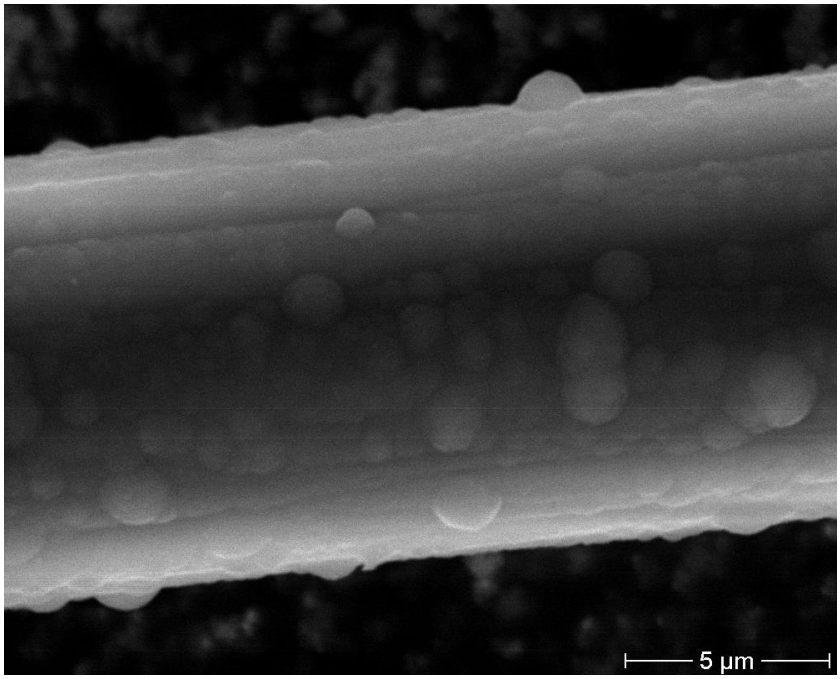

Figure4.5.1 SEM picture of PNVCz coated on carbon fiber by CV with 3 cycle

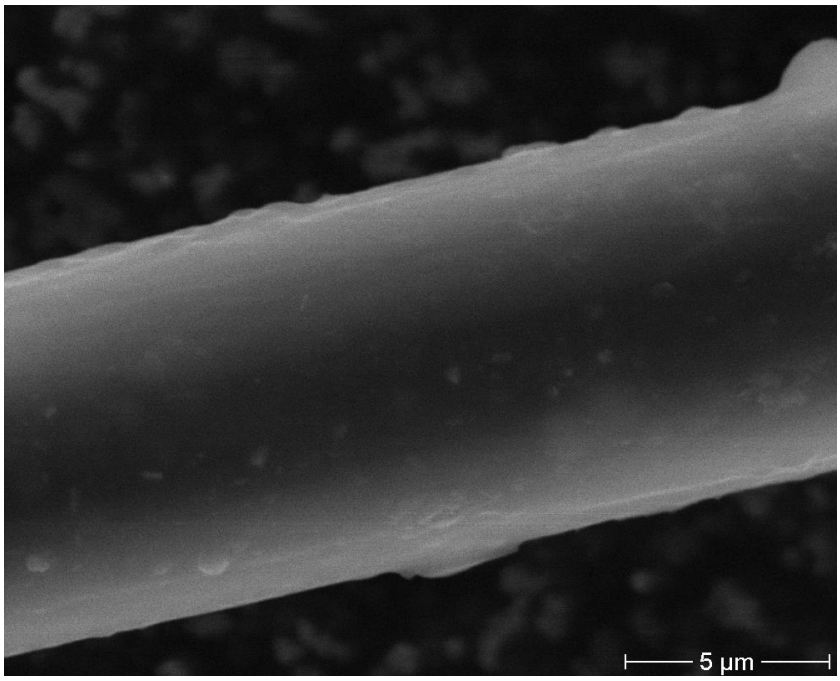

Figure4.5.2 SEM picture of P[NVCz-co-St] coated on carbon fiber by CV with 3 cycle

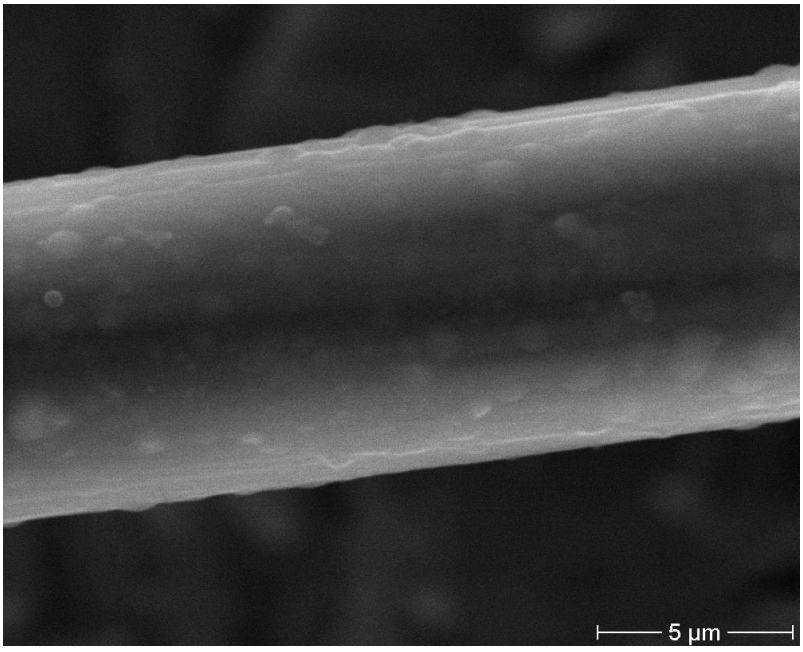

Figure4.5.3 SEM picture of P[NVCz-co-AN] coated on carbon fiber by CV with 3 cycle

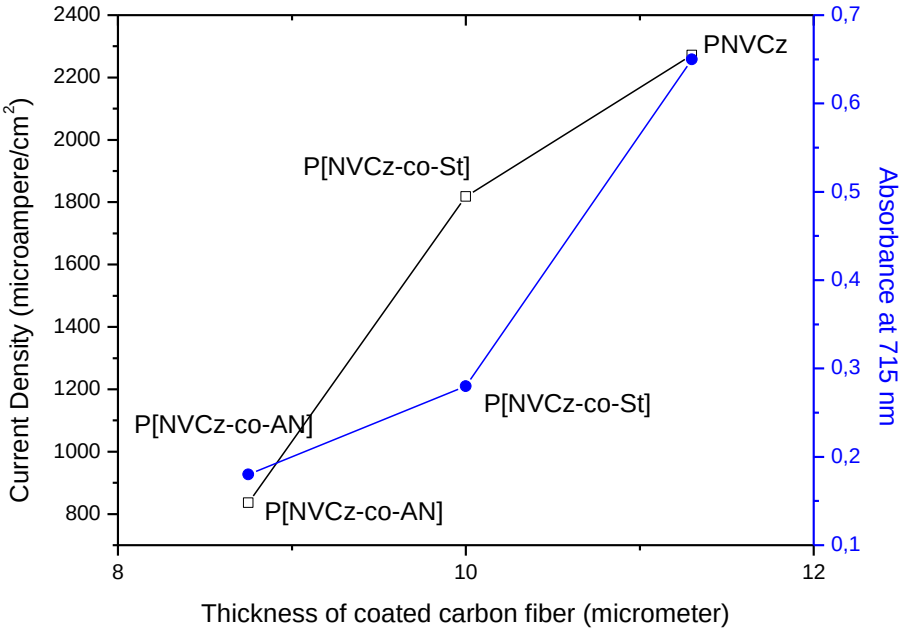

Figure4.5.4 Current Density and Absorbance -Thickness- Graphic (Thickness of electrografted carbon fiber by 3 cycle, Current density results are calculated from CV at 3. Cycle and absorbance results are obtained from ITO coated polymers)

4.6 FTIR Reflectance Spectra (ATR-FTIR)

FTIR reflectance spectra of electrografted P[NVCz-co-St] and P[NVCz-co-AN] are depicted in Fig 4.6.1. The peaks observed at 1636,1234 cm^{-1} are due to -C=C

streching of benzene rings present . The peak at 1348 cm^{-1} is due the C-N bond of carbazole ring. The peak at 882 cm^{-1} are attritubed to the out-of-plane deformation of C-H bond in benzene rings. The peak at 2332 cm^{-1} appears both on in the spectrum of P[NVCz-co-AN] P[NVCz-co-St] this could be due to the CN streching and C-H but it appears to be more clearly in the spectrum of P[NVCz-co-AN] because of CN group in addition to C-H which is present only in P[NVCz-co-AN]. Also the peak at 1459 cm^{-1} appear only in P(NVCz-An). The peak at 1114 cm^{-1} appears only in the spectrum of P[NVCz-co-St] this is due to chracteristic peak of benzene C-H for styrene.

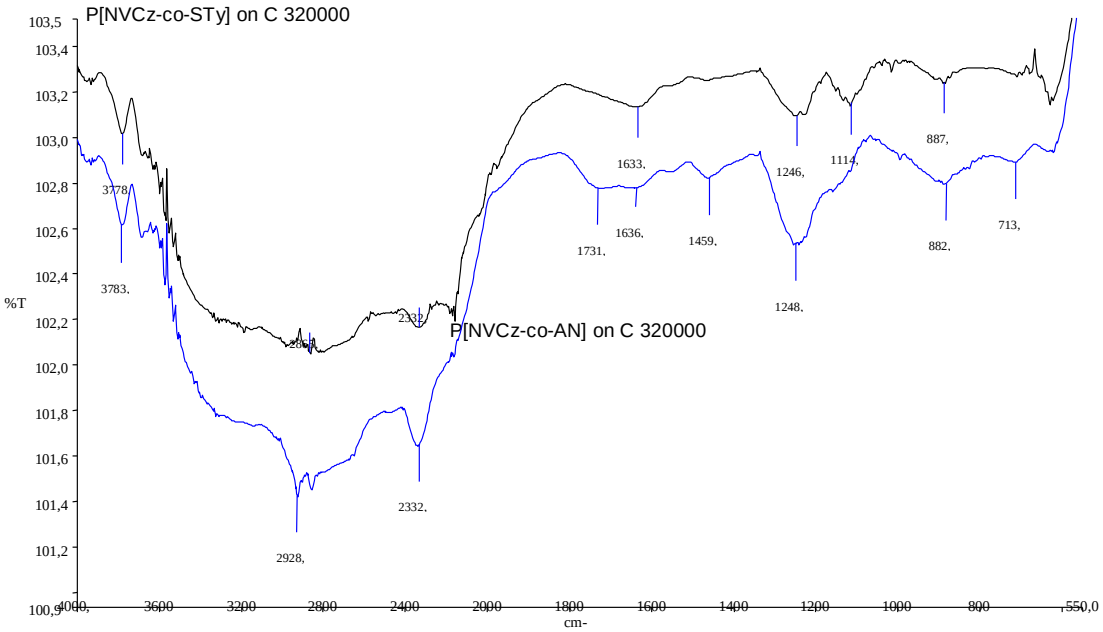

Figure 4.6.1 FTIR-ATR of P[NVCz-co-St] and P[NVCz-co-AN] on carbon fiber coated with CV by 3 cycle

4.7 FTIR Results

NVCz can be polymerized through the vinyl groups if it was provided that monomer concentration is five times greater than oxidant concentration(12), under these conditions resulting polymer (PNVCz) was white color.In the FTIR spectrum of white PNVCz, the intensity of vinyl bands at 916 and 850 cm^{-1} decreased compared to monomer's and there's no decrease in the intensity of C-H out of plane deformation (21) . These results showed that polymerization takes place through vinyl group.

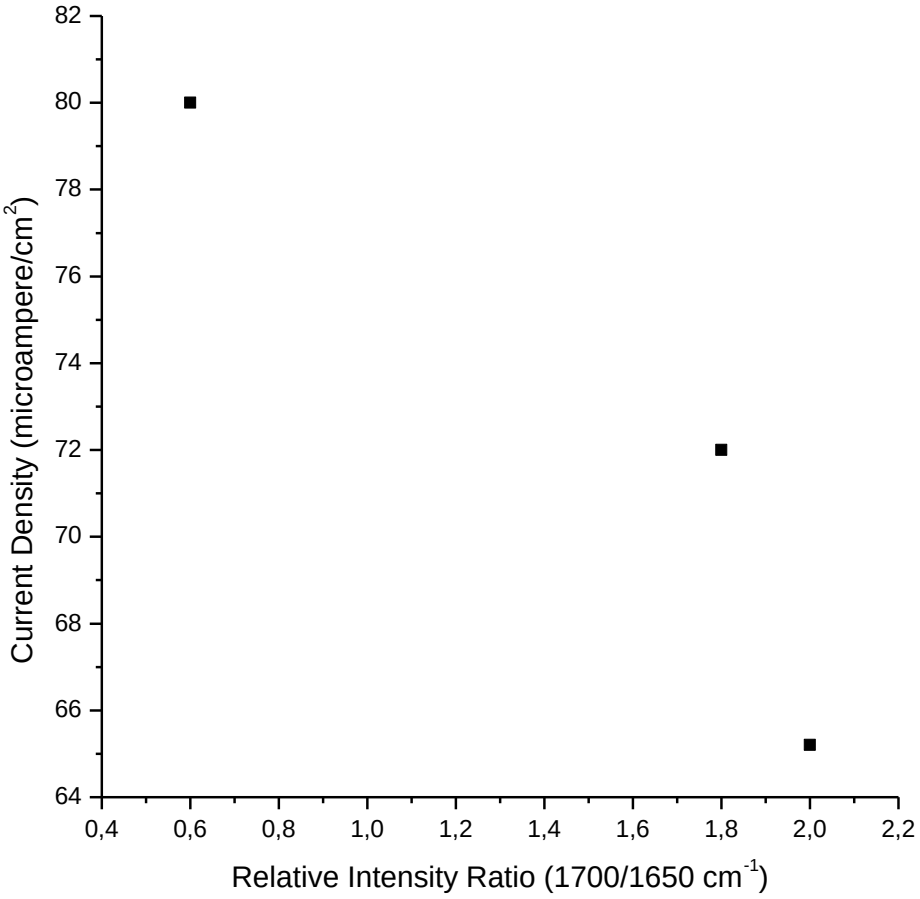

Figure 4.7.1 Current Density with changing ratio of $[St]_0/[NVCz]_o$-Relative Intensity Ratio (1700/1650 cm^{-1})- graph

The ratio % transmission intensity of the peaks in the PNVCz and P[NVCz-co-St] and P[NVCz-co-AN] changes with increasing styrene or acrylonitrile in the copolymer. The relative intensity ratio of bands 1700/1650 cm^{-1} (which corresponds to –C=C streching) is 0.66 for PNVCz , in the case of P[NVCz-co-St] with changing the amount of styrene during chemical polymerization the ratio of the peaks becomes 1.8 and 2.0 for St/NVCz=1,St/NVCz=5 respectively. In the homopolymer of PNVCz the relative intensity ratio of bands 725/750 cm^{-1} (C-H out of plane bending) 1.33 in the case of P[NVCZ-co-AN] with changing amount of Acrylonitrile during chemical polymerization the ratio of the peaks changes 1.5 and 1.6 for $[AN]_0/[NVCz]_0$=1 and $[AN]_0/[NVCz]_0$=5 respectively..

Figure 4.7.1 and Figure 4.7.2 shows with changing ratio of peaks observed the current density of the polymers change .This is due to increase of $[St]_0/[NVCz]_0$ or $[AN]_0/[NVCz]_0$, (changing ratio of the peaks observed), the current density decrease because of the observed polymers are less conductive compared with the homopolymer of PNVCz. Figure 4.7.3 shows the FTIR spectrum of PNVCz,P[NVCz-co-St] ($[NVCz]_0/[St]_0$=1/5), P[NVCz-coAN],$[NVCz]_0/[AN]_0$=1/5).

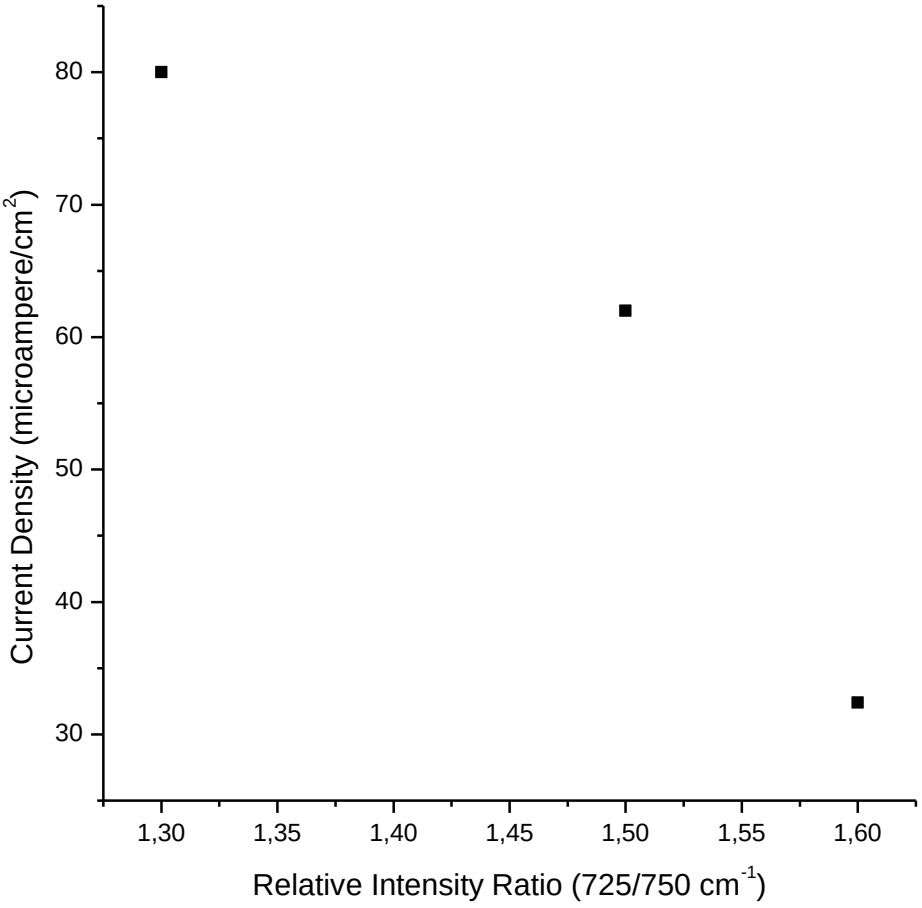

Figure 4.7.2 Current Density with changing ratio of $[AN]_0/[NVCz]_o$-Relative Intensity Ratio (725/750 cm^{-1})-

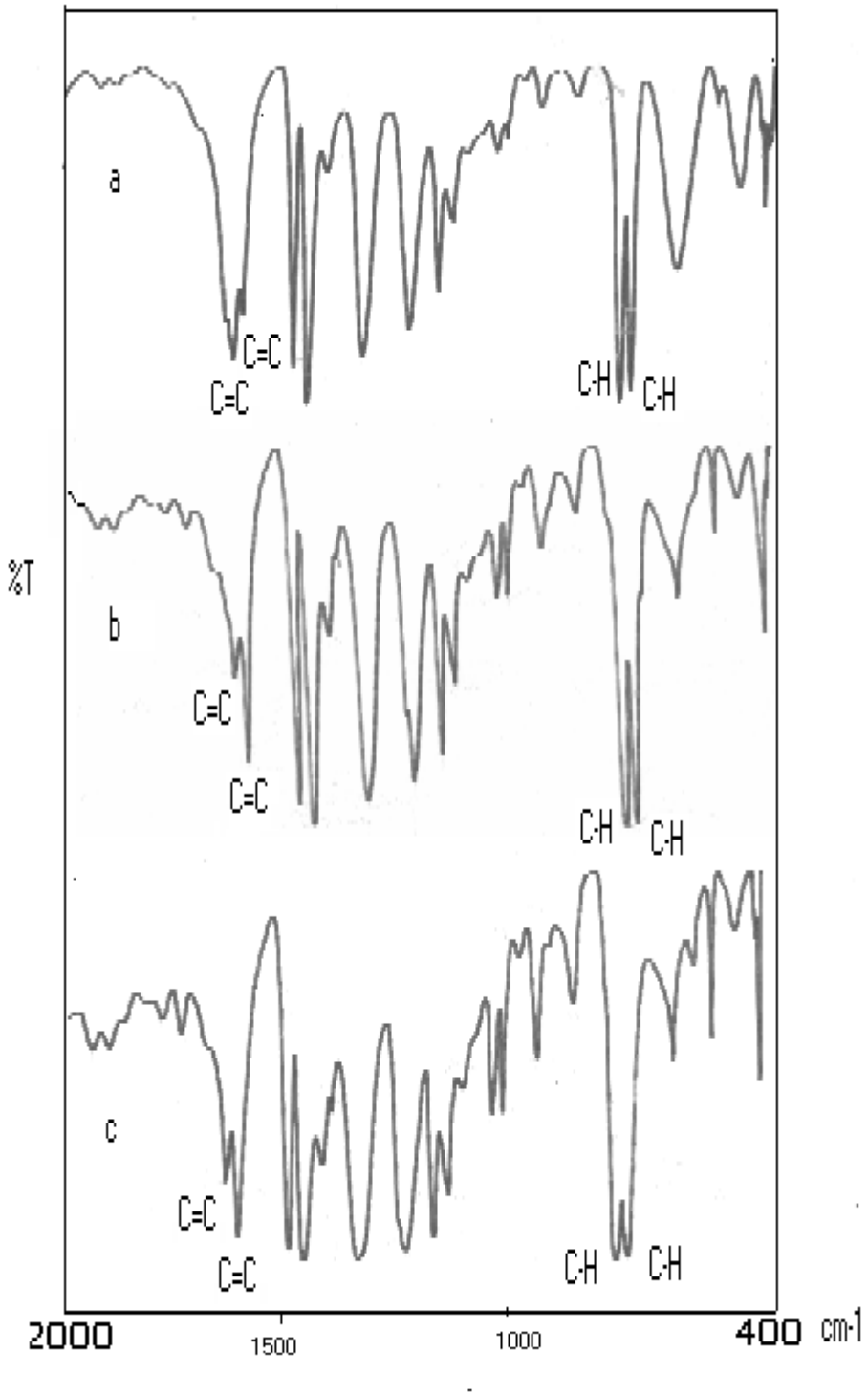

Figure 4.7.3 FTIR Spectrum of a) PNVCz b) P[NVCz-co-St] c) P[NVCz-co-AN]

4.8 PROPOSED MECHANISM

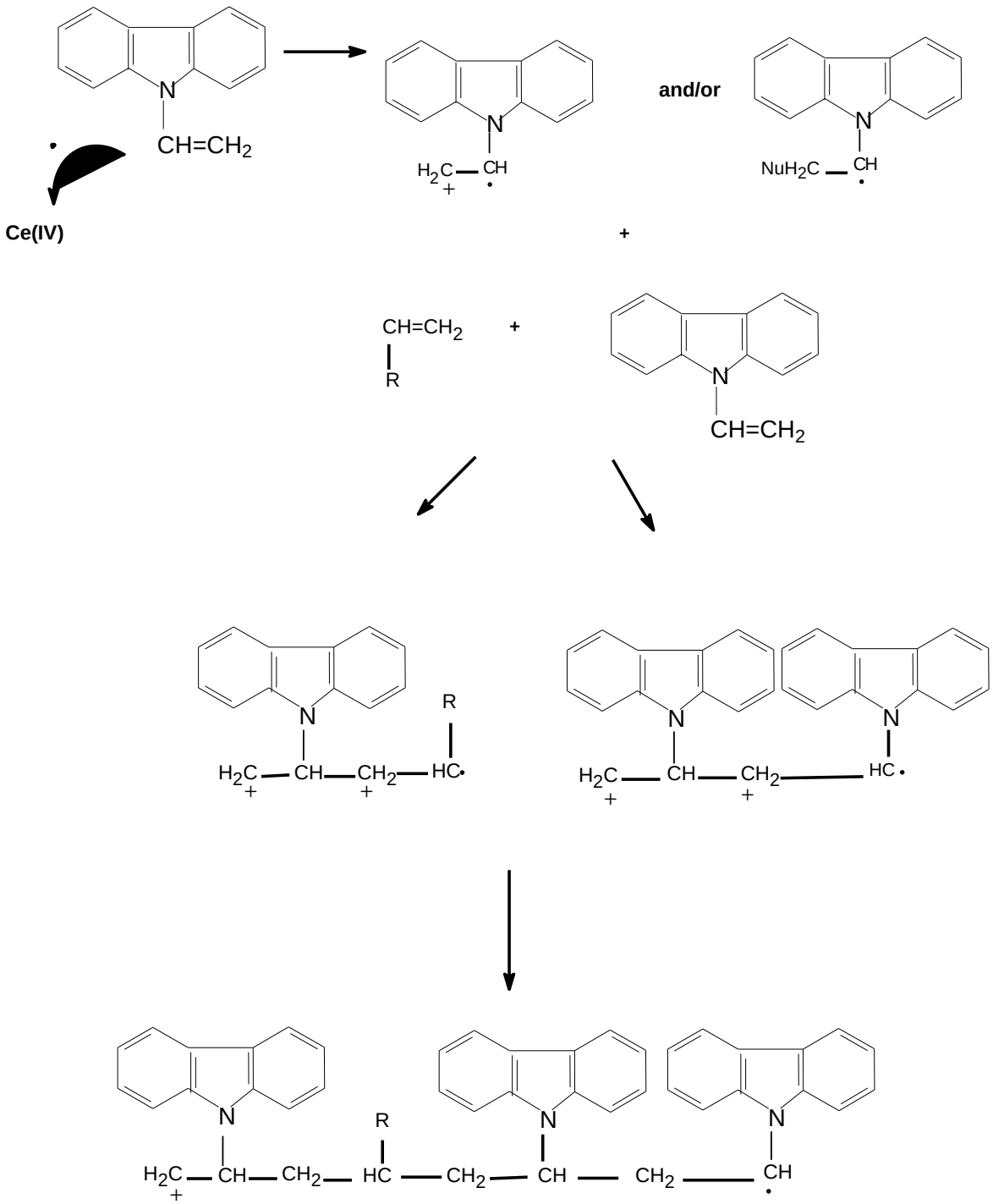

Figure 4.8.1 Chemical Polymerization Mechanism

For chemical polymerization we proposed a similar Mechanism with the literature as it has been mentioned if the oxidant concentration is five times lower tan the monomer concentration a white polymer is formed for NVCz indicating that polymerization proceeds through the vinyl groups(22). Also Tazuke has suggested

that the initiation process for the polymerization of NVCz catalyzed by oxidizing metal salts is mostly like to be of an electron transfer type(11) so we suggest a mechanism that an electron transfer from NVCz to CAN , results radical cation which can be reacted by a nucleophile (NO_3^-) forming a radical by the addition reaction of this active radical cation or radical with NVCZ or St,AN and polymerization growth is obtained. Figure 4.8.1 shows the tentavive mechanism proposed for chemical polymerization.

For electrochemical and chemical oxidation of this polymer we suggest a similar mechanism to copolymerization Carbazole-Acrylamid (18-23) electrochemical and chemical oxidation of this polymer can be achieved mostly takes place from 3-position which is most reactive by a electron transfer yields to radical cation and coupling of this radical cations cause the elimination of H^+ and forms a conjugated system which is conductive.Figure 4.8.2 and Figure 4.8.3 shows the tentavive mechanism proposed for chemical and electrochemical oxidation respectively.

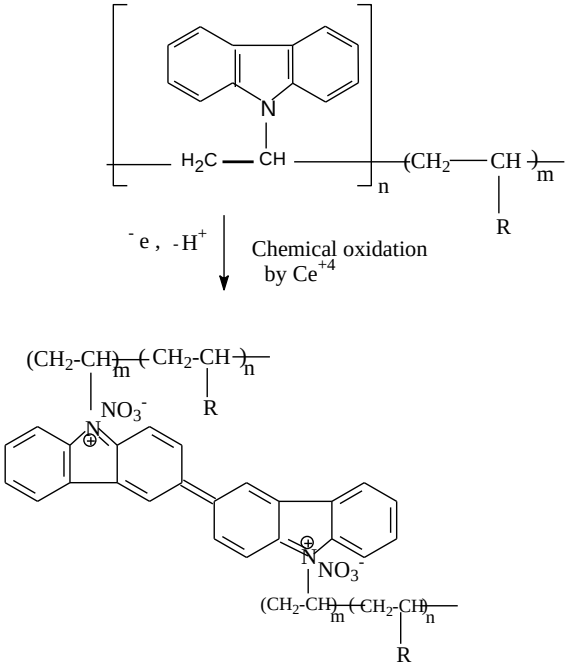

Figure 4.8.2 Mechanism for Chemical Oxidation

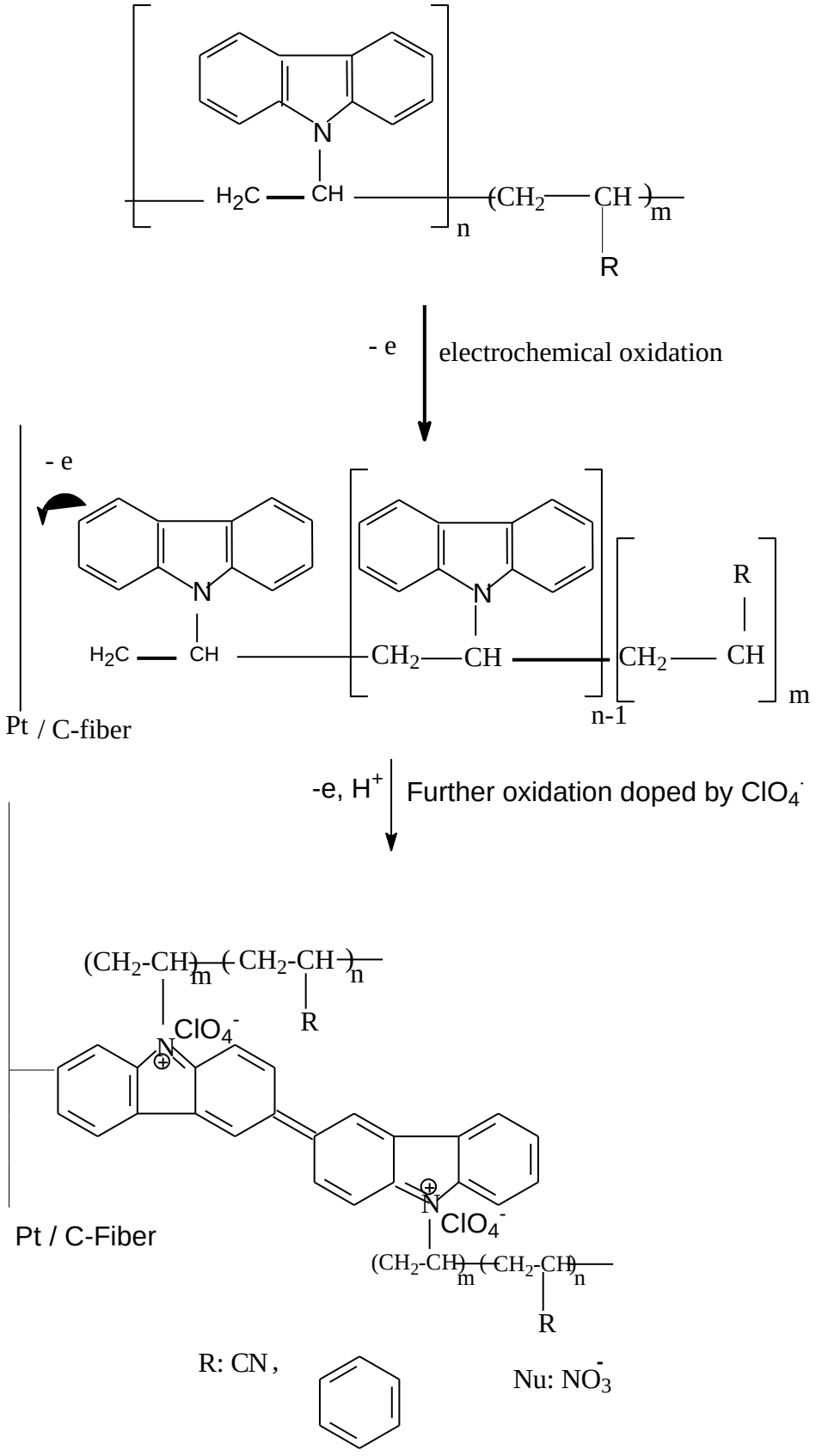

Figure 4.8.3 Mechanism for Electrochemical Oxidation

4.9 ELECTROCHEMICAL Response to Dopamine

Obtained Polymers PNVCz, P[NVCz-co-St], P(NVCz-co-AN] were coated on platium and carbon fiber electrodes by dissolving 0.0040g homopolymer of PNVCz and P[NVCz-co-St], P[NVCz-co-AN] copolymers in 4 ml of CH_2Cl_2 and 0.05 M TEAP is used as supporting electrode. Anode was Pt wire and cathode was Pt wire or carbon fiber. All polymers were oxidized again by application of potential between 0-1.3 V vs Ag scan rate at 20 mV s^{-1} by 2 cycle. These polymer modified electrodes was than taken to pH 7 buffer solution contaning 0.0085g/5ml dopamine. Polymer modified electrodes were tested for their response to dopamine by applying potential between –0.5-1.0 V vs Ag at 500 mV sn^{-1} scan rate. $\Delta E_p/2$ is determined for the polymer electrodes table(4.9.1) shows the $\Delta E_p/2$ for PNVCz, P[NVCz-co-St], P[NVCz-co-AN] on Pt and carbon fiber.

Table 4.9.1 $\Delta E_p/2$ values for Polymer coated Pt and carbon fiber in dopamine solution

	Pt	**Carbon Fiber**
PNVCz	310 mV	245 mV
P[NVCz-co-St] ([St]/[NVCz]$_0$=1)	300 mV	220 mV
P[NVCz-co-St] ([St]/[NVCz]=5)	280 mV	200 mV
P[NVCz-co-AN] ([AN]/[NVCz]=1)	220 mV	150 mV
P[NVCz-co-AN] ([AN]/[NVCz]=5)	185 mV	75 mV

All polymer electrodes show quasi reversibility to dopamine. It can be seen that $E_{1/2}$ of the copolymers are smaller than the homopolymer of PNVCz. Figure(4.9.1-4.9.2) shows the CV of P[NVCz-co-AN] on carbon fiber to dopamine. Also $\Delta E_p/2$ decrease on carbon fiber electrode for polymers when compared with the Pt electrode which is much convential for in-situ determination of Dopamine. CV of the polymers are given AppendixC(1-4)

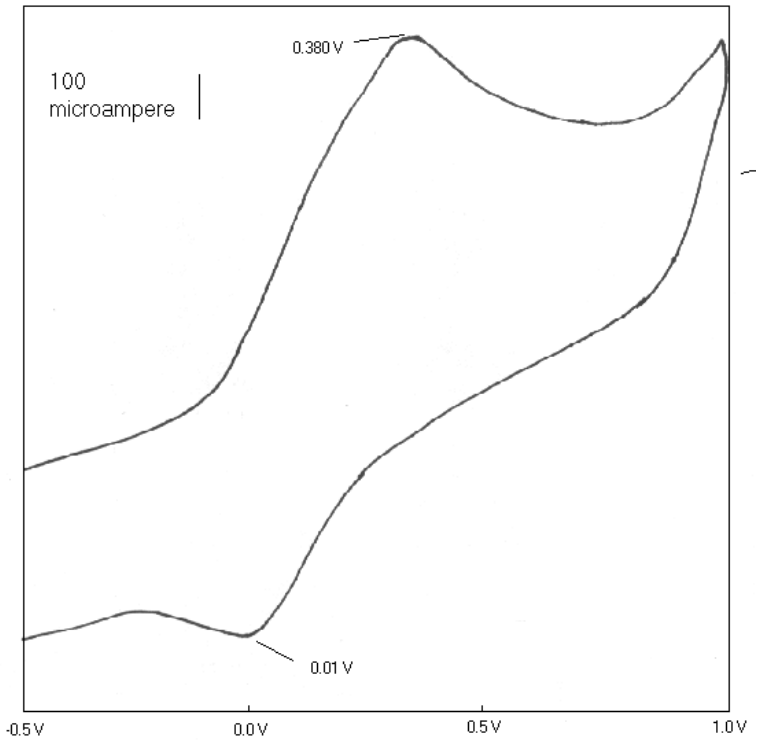

Figure 4.9.1: CV of P[NVCz-co-AN] on Pt in dopamine solution (0.0085 g/5 ml pH=7 buffer solution) between –0.5 V-1.0 V at 500 mV s^{-1} scan rate

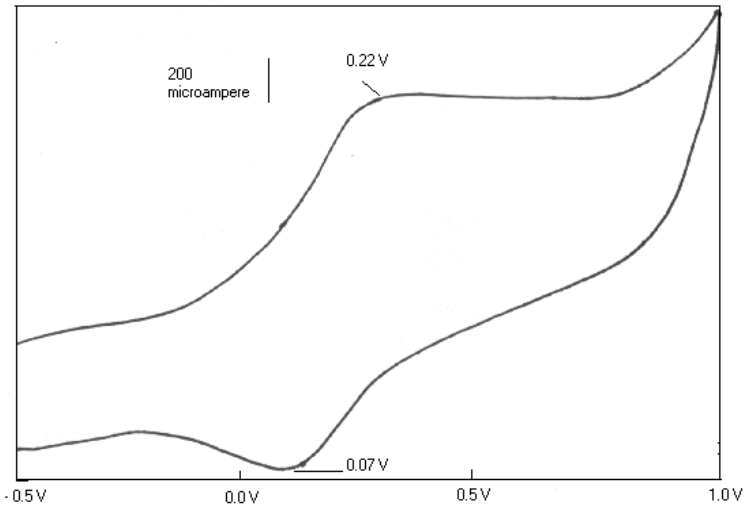

Figure 4.9.2: CV of P[NVCz-co-AN] on carbon fiber in dopamine solution (0.0085 g/5 ml buffer pH=7 solution) between –0.5 V-1.0 V at 500 mV s^{-1} scan rate

5. CONCLUSION

In this study copolymerization of N-Vinyl Carbazole with styrene and acrylonitrilewere achieved by using CAN as a oxidazin agent in the suitable ratio so that the polymerization leads from vinyl group.

Electrochemical coating random copolymers of P[NVCz-co-St], P[NVCz-co-AN] which is obtained by free radical polymerization by Ce(IV) ,on Pt and carbon fiber was probably achieved first time for this type of vinyl-conjugated copolymer.The main reason for this was to obtain flexible material comparing to NVCz ,and presence of both monomers and their electropolymerization gives Homopolymer of NVCz probably reacting mainly through aromatic ring at high potentials and inclusion of vinyl monomer will not be realized .This system also gives a better control of pre-copolymer which can be easily synthesized and its properties can be tailor made before electrocoating .

In this study we examined the electrochemical oxidation of PNVCz, P[NVCz-co-St),P[NVCz-co-AN] on carbon fiber microelectrode which are characterize on Pt in the previous study. Also we examined the of dopamine behaviour of Pt and carbonfiber electrodes modified by PNVCz, P[NVCz-co-St], P[NVCz-co-AN]. The results shown that polymer coated carbon fiber electrode is much better than polymer coated Pt electrode also it is clear that polymer modified carbon fiber microelectrode may be used for in-situ determination of dopamine in brain with the future investigation.

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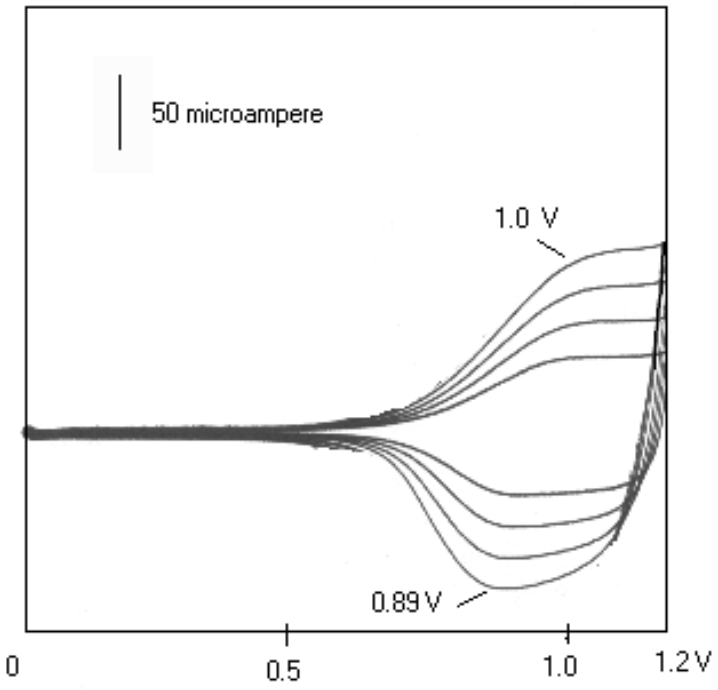
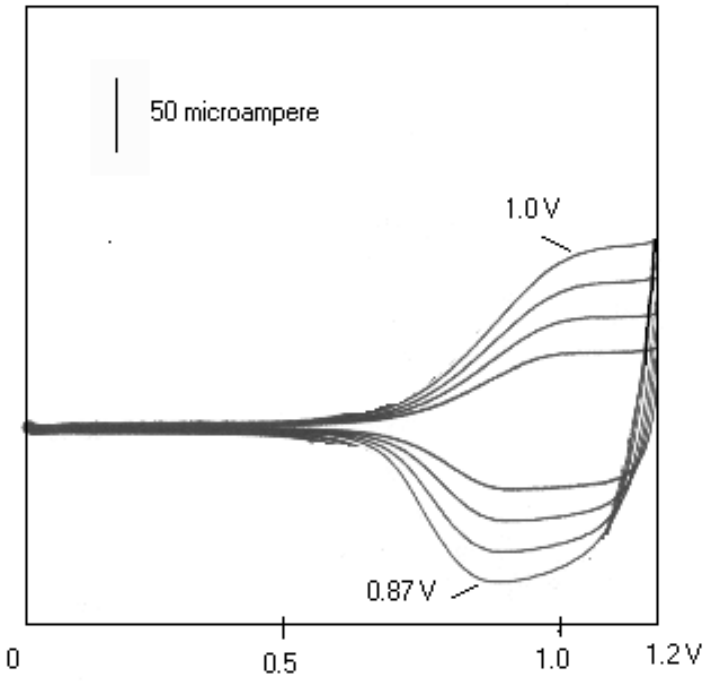
APPENDIX A

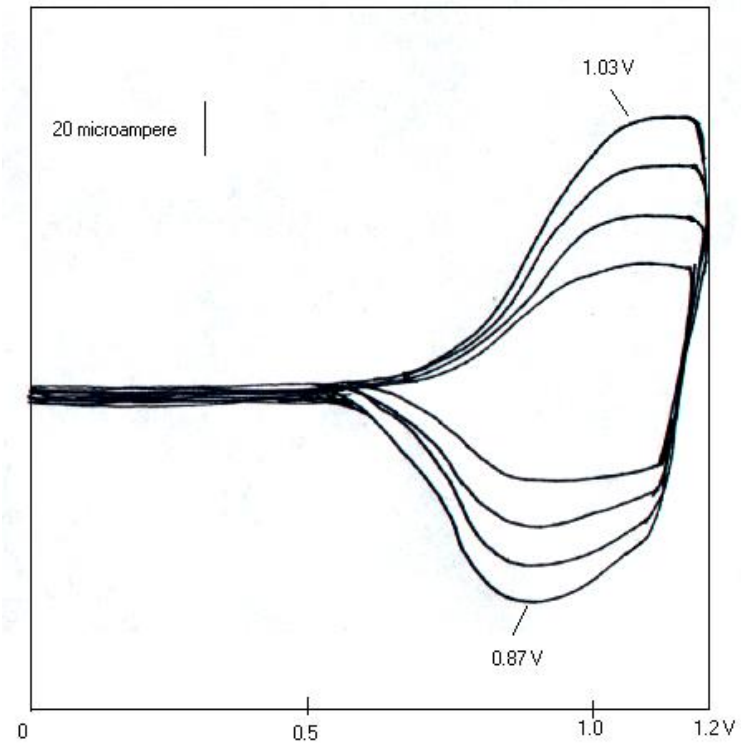
A1 CV of PNVCz in monomer free solution on Pt between 0-1.2 V and 60-120 mV s^{-1}



A2 CV of P[NVCz-co-St] in monomer free solution on Pt between 0-1.2 V and 60-120 mV s^{-1}

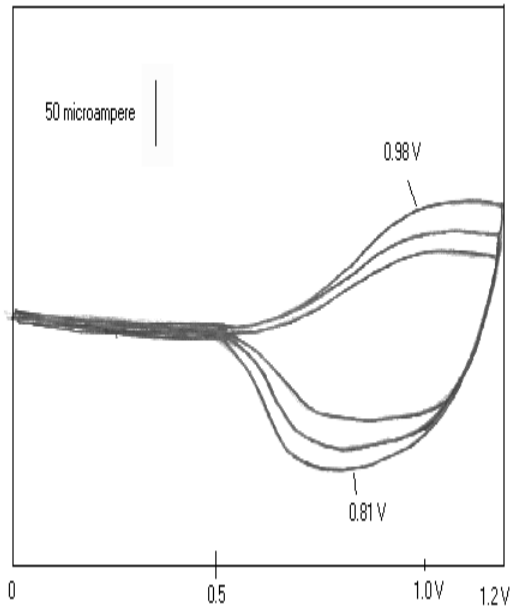


A3 CV of P[NVCz-co-AN] in monomer free solution on Pt between 0-1.2 V and 60-120 mV s^{-1}

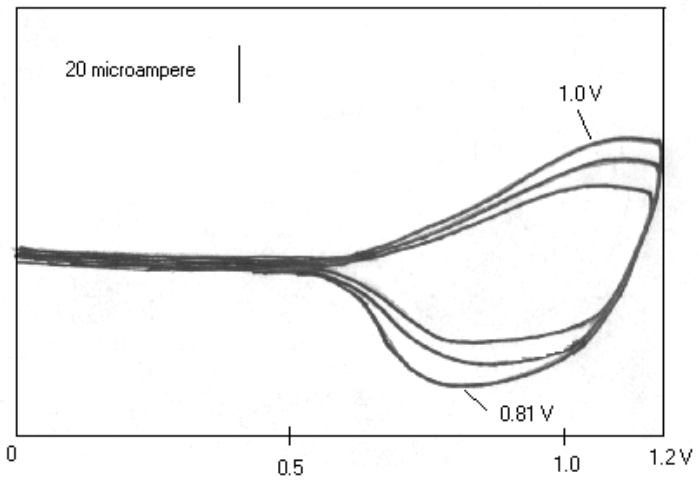


APPENDIX B

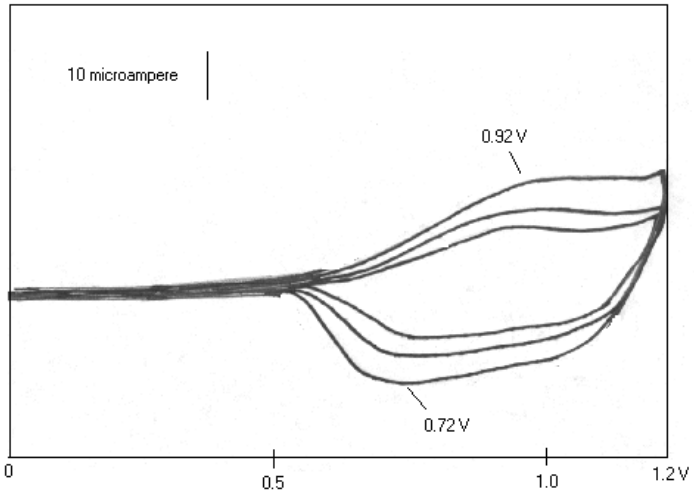
B1 CV of PNVCz in monomer free solution on carbon fiber between 0-1.2 V and 60-100 mV s^{-1}



B2 CV of P[NVCz-co-St] in monomer free solution on carbon fiber between 0-1.2 V and 60-100 mV **B4** CV of PNVCz in monomer free solution on carbon fiber between 0-1.2 V and 60-100 mV s^{-1}

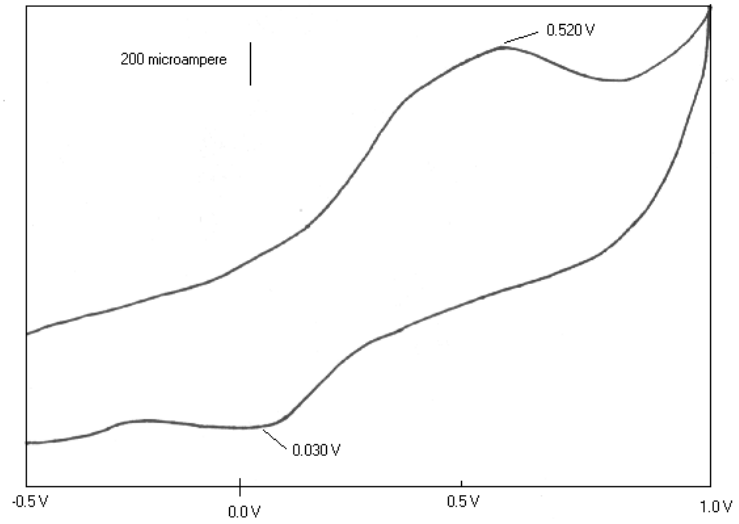


B3 CV of P[NVCz-co-AN] in monomer free solution on carbon fiber between 0-1.2 V and 60-100 mV s^{-1}

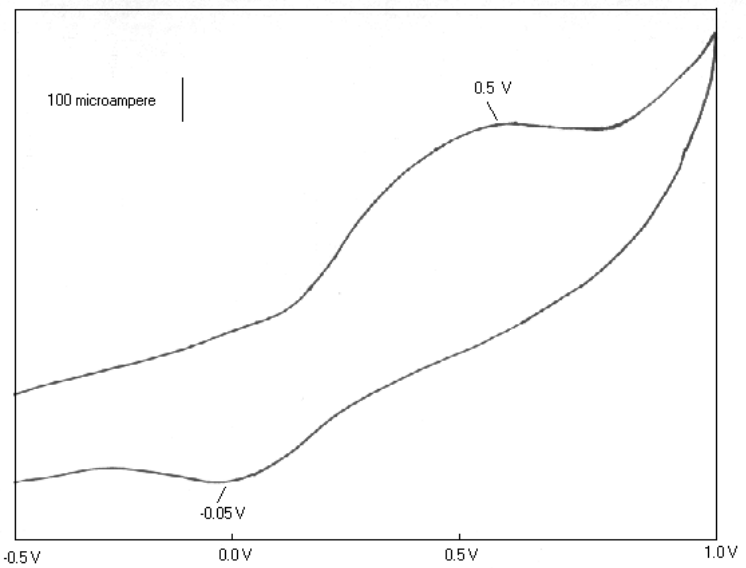


APPENDIX C1

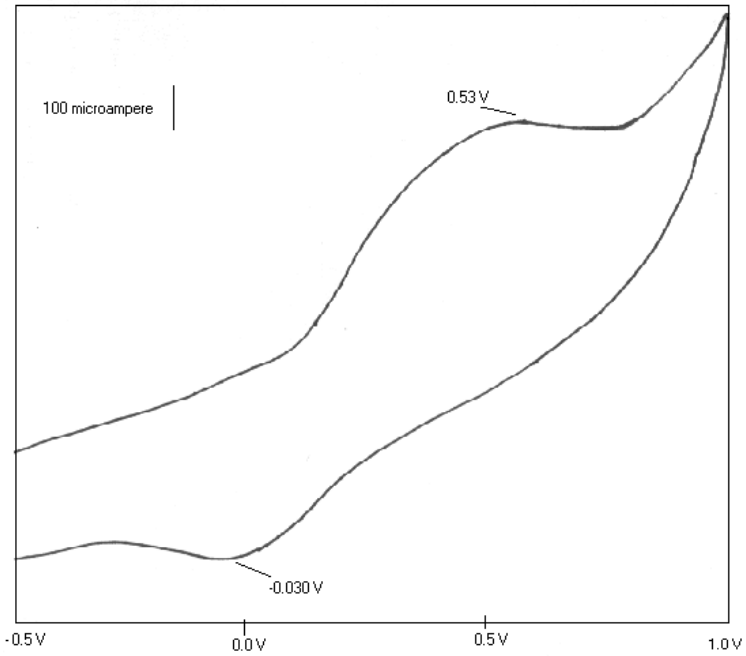
C1 CV of PNVCz coated Pt in dopamine solution (0.0085 g/5 ml in pH=7 buffer solution) between –0.5 V-1.0 V at 500 mV s^{-1}



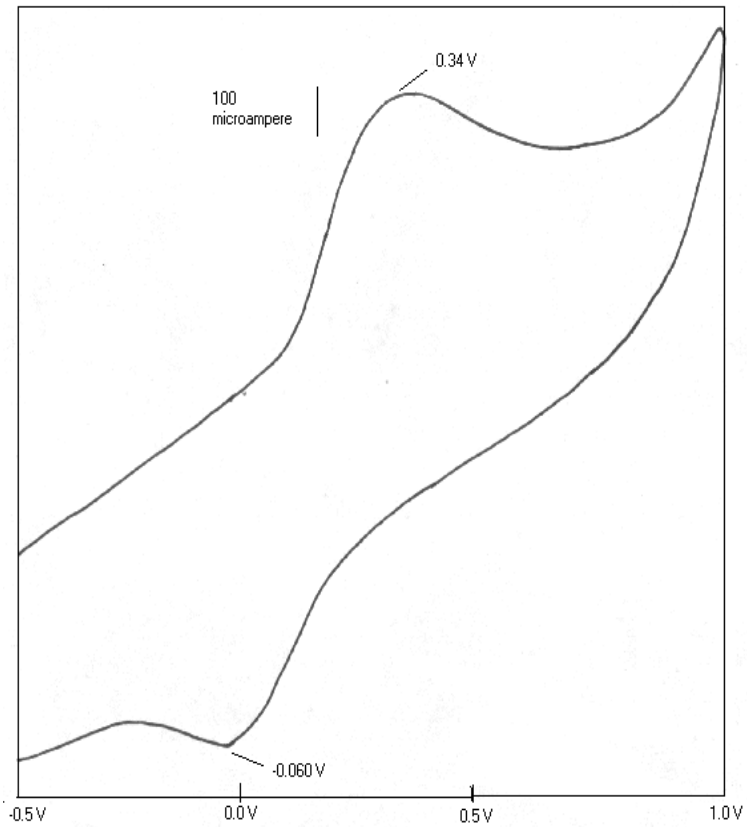
C2 CV of PNVCz coated carbon fiber in dopamine solution (0.0085 g/5 ml pH=7 buffer solution) between –0.5 V-1.0 V at 500 mV s^{-1}



C3 CV of P[NVCz-co-St] coated on Pt in dopamine solution (0.0085 g/5 ml pH=7 buffer solution) between –0.5 V-1.0 V at 500 mV s^{-1} scan rate



C4 CV of P[NVCz-co-St] on carbon fiber in dopamine solution (0.0085 g/5 ml pH=7 buffer solution) between –0.5 V-1.0 V at 500 mV s^{-1}scan rate



BIOGRAPHY

Yusuf Bardavit was born in Istanbul in 1978. He was entered to Istanbul Techical University, Department of Chemistry, in 1996, and was graduated in 2000.

He was registered as a M.Sc. candidate to the Institute of Science and Technology of Istanbul Techical University in 2000. He has been working as a research assistant in Physical Chemistry Department since 2001.