SUMMARY

Electrically conducting polymers made from heterocyclic monomers have been the subject of much research in recent years. Due to its interesting electrical and optoelectronic properties, chemical and electrochemical polymerizations of N-vinylcarbazole (NVCz), have been extensively studied. Also Polycarbazole is a conductive polymer but there is no much applications because of its brittle property. And Poly(N-ethylcarbazole) is investigated as a model compound with poly(N-vinylcarbazole).

Despite its long history, the mechanism of carbazole polymerization under oxidizing conditions is not well understood, because of the polymers are insoluble powders a and can not be characterized by conventional methods.

In this thesis, the chemical and electrochemical oxidation of carbazole and derivatives by the use of oxidants and metals with ethyl methyl ketone resin has been studied. Th effect of monomer, resin and metal ion concentration were investigated. Products were characterized by FT-IR, NMR, AAS, DSC, UV-Visible, elemental analyses, conductivity measurements.

A new class of totally soluble conducting Carbazole, Ethyl Carbazole and N-Vinyl Carbazole- Ketonic resin copolymers have been developed both chemically and electrochemically.

ÖZET

Polimerik malzemeleri metallerden ayıran temel özellik yalıtkan olmalarıdır. Bu özellik, örneğin ellektrik tellerini polimerle kaplayarak oluşabilecek kayıpları minuma indirme gibi birçok üstünlük sağlar. Ancak son yıllardai elektrik akımını iletebilen yeni bir organik polimer sınıfı geliştirildi. Asetilen, pirol, tiyofen, karbazol ve çeşitli benzen türevlerinedn sentezlenen ve "organik metaller" olarak da isimlendirilebilen bu polimerler korozyon önleyici kaplama olaraki pillerde ve kararlılıklarına bağlı olarak mikroelektronikte önemli bir yere sahiptir. Bu polimerler arasında karbazol ve türevleri son yıllarda yoğun bir şekilde incelenmeye alınmıştır.

Karbazol ve türevlerinin çözünme problemi nedeniyle bu güne kadar karakterizasyonunda oldukça zorlanılmıştır.

Bu tezde karbazol, etilcarbazol ve N-vinyl karbazolun etil metil-keton formaldehit reçinesi ile kimyasal ve elektokimyasal kopolimerizasyonu çeşitli metaller ve oksidantla polimerizasyonu çalışılmıştır. Elde edilen ürünler, FT-IR, NMR, AAS, DSC, UV-Visible , elementel analiz ve iletkenlik ölçümleri ile karakterize edilmiştir. Sonuç olarak ilk kez olarak tamamen çözünür ve iletken kopolimerler elde edilmiştir.

1.INTRODUCTON

Conducting polymers have novel electrical and optical properties that are potentially useful for applications in electroluminescence display, rechargeable batteries, electrochromic windows, chemical sensors, electromagnetic shielding and anti-electrostatic films.

However, these new materials are less adaptable to industrial processes, because of the solubility problem. Therefore to elaborate the solubility problem of such polymers is vey important.

Among the conducting polymers, Polycarbazole (PCz), Polyethylcarbazole (PECz), Poly (N-Vinylcarbazole) (PNVCz) have poor processing properties which need to be improved for practical application.

Recently years, one of the target in chemistry of electroactive polymers, has been the synthesis of soluble and processable materials. Water soluble, neutral polymers have been used as a medium for the polymerization of pyrrole to overcome the solubility, however products had very low conductivities.

In this work, a new polymerization route, proceeding by oxidative polymerization in the presence of resin with several metals is described. This method was first applied to pyrrole, but it is the first time for Carbazole and derivatives.

The advantage of this polymerization system is to obtain totally soluble polymers.

2.THEORY

2.1.General Definition of Polymers

Polymer is a large molecule built up by linking together of large number of simple chemical units. Monomers are small molecules that combine with each other to form polymer molecule.

If the polymer chain has one species of monomer it's called "homopolymer" or has two or more called "copolymer". Copolymers from two, three, four species of monomer are called bipolymers, terpolymers and quarter polymers.

Copolymers are subdivided into:

Random Polymer	...abbbaababaaab...	poly (A-ran-B)
Alternating Polymer	...ababababab...	poly (A-alt-B)
Periodic Polymer	...abbabbabbabba...	poly (A-per-B-per-B)
Block Polymer	...aaabbbaaabbb...	poly (A)-block-poly (B)
Segmented Polymer	.$(a)_n$-$(b)_m$-$(a)_p$-$(b)_q$...	
Gradient Polymer	$(a)_n$baaaababbaabba$(b)_m$	
Graft Polymer	...aaa...aaa...aaa b_m b_n	poly(A)-graft-poly(B)

It's possible to make a group of polymers due to their structural and functional differences.

- Natural Polymers
- Synthetic Polymers
- Elastomers

Natural polymers don't have much importance in industry as synthetic polymers because of their complex structures.

Elastomers are both natural and synthetic materials like rubber.

In 1929, Carothers suggested a classification of polymers into two groups as addition and condensation polymerization according to the mechanism of polymerization.

2.2.Classification of Polymerization Reactions

2.2.1. Addition Polymerization

Addition polymerization of unsaturated monomers lead to the formation of high molecular weight products by chain growth mechanism.

During chain-growth polymerization, high molecular weight polymer is formed early during polymerization and the polymerization yield or the percent of monomer converted to the polymer, gradually increases with time.

In the chain-growth reactions, the initiation is required to begin chain growth by means of a free radical initiator. This free radical R* quickly adds to monomer to obtain a monomeric radical. This new active monomer adds to another monomer and so on. This growth continues until some termination reaction occurs to make the chain active.

$$I^* + M \longrightarrow IM^*$$

$$IM^* + M \longrightarrow IMM^* \qquad \text{Initiation}$$

$$I\text{-}(M)^* + M \longrightarrow I\text{-}(M)\text{-}M^* \qquad \text{Propagation}$$

$$I\text{-}(M)_n + M^* \longrightarrow \text{Inactive Polymer} \qquad \text{Termination}$$

Chain-growth polymerizations are always initiated initiator fragments are the end groups of the chain, while step growth polymerization is catalysted and catalyst molecules don’t become the part of the molecules.

2.2.2. Condensation Polymerization

Condensation polymers are obtained from by the random reaction of two molecules. Typically, condensation polymerization occurs by the liberation of a small molecule.

In condensation polymerization molecular weight of polymer increases steadily through out the reaction, so long reaction time is needed to obtain high molecular weight polymer. At any stage all molecular species are present in a calculable distribution and monomer disappears early in the reaction.

2.2.3. Free Radical Polymerization

Free radical polymerization are initiated by radicals and propagated by macroradicals. These radicals exhibit an unpaired electron. Traditionally, the free radical systems go on 3 steps:

1- Initiation:

Initiating radicals are rarely formed by monomers themselves but rather thermally, electrochemically from deliberately added initiators. The initiation consist of two steps in a free radical polymerization:

a) A dissociation of the initiator to form two radical species.

$$\text{Initiator} \xrightarrow{k_d} 2I^*$$

b) Addition of a single monomer molecule to the initiating radical. (association step)

$$R^* + M \xrightarrow{k_i} M^*$$

k_d and ki are the rate constants of decomposition and initiation step.

2- Propagation:

Propagation contains the growth of the monomer. By the successive of large numbers of monomers, it can be figured as shown where kp is the rate constant of propagation.

$$m_1 + m \xrightarrow{kp} m_2$$

$$m_2 + m \xrightarrow{kp} m_3$$

$$m_3 + m \xrightarrow{kp} m_4$$

$$m_n + m \xrightarrow{kp} m_{n+1}$$

Propagation takes place very rapidly. The value of k_p for most monomers are in the range of 10^2-10^4 lt/mole. sec.

3-Termination:

The propagating polymer chain stops growing and terminates. Two radicals react with each other by combination, or more rarely, by disproportionation in which hydrogen abstraction from one end to give two dead polymer chains, one is being an unsaturated and other is saturated.

Termination by combination;

$$m_n^* + m_m \xrightarrow{k_{tc}} m_{n+n}$$

Termination by disproportionation;

$$m_n^* + m_m \xrightarrow{k_{td}} m_n + m_m$$

k_{tc} and k_{td} are the rate constant of termination by coupling and disproportionation, respectively.

Typically termination rate constants are in the range of 10^6-10^8 liter/mole. sec. And higher than propagation reactions.

2.3. Monomers

N-Vinylcarbazole (NVCz) is a white crystalline material, m.p.=65 ^{0}C. It is soluble in most aromatic, chlorinated and polar organic solvents and somewhat soluble in hot alcohols and aliphatic solvents. Working with N-vinylcarbazole can pose significant danger when the material is handled improperly. Severe cases of skin irritation on humans and test animals have been reported. The compound produced death in mice at 0.05 g/kg perorally.[1] Insufficient data are available as to the carcinogenic behavior of the monomer. However, N-Vinylcarbazole belongs to the general category of aromatic amines, several members of which are known to be carcinogens.

Carbazole (Cz) is a dull white monomer and produced from petroleum products, m.p.=245 ^{0}C. It can be crystallized in alcohol, benzene, toluene and pure acetic acid. It is not soluble in water but soluble in ether, acetone, benzene, pyridine. Carbazole is used in the UV sensitive photographic panels.

N-Ethylcarbazole is a yellowish material, m.p.68-70 ^{0}C. Generally solved in solvents which carbazole and N-vinylcarbazole solved.

Methylethyl ketone formaldehyde is a thermoplastic solid resin produced from the reaction of methyethyl ketone with formaldehyde[2]. The chemical structure of resins are not completely known.

The methylene bridges, shown here in a regular arrangement, might occur in a random manner on both sides of the carbonyl group, or they might be concentrated on the methyl side.

If ketones containing α- hydrogen react with formaldehyde powerfully than usual aldol condensation they give keton-formaldehyde. Ketonic resins are produced commercially since 1920 and nowadays aceton, methylethyl keton, cyclohexanone and acetofenon have practically importance.

The condensation reaction of ketons which have small molecules with formaldehyde goes on preferentially 2 steps. First step of the reaction, usually water-soluble addition products are obtained and supplied at pH = 9-10. When NaOH is added as a bases coloured, complex, insoluble products are obtained.

All the condensation reactions of formaldehyde, pH of solution must control continuously. Otherwise the side reaction of Cannizaro might be occur and formaldehyde may loose alkali continuously.
Thermoplastic resins soften by heat, reshaped easily and stick. These resins are used in coating, paint, ink industry and adhesive industry as a additive material.

2.4. Polymers

2.4.1. Poly (N-Vinylcarbazole)

The polymer (PNVCz) is a glassy, brittle material. It was produced commercially in the 1940s in both Germany and the US, primarily for application as a high temperature dielectric capacitor. The discovery in the 1957 of its photoelectronic behavior created a strong industrial interest in finding a commercial utilization for this interesting property. This was in fact realized in 1970 when IBM Corporation introduced the first commercial organic polymeric photoconducter, based on PNVCz, in its Copier I series of electrophotographic (photocopying) machines.

The bulkiness of the pendant carbazole group and the hindered rotation around the C-N bond linking it to the backbone dominate the structural and physical properties of the material. The polymer chains are rigid and rod-like in nature. In the solid, the polymer forms ordered paracrystalline structures induced by the pendant group packing rather than stereoregularity in the chain, a phenomenon not encountered in other vinyl polymers. The T_g for PNVCZ 227 ^{0}C, among the highest known for a vinyl polymer, and the material exhibits excellent thermal stability. Unfortunately, this property has never been exploited because of the extreme brittleness of the polymer. Attempts to improve the mechanical and processing properties by conventional techniques (plasticization, orientation, copolymerization) have been successful enough to overcome this limitation.

Perhaps the most intriguing properties of the polymer are its photophysical and photoconductive characteristics and its ability to form charge transfer complexes with suitable electron acceptor molecules. The spectroscopic behavior of PNVCz (absorption, emission and energy transfer phenomena) has been investigated in detail both in solution and in the solid state. PNVCz is the only known vinyl aromatic polymer which exhibits emission from two characteristic excimer states, reflecting its unique structure and interchromophoric effects. Photoconductivity studies on the polymer have contributed significantly to the understanding of the mechanism of the photogeneration and transport of electronic charge carriers in organic and polymeric solids. PNVCz based materials have been the most extensively studied and are among the best understood polymeric semi- and photo-conductors.

The stereoregular polymerization of NVCz by the homogeneous catalyst systems, $CoCl_2$-quinoline/pyridine-$ZnEt_2$ in toluene, has been described by Biswas and Mishra [3.4]. PNVCz obtained from these systems shows partial solubility in methyl ethyl ketone (MEK).

2.4.2. Poly (Carbazole)

Carbazole is a relatively unimportant molecule in the past, is of considerable interest at present due to the uses of substituted carboles in the polymerization studies. [5] Since the carciogenic activity of carbazole molecules may be associated with their redox properties, and considering that present and future studies may verify the presence of other substituted carbazoles. Carbazole is a prototypical organic molecule that has shown potential for technological applications. Polymers based on this molecule have good electro- and photo- active properties due to their high hole-transporting mobility, strong absorption in the ultraviolet spectral region and blue-light emission well. Already, within the xerographic industry, such as polymers have been considered for use as photoconductive charge-transport layers. [6]

Poly (N-Carbazole) is a dark green conductive polymer, is formed by electropolymerization of 10^{-3} M carbazole with 0.1 M tetrabuthylamonum perchlorate in acetonitrile at 1.3 V (vs SSCE) on Pt anode. A brittle conductive film is formed and its conductivity is between
$10^{-4} < \sigma < 10^{-1}$ Scm^{-1} at 300 ^{0}K. The structure of the film is likely the mixture of low molecule weight oligomers.

Carbazole oligomers can polymerize in liquid iodine [7], iodine complexes of nitrobenzene soluble polycarbazole which are indefinitely stable in air at room temperature and have conductivities as high as 6 ohm^{-1} cm^{-1}.

Carbazole Modified PolySiloxanes (CMPSs) have been shown to undergo facile electrochemical cross-linking with the formation of dicarbazolyl units [8]. Electrochromic properties of dicarbazolyl groups has focused largely on polyvinylcarbazole [9] where owing to the comparitive rigidity of the polymer backbone, cross-linking efficiencies and consequently the density of colouration centres was found to be relatively poor.

2.4.3. Poly (N-Ethylcarbazole)

There is no more studies about poly (N-ethylcarbazole)'s conductivity and photoconductivity. The achievement of N-substituted carbazoles as coherent films bound to the anode substrate depends strongly on the nature of the substituent.

Dubois and co-workers [10] found that the anodic oxidation of N-ethlcarbazole in acetonitril does not produce filming: the green colour, ascribed to oxidized 3,3'-dicarbazyl units, was seen to diffuse into solution.

Copolymer and composites of Ecz in the presence of Pyrrole has advantages of high conductivity and a alternative to electrochemical methods.[11]

Following the findings, N-ethyl carbazole produced by anodic oxidation of the relevant monomer in acidic aqueous solutions. The analytic data indicated that the material is a C-C coupled Ecz oligomer: voltammetric and coulometric runs suggest that at least tetramers are the basic constituents. This may be totally oxidized to iminium salts by two separate stage involving similar charge amount: however, only the fist system, engaging the oxidation of one nitrogen out or two, represents a stable form of the material.

Except the electrochemical polymerization of N-ethylcarbazole, it is possible to obtain blue or green colored insoluble polymers from the chemical reaction (as a Friedel Crafts reaction) of alumınıum chlorur with methylen chlorıde.[12]

The conductivities of Cz and derivatives prepared by oxidative polymerization can be controlled and a wider range of properties obtained in terms of solubility as well as conductivity shown than electrochemical polymerization [13].

The structure and the abbreviations of monomers and polymers are shown in the Table 2.1.

2.5. Electropolymerization of N-Carbazole Derivatives

2.5.1 Electropolymerization of N-Carbazole

Previous work had established, upon anodic oxidation, form a very unstable cation radical reacts via coupling-deprotonation to 9,9'- and 3-3'-bicarbzyls [14], higher polymers were thought to form upon prolonged electrolysis. [15] When alkyl and phenyl groups were placed on the carbazole nitrogen only the corresponding 3,3'-bicarbazyls formed, in quantative yields, and they appeared to be quite stable under electrolytic conditions.

The electrochemistry of these molecules has been presented in detail previously. [16] When carbazole is oxidized in ACN (TEAP) at platinum, the initial step is a (proposed) removal of one electron to form a very unstable cation radical. This cation radical reacts by deprotonation-coupling to form the 9,9'- and 3,3'- bicarbazyl is two reversible one electron steps to yield a moderately stable dication with extensive conjugation. The 9,9'- bicarbazyl is only formed initially under cyclic voltammetric conditions and could not be isolated from controlled-potential electrolyses in unbuffered ACN. The 9,9'- bicarbazyl is only formed initially under cyclic voltrammetric conditions and could not be isolated from controlled-potential electrolyses in ACN; the 3,3' – bicarbazyl was isolated in moderate yields. The 9,9'-bicarbazyl was to form quantatively, however, when electrolyses were carried out in the presence of an organic base such as pyridine. This fact led to the conclusion that the carbazole cation radical forms the 9,9'- bicarbazyl by diffusing out into solution, followed by deprotonation of the central nitrogen and subsequent coupling of the resultant free radicals in solution before they can diffuse back to the electrode to be further oxidized.

Ambrose and Nelson [16] have shown that the electrochemical oxidation of carbazole displays all the characteristic of a classical ECE mechanism, and proposed the following reaction scheme:

Structures A, B and C in the above scheme are the most important resonance forms for the carbazole cation radical. According to these authors, when there is no proton scavenger such as pyridine the dimerization of cation radicals (A) occurs at the 3 position and leads to the formation of 3,3’-dicarbazyl (C) ; this compound, which oxidizes more easily than carbazole, then gives the quinoidal dication (E) which precipitates in the electrolyses cell.

Although the films could be reduced by chemically, neither the redox properties nor he film stability was tested by Bargon et al. [17] are described a very poor.

Electrochemical oxidation of carbazole in acetonitrile containing TEAP versus SSCE yields an amorphous conducting film which adheres to the Pt anode. Unlike polypyrrole, polythiophene or polyazulene, these film are very brittle and crack easily. The film have very low electrical conductivities of $10^{-4}<\sigma<10^{-1}$ $\Omega^{-1}cm^{-1}$ at 300 ^{0}K, and the elemental analysis data, $(C_{12}H_{13}N)$ $(ClO_4)_{0.14}$, reveal that they are very rich in hydrogen and contain a high level of perchlorate anions. The films are more likely a mixture of low molecular weight oligomers, but certainly different from the crystalline radical cation salt.

A better morphology and adhesion of the coating to the substrate were achieved by pulse galvanostic oxidation of carbazole in DMF [18], although the electrochemical properties of the deposits were not described in this case either. And, the oxidation of carbazole in protic acid medium provides an easy, straight route for synthesizing films bound to an inert electrode substrate which, in a suitable acid electrolyte, exhibit fair conductivity and stable redox behaviour [19].

According to Maitland and Tucker [20], the reaction medium affects the isomer distrubution drastically: In the presence of sulfuric acid, using dichromate as the oxidant, only the 3,3’- dicarbazyl is obtained, whereas in the absence of sulfuric acid the 9,9’-carbazyl is also formed. Electrochemical oxidation studies of Ambrose et al. [21] revealed that the 3,3’-dicarbazyl is typically the dominating electro-oxidation product. The 9,9’- dimer was only formed very early during electrolysis, before the proton concentration build up. Addition of H_2SO_4 suppressed the formation of the 9,9’- dimer altogether, whereas addition of base as a proton scavenger (pyridine) increased its yield significantly.

Santhanam has been reported polycarbazole as an electrode by oxidation of L-dopa an showed remarkable reproducibility and stability without any pretreatment [22] and reported the electrodeposition of polycarbazole by passing a constant current through a solution carbazole in DMF containing 0.1 M TBAP and the deposited film was used as an electrode in the electrochemical oxidations [23].

Copolymer and composites of carbazole with pyrrole were synthesized on a platinum substrate and an electrochemical study of polymeric films was performed and found that homopolymer, copolymer and composite electrodes of N-substituted carbazoles with pyrrole seem to be stable and sufficiently electroactive for potentially different applications (i.e., sensors, battery and corrosion inhibition) and thicker films obtained than expected [16].

2.5.2 Electropolymerization of N-Vinyl Carbazole

It should be noted that up till 1982 the electrochemical polymerization of NVCz has been undertaken for preparative purposes [24,25], and that only products obtained in solution have attracted attention. Ambrose and Nelson [16], who are the first to have studied the mechanism involved in the electrochemical oxidation of a certain number carbazoles, reported a complex behaviour for NVCz which they did not attempt to elucidate.

Electrochemical polymerization of N-Vinylcarbazole is different from that of pyrrole, thiophene etc. [26,27]. In comparison with the rather simple molecules of these five membered heterocycles, N-vinylcarbazole represents a more developed π-electron system with more mesomeric forms of the cation radical and with polymerization centers on both the benzene ring and the vinyl group [28]. 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 [29].

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 electochemical 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 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) $^{*+}$,as proposed by Breitenbach.

When there is an excess of NVCz, the cation radical (NVCz)*+ yields the 1,2-dicarbazylcyclobutane (DCB) cation radical, as follows:

Reaction (2) also occurs in photochemical or thermal studies of NVCz [29]. It does not compete with the 3,3’ coupling observed for carbazole and some of its N-alkyl derivatives [11].

Nor with the ensuing electrochemical oxidation of 3,3’- (NVCz)$_2$ into the corresponding cation radical 3,3’-(NVCz)$_2^{*+}$.

DCB, which oxidized at the same potential as NVCz, displays an electrochemical behaviour analogous to that of N-alkylated carbazole derivatives [16]. It is therefore highly likely that its electrochemical oxidation leads to the 3,3’coupling product and the release of protons:

Thus, the resulting 3,3’-(DCB)$_2$, which oxidizes at a lower potential than DCB, could yield the corresponding cation radicals:

Which can associate with CIO$_4^-$ ions to form perchlorate salt films that can be reduced by electrochemical or chemical means.

Several authors have reported that polypyrrole, polythiophene and poly (N-vinylcarbazole) films obtained solutions containing added water are uniform and adherent, although they exhibit lower conductivity than films prepared in dry acetonitrile [28,30-34]. 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 [30]. During redox cycling of the polymers, ion and solvent exchange occur and nucleophilic solvents such as H_2O can react with the cation radical cations or dications produced during oxidation leading to degradation of the polymer [28,34 - 35].

The redox behavior of poly(N-vinylcarbazole) 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_2O + 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_2O + 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.

It has recently been shown that the level of conductivity can be significantly enhaced (up to $6x10^{-4}$ S/cm) by employing electrochemical oxidation of PVCz in thin films coated onto a platinium electrode [36].

Stable polymer coats with good adhesion characteristics were prepared by evaporation of a small quantity of a solution of PVCz from a platinum foil [37].

Kanega and Shirota has been showed the effect of doping on the conductivites of thin films coated on the electrode and for solutions by means of controlled potential electrolysis using a three-electrode system [38].

2.5.3. Electropolymerization of N-Ethylcarbazole

The best defined electrochemically activity is shown by PECz which, however, has the lowest solid state dc conductivity in the homologue series explored. Therefore, other properties such as permeability to the electrolyte, morphology and overall ionic conductivity appear more important for characterizing modified electrodes. In aggrement with this point, ac investigation revealed that the close similarity of the PECz film with a redox polymer film, in which electroactive species are dispersed inside a non (electrically) conducting matrix.

Further, it was assessed that the second oxidation state of PECz is more stable than the corresponding state of PCz. These thermodynamic stability conditions require high energy to be distrupted and PCz does show the further oxidation stage at a definitely more positive potential than PECz : at this potential other oxidative degradation reactions probably occur [39]. In agreement with this explanation, the second oxidation of PECz, though showing better reversibility than PCz, occurs at approximately the same potential and thus leads to the degradation.

Polymerization of N-ethylcarbazole (NECz) in the presence of acrylamide has been investigated by in situ and ex situ UV-visible spectrophotometric measurements to obtain information about the reaction pathway, because NECz gives soluble oligomeric species allowing such measurements [40].

2.6. Other Polymerization Type of Carbazole Derivatives

A great deal of attention has been given to poly(N-vinylcarbazole) over the years because of its unusual electrical and photoelectrical properties. Earlier work on PVCz focused on its dielectric chracteristics while more recently its electrophotographic properties have been utilizied in commercial photoreceptors. Its unusual electrical behavior, high glass-transition temperature (227 ^{0}C) and brittleness, ease of polymerization by a variety of techniques, and intriguing morphological features and solutions properties combine to make PVCz a polymer of considerable current interest.

NVCz is a reactive monomer towards radical and cationic polymerization because of its ability to stabilize electron-deficent centers by resonance involving the nonbonding electron pair on the nitrogen atom in the carbazole ring.

2.6.1. Free Radical Polymerization

Free radical polymerization carried out in dispersion and suspension with azocompounds, peroxides and systems that can produce free radical [41,42].

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 [43]. 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/lt. 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.

To understand the mechanism the best method is the polymerization with styren. It's proposed that the cationic mechanism with base solvents such as DMF [44].

Copolymerization with ethylen glicol bis (methyl fumarate) results with free radical, obtained 1:1 alternate copolymer and ring-advenced mechanism is dominant while NVCz concentration increased [45].

Copolymerization with alkyl metacrylat proved that the reactivity ratios change depends on the solvents [46].

2.6.2. 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 [47]. Even the generally accepted

concept that basic solvents preclude cationic polymerization can not be applied to NVCz.
Boweher et al. [48] have stuied the cationic polymerization of NVCz by tropylium hexachloroantimonate 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.

Ledwith and Sherrington [49] have also reported the only example of a propagating dication by reaction of NVCz with the stable cation-radical tris-(p-bromophenyl) aminium hexachloroantimonate. Although this system with the propagating dication is extremely interesting and important, a question remains as to why relatively large amounts of catalyst must be used and why a molecular weight of ≈ 10.000 can be achieved. Ledwith [50] 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 [51]. Among the most recent studies are those by Pielichowski [52] who described the polymerization of NVCz initiated by hydrogen halides, HF, HCl, HBr and HI [53].

2.6.3. Anionic Polymerization

The polymerization of NVCz with metallic Na, -S-, n-BuLi did not result successfully [54]. Depending on the ESR and UV-Visible spectrums, radical anion (NVCz) is stable only at low temperatures. This radical anion can not be formed its own dimer or polymer but can start the polymerization of the other monomers such as styrene. At high temperatures, break into carbazole and ethylene.

Mulvaney put forward that NVCz can polymerize with R_2CuLi (Litium di-n-buthyl copper (II))and the mechanism is the coordinate anionic mechanism [55].

Ledwith et al. [56] and Pearson et al. [57] have demonstrated that the related monomers, N-alkyl-2-vinylcarbazole(N2VK), N-alkyl-3-vinylcarbazole(N3VK) and N-alkyl-4-vinylcarbazole(N4VK) can be polymerized by both addition and electron transfer initiators. These systems are typical living polymers in that they give high molecular weight ($M_n \approx 10^6$), narrow molecular weight distribution (MWD<1.4) homopolymers and AB and ABA type block copolymers, e.g., with styrene.

2.6.4. Charge Transfer Polymerization

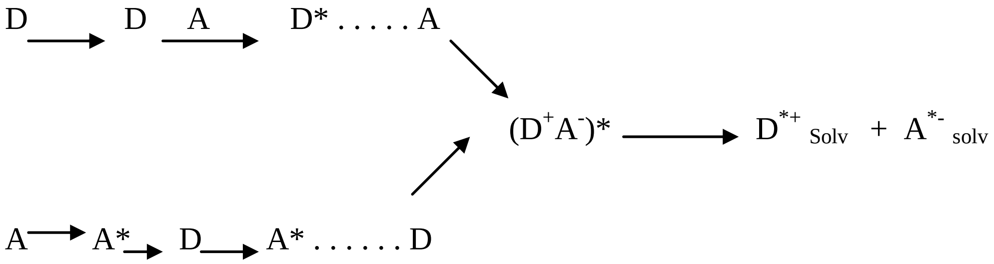
Polymerization reactions involving electron donor-acceptor interactions (charge transfer interactions) have been of considerable interest since Labes [58] and Ellinger [59] independently reported in 1963 that donor monomers such as NVCz could be spontaneously polymerized in the presence of electron acceptor molecules.

First, induced by electron acceptors such as chloranil, TCNE, halogens, maleic anhydride, acetonitrile and fumaronitrile, involved formation of an electron donor-acceptor or charge transfer complex (CTC) followed by electron transfer to produce an initiating species.

Labes [58] proposed the monomer radical cation, NVCz $^{*+}$, formed by one electron oxidation, as the initiating species. Ellinger [59,60] favored a mesomeric polarization mechanism involving partial electron transfer.

A considerable number of publications on the charge transfer polymerization of NVCz, initiated both thermally and photochemically, have appeared since the early studies of Ellinger and Labes. Unfortunately, many of these investigations have added to the mechanistic confusion, since purity considerations and alternative reaction pathways were largely ignored. Mikawa et al. [61] and Stille [62] first demonstrated that no polymerization occurs in the presence of highly pure chloranil or TCNE. Even with highly purified chloranil, a slow polymerization of NVCz in benzene is still observed. In a polar medium, nitrobenzene, the polymerization is rapid [63].

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 complex, [DA] $[D^+A^-]^*$, or by diffusion controlled collision between locally excited donor (or acceptor) and ground state acceptor (or donor):



2.6.5. Ziegler-Natta Polymerization

Early reports [64,65] that NVCz can be polymerizaed by conventional heterogenous Z/N catalyst systems to produce stereoregular, crystalline polymer have been questioned. The high reactivity of NVCz to cationic polymerization suggests that this process dominates the reaction and that the coordinated Z/N type mechanism is not involved [66]. Polymers isolated from free radical, cationic and Z/N systems are essentially atactic (certainly not highly stereoregular) and amorphous.

2.6.6. Cyclodimerization

The cyclodimerization of NVCz to the trans-1,2-dicarbazyl-cyclobutane is readily achieved by electrochemical (anodic) [67], thermal (metal oxidant) [68], photochemical [69] and radiolytic techniques [70]. In most instances, the cyclodimerization is accompanied by free radical or cationic polymerization NVCz.

2.6.7. Solid State Polymerization

There have been several publications describing the solid state polymerization of NVCz in the crystalline state initiated by high energy radiation [71-73], cationic catalysts [74], halogen vapors [75] and redact systems [76]. Both free radical and cationic mechanisms have been proposed, primarily on the basis of kinetic and polymer molecular weight analysis. Solid state polymerization of NVCz is important to obtain stereoregular crystalline and high molecular weight polymer.

2.6.8. Polymerization in Water

There is no more studies about NVCz, Cz and EtCz because of the solubility problem of the monomers. It is known that an increase is obtained from the polymerization of conductive polymers in watery conditions [77]. Besides, if there is a polymer in an environment conductive polymer can be obtained by dispersion polymerization [78]. PVCz can polymerize in the presence of toluene/water by $FeCl_3$ catalyst and the product is more conductive than the products obtained from conventional methods.

2.7. Mechanical Properties of Polymers

PVNCz is a glassy polymer with unusually high thermal stability for a vinyl polymer. The glass transition temperature of $>200^0C$ is the highest among known vinyl polymers. This excellent thermal stability is, however, offset by the extreme brittleness of the material.

Glass transition temperatures of PNVCz ranging from 150 to 248^0C have been reported [79,80,81]. The highest reported value of T_g of 248^0C was for PVNCz prepared by cationic polymerization [81]. This polymer is claimed to be somewhat more isotactic than polymers prepared free radically, and the high T_g value was attributed to isotacticity.

For purified samples prepared by free radical techniques, covering a molecular weight range Mn 3500-1.200.000, the T_g is linearly dependent on M^{-1}.

$T_g = T_{g\,\infty} - K/Mn$

in which K is related to the chain end free volume.

T_g is relatively independent of molecular weight distribution, but is very sensitive to impurities.

The intrinsic viscosity-molecular weight relationship for PVNCz in benzene at 25^0C:

$[\eta\,] = 3.05 \times 10^{-4}\ (cm^3/g)\ M^{0.58}$

2.8. Degradation and Stability of Carbazole Derivatives

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

Since PVCz is a vinyl derivative with a high T_g, requires high processing temperatures (≈230 ^{0}C), and sees enviromental 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 [82]. 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 [83]. Generally, the aromatic groups oxidized to form quinones, which can then undergo further reactions to form alcohols [84].

Thermal, oxidative and enviromental degradation tests have been performed on several commercial and fractionated PVCz materials as a function of ambience, temperature and time [85]. Low molecular weight samples were the most resistive to degradation in air and argon at 180, 280 and 330 ^{0}C. High molecular weight PVCz performed better than an “as received “ 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.

The thermal degradation of phosphorylated PNVCz also was studied by thermogravity. The onset degradation temperature decreases with respect to that of unmodified PNVCz indicating a lower thermal stability for the phosohorylated sample [86].

Ferric 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) <PNVCz (255^{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 degradation occurs in the range 250-520 ^{0}C in these systems [87].

2.9. Electrical Properties

2.9.1. Conductivity of Polymers

PVCz can be useful either as an insulator or a photoconductor, depending on the circumctances. The polymer has also shown promise as an interesting p-type semiconductor. By the chemical [88] and electrochemical [89] oxidation of polymer radical catıon centers formed, the film colored and become conductive. Conductivity (σ) depends on the mole ratio of the carbazole groups turn into cationic radicals (χ). The film has high resistance in air. For example a sample with a value of conductivity 6.65x10^{-3} can be stable for six months.

Polycarbazole has a conductivity value between 10^{-4}-10^{-1}. It is obtained for electrochemically prepared PECz in acidic alcohol solutions, the conductivity values change between 10^{-4}-10^{-6} [90].

Conductivity of polyvinylcarbazole and other organic photoconductors increase when they exposed to light it will continue for a long time. This fact is called continuous conductivity and can be stable due to the temperature and nature of the of the material. But it doesn't permanant, can be vanished by heat or light.

PVCz : o- dinitrobenzene doped with trichloroaceticacid system was investigated and observed while light exposed to material conductivity increase and after the light was turned off obtained high conductivity [91].

The formation of the long lived persistent conductive state was attributed to complexation of the acidic proton with the excited donor-acceptor complex to yield a free radical cation D^{-+} of the carbazole moiety (hole) and a proton-complexed nitroaromatic radical cation:

$$\mathrm{D(PVCz)} + \mathrm{A(o\text{-}DNB)} \rightleftarrows [D^{+}A^{-}]$$

$$\mathrm{HB\ (acid)} \rightleftarrows H^{+} + B^{-}$$

$$[DA]^{*} + H^{+} \rightleftarrows [H^{+}A^{*-}] + D^{*+}$$

the decay of persistent photoconductivity is viewed as a reversible bimolecular reaction between the complexed acceptor $[H^{+}A^{-}*]$ and the hole $D^{+}*$

$$D^{+}* + [H^{+}A^{*-}] \longrightarrow DA + H^{+} + \mathrm{energy}$$

The stability of the persistent conductive state depends on several factors:

- the affinity of the radical anion A^{*-} for the proton
- steric factors influencing the activation energy and the rate of the reverse process
- affinity of the acid anion B- for the radical cation D^{*+}
- relative strengths of B^- and A^{*-}

2.9.2. Photoconductivity

The discovery of phtoconductivity in PVCz [92] situmalated the development of photoelectrically active organic materials which ultimately resulted in commercial applications. PVCz 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 electrode. Moreover, the generation of charge carriers can be shifted into the visible and near infrared range of wavelengths by appropriate sensitizers.

It is known that the presence of dopants phtoconductivity increase [93]generally these are acceptors. The most important one is 2,4,7, trinitrofluorene (TNF). PVCz :TNF system has a practical importance in electrophotograph as a photoreceived [94].

Except the electron receivers dyes used in conducting [95,96]. The most used ones are siyanin, methine and azo dyes. The photoconductivity of the intermolecular charge transfer complexes of NVCz, polycarbonates and azo dyes and obtained high photo-current [97].

Good photoconductivity of NVCz is related to prepare good thin films. There are dry and fresh methods to prepare films in recently years. One of them is plasma-CVD method [98]. But it is a difficult method because of the controlling all parameters.

2.10. Miscellaneous Applications

The major utilization of PVCz based materials has been as an organic photoconductor in electrophography. Several other possible applications have been reported in the literature which have yet to be exploited commercially. A few of these are covered here.

2.10.1 Image Storage Systems

Formation of an electrostatic duplication master in a PVCz : TNF : leuco dye film has been recently described [99]. Kumada et al. [100] have created long lived latent images in dual layer ferroelectric (FE)-PVCz : TNF structures which can be developed using liquid toner systems. Problem of sensitivity, image stability, quality and erasure have to be overcome before this approach to image retention/utilization becomes practical.

2.10.2. Photothermoplastic Imaging

direct optical relief recording on thermoplastic organic photoconductor layers has been demonstrated [101,102], and the technology has been considered for display devices, “add-on-image” microfiche and “instant” microfilm. A single layer device has recently been described [103,104] which is based on copolymers of NVCz with acrylates, methacrylates or styrenes. PVCz based photoconductors have also been used in devices suitable for holographic recording, image intensification and optical buffer storage [105,106].

2.10.3. Photovoltaic Devices

The development of low cost, readily fabricated, large area phovoltaic cells for solar energy conversion is highly desirable, and organic polmeric systems based on PVCz have been examined. An estimate of the photovoltaic conversion efficiency for the PVCz :TNF (1:1) system has been made [107].

2.10.4. Non-Conventional Imaging Systems

A non-silver photographic process utilizing the polymerization of NVCz was described by Yamada, Garland and Bruck [108]. 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 colorless PVCz product.

Hasegawa et al.[109] have described a light sensitive paper based on the above NVCz :CBr_4 emulsion, which can be used to produce copies from a CRT printer and as a high speed facsimile receiver sheet.

3. EXPERIMENTAL WORK

3.1. Materials

Methyl ethyl ketone formaldehyde-resin (MEKF-R) was prepared as described earlier.[110] Its molecular weight is about 700 g/mol. N-carbazole (Cz), N-ethylcarbazole (ECz),, N-vinylcarbazole (NVCz), acetonitrile (ACN), dimethyl formamide (DMF), dichlorometan tetraethylammonium perchloride (TEAP), Ceric ammonium nitrate $(NH_4)_2$ $[Ce(NO_3)_6]$, Acetone (Ac) and sodiumperchloride ($NaClO_4$) were all Merck reagent grade chemicals of the highest purity and used without further purification. All solutions were prepared fresh before each run.

3.2. Instrumentations

Infrared spectra were recorded on a JASCO FT-IR 5300 Fourier transform infrared spectrometer on a KBr disk.

DSC thermograms were obtained by using Perkin-Elmer DSC-6 instrument; the heating rate was 10 ^{0}C/min under nitrogen atmosphere.

In order to measure the electrical conductivity of powders were compacted under 10 tons of pressure to obtain thin pellets. Typical sample dimensions were 13 mm and the thickness were 0.30 mm and 0.80 mm. Conductivity measurements were performed in air by using Four Probe Technique and calculated from the following equation:

$$\sigma = V^{-1} * I \, (\ln 2 / \pi \, dn)$$

where V is the potential in volts, I is the current in amper and dn is the thickness of the samples in cm.

Viscometric data were collected using Ostwald viscometer at 25 ^{0}C.

UV-Visible spectra of polymers were performed by using Shimadzu 164 A Recording Spectrophometer.

^{1}H-NMR were obtained for DMSO-d_6 solutions on a Bruker AC-(200 MHz).

Elemental Analysis were done with Carlo Erba 1106 equipment.

The electrochemical measurements were carried out using a Wenking POS 73 Model Potentiostat.

Samples were being solved in “MARS-5” Microwave solving system in teflon cups under 175 psi pressure and maximum 205 ^{0}C by adding %65 HNO_3 and %30 H_2O_2. After cooling filtrated and Fe, Cu, Zn and Cu were analyzed in AAS (Atomic Absorbtion Spektrofotometer) in the modulus of [Flame (Air/Acetylen)].

3.3.Preparation of Methyl Ethyl Ketone Formaldehyde-Resin and Carbazole Copolymers

3.3.1. Chemical Polymerization

First, the ketonic resin, CAN, Cz, EtCz and N-VnyCz were dissolved in acetonitrile separately. Then CAN solution was added to the mixture of Cz and MEKF-R solutions dropwise under stirring. A green powder formed almost instantaneously except in the case of NVCz. If the oxidant concentration is five times lower than the monomer concentration, a colourless polymer is formed for NVCz indicating that polymerization proceeds through the vinyl groups, whereas the colour of polymers are dark green in the case of Cz and Ecz at the same concentrations. When the molar ratio of n_{CAN} /n_{mon} become higher than 0.2, dark green polymer could also be obtained for NVCz. After one hour the powder was filtered and the precipitate was called as the precipitate I and the precipitate obtained by pouring the filtrate to the water was called as the precipitate II. Polymerization experiments were carried out at 25^{0}C while stirring with a magnetic stirrer. The reaction volume was about 40 ml in all experiments.

The white product of PNVCz was converted to the green form by chemically by taking Sample 3 and oxidize with CAN again.

In the standart experiments the monomer concentrations are 0.12 M for Cz, NVCz, EtCz and $8.6x10^{-3}$ M for MEKF-R and 0.06 M for CAN. But for NVCz to obtain colourless polymer CAN concentration is $1.5x10^{-3}$ M. These are listed in Table 3.1.

3.3.2. Electrochemical Polymerization

In order to compare with chemically prepared polymers, Cz, EtCz and NVCz were electrochemically polymerized in the presence of MEKF-R in ACN. $NaClO_4$ and TEAP were used as electrolyte and stainless steel plates were used as electrodes (10 cm^2). 3 V was applied for one hour, electrocopolymers were recovered as green films and washed with ACN and dried at room temperature.

Electrochemical polymerization was realized at different concentrations for each Cz and its derivatives. For comparing the results of chemically and electrochemically polymerized copolymers the same concentrations are used both homolpolymers and copolymers (Cz=0.12, MEKF-R=$8.6x10^{-3}$, $NaClO_4$=0.1 M).

On the other hand MEKF-R concentrations were changed from $1.55x10^{-3}$ M to $1.63x10^{-3}$ M while Cz concentration is equal $1.55x10^{-2}$ M to see the effect of resin in the electrocopolymers.

The white form of homopolymer and copolymer of NVCz is polymerized by electrochemically and converted to conductive green form.

3.4. Preparation of MethylEthyl Ketone Formaldehyde-Resin and Carbazole Copolymers With Other Metals

Cz, EtCz and MEKF-R were dissolved in ACN separately, then metal solutions added to the solutions dropwise under stirring. After a week green products were filtered. Polymerization reactions were carried out at 25 ^{0}C. Due to the different oxidation potentials of metal used, different concentrations of metal solutions were used for oxidizing the same amount of monomer. That’s why the volume of the reaction media were different. .

4. RESULTS AND DISCUSSION

In this study a new class of soluble conducting carbazole (Cz), ethylcarbazole (Ecz) and vinylcarbazole (NVCz)- ketonic resin copolymers have been developed. This was accomplished by chemically and electrochemically polymerizing carbazole monomer and its derivatives with MEKF-R by Ce(IV) in chemical method and by $NaClO_4$ and TEAP by electrochemical method.

On the other hand instead of CAN different metal solutions were used in chemical polymerization and the metal content in soluble and insoluble products are obtained.

Solid and solution conductivities, solubility, yield, viscosity and the character of the result products were compared due to the monomer, oxidant and resin concentrations.

4.1. Chemical Polymerization

Because of the solubility problem of carbazole and its derivatives the characterization and application of them is very difficult. From this idea we copolymerized Cz, EtCz and NVCz with ethyl methyl ketone formaldehyde resin (MEKF-R) in the presence of Ceric ammonium nitrate (CAN) by chemically firstly. We have choose a suitable ratio between monomer and oxidant to obtain both conductive and soluble copolymers (n_{CAN}/nmon =0.5). Copolymers were obtained at the same monomer,MEKF-R and CAN concentration and homopolymers obtained in the absence of MEKF-R at the same conditions. (Sample no 1, 4, 7 and 10, 11, 12). In this experiment NVCz/oxidant ratio is higher than 0.2, so the polymer is green. Their conductivity, yield and the solubility results are listed in Table 1.

From these results we can say the highest conductivity is obtained while MEKF-R was absent and the lowest conductivity is obtained when the highest MEKF-R is used. The precipitate I and II of copolymers have conductivities between 10^{-3} and 10^{-4} (S/cm), little changes mean the inclusion MEKF-R is nearly the same in precipitate I and II. When we compare the conductivities of precipitate I and precipitate II, slightly decreases in the case of precipitate II is due to the inclusion of MEKF-R to the structure.

From the solubility results, all copolymers are totally soluble in DMF, although homopolymers are partially soluble All these results show us the presence of MEKF-R in copolymers.

In case of NVCz, first, PNVCz homopolymer is synthesized (Sample 3/Table 3.1) to obtain colorless polymer and NVCz/MEKF-R copolymer(Sample 8) is obtained at the same concentration of CAN. Homopolymer and copolymer are insulators as expected. If MEKF-R concentration is taken half of sample 8, there is no precipitate. Pink solution is obtained and this might be due to the matrix polymerization of NVCz on MEKF-R matrix (Sample 2).

4.2. Role of Ceric Ammonium Nitrate (CAN) Concentration

The role of CAN concentration on the yield and conductivity of copolymers was investigated. In order to understand the effect of CAN concentration on the polymerization, the ratio of nMEKF-R/nCz, nMEKF-R/nNVCz and nMEKF-R/nECz =0.071 is held constant and CAN concentration is changed from 0.015 to 0.06. Yield and conductivity increase when CAN concentration increases in precipitate I of Cz copolymer (Figure 1a). The yield and conductivity of precipitate I of NVCz copolymer remain constant by increasing CAN concentration until the 0.056 M CAN concentration, then increases (Figure 1b). This result supports the knowledge that NVCz polymerized with MEKF-R by CAN both via the vinyl and carbazole groups according to CAN groups. During vinyl polymerization yield and conductivity stay constant.

Precipitate II of Cz copolymer yield decrease until 0.03 M, then starts increasing and related with this result conductivity increase up to 0.03 M then decreases. This might be due to the termination of chains with CAN till 0.03 M concentration, then termination between long chains presents in the medium (Figure 2a and 2b)

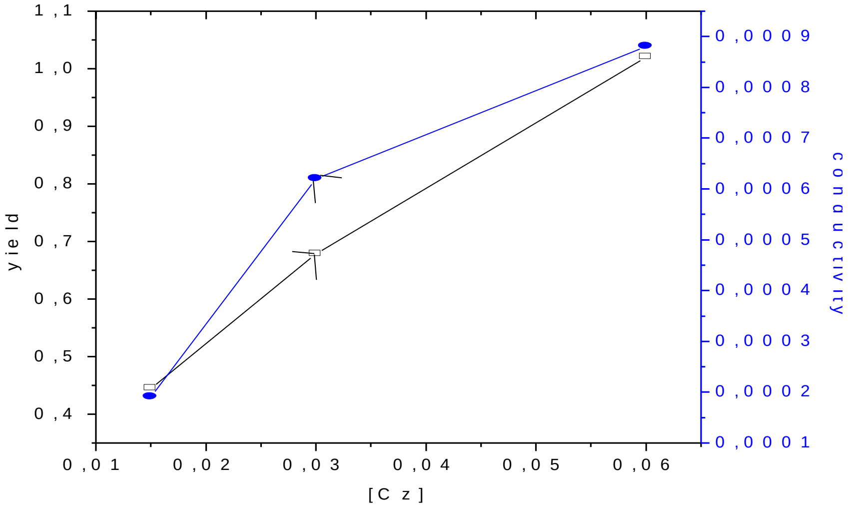


Figure 1a. The role of CAN concentration on the conductivity and yield of Cz copolymers for precipitate I

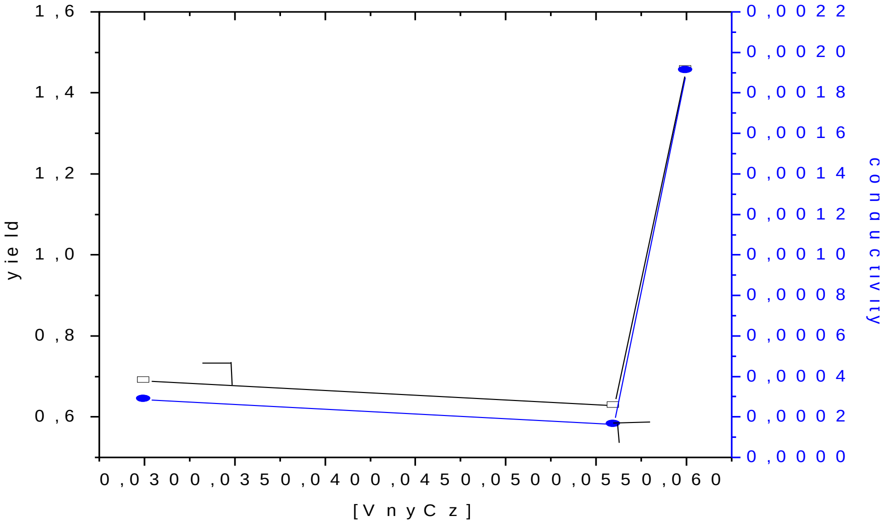


Figure 1b. The role of CAN concentration on conductivity and yield of NVCz copolymers for precipitate I.

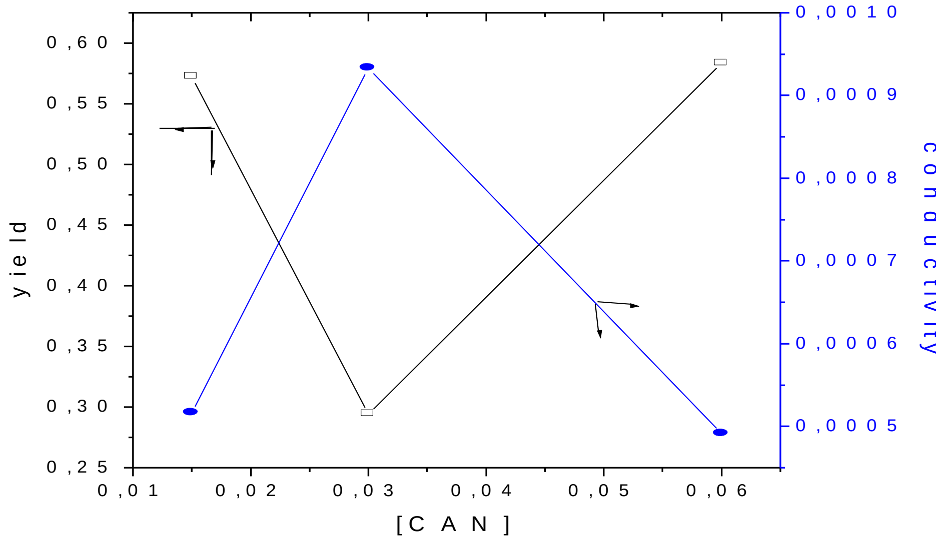


Figure 2a. The role of CAN concentration on conductivity and yield of precipitate II for Cz.

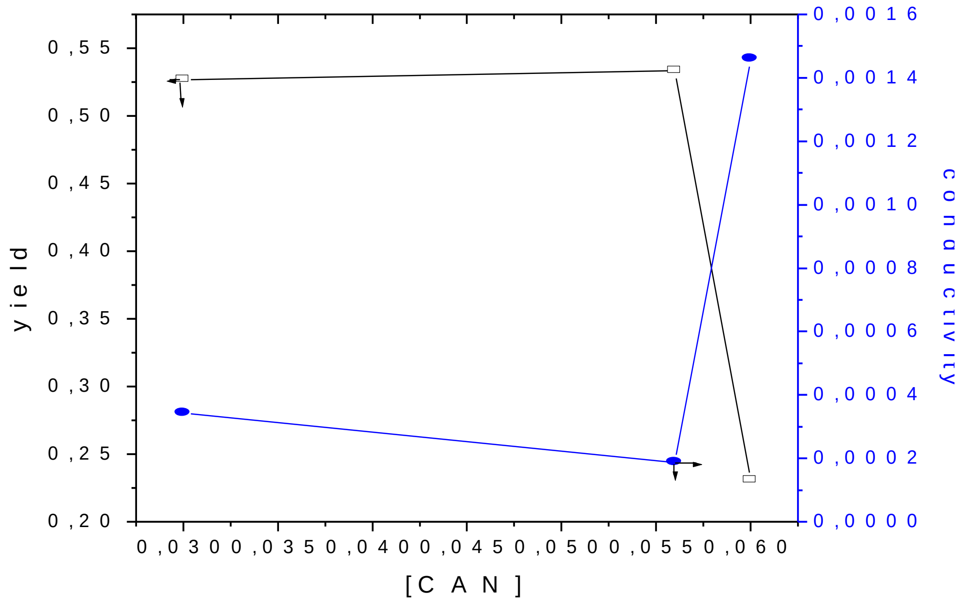


Figure 2b. The role of CAN concentration on conductivity and yield of precipitate II for NVCz.

4.3. Role of MEKF-R Concentration

While monomer and CAN concentrations held constant MEKF-R concentrations changed from $4.3x10^{-3}$ to $7.2x10^{-2}$ M. Increasing MEKF-R in copolymer does not change the yield and conductivity so much, there is little changes. It is due to the less inclusion of MEKF-R to structure than Cz and derivatives (Figure 3a and 3b).

4.4. Role of Cz, Ecz and NVCz Concentrations

The effect of Cz concentration on the yields and conductivity was examined for different concentration of Cz, Ecz and NVCz, keeping the concentration of MEKF-R and CAN constant. Yields in precipitate I and II were increased by inrcreasing Cz, Ecz and NVCz concentrations (Figure 4b, 5a). But conductivities of resulting products are decreases by increasing Cz, while Ecz and NVCz copolymers conductivities stay constant (Figure 4a, 5b).

These results show that since CAN is partially used by MEKF-R in the polymerization medium, longer conductive chain can not be obtain if necessary amount of CAN is absence. On the other hand, although increasing in yield conductivities are decreasing, shows the inclusion of MEKF-R to the conductive chain.

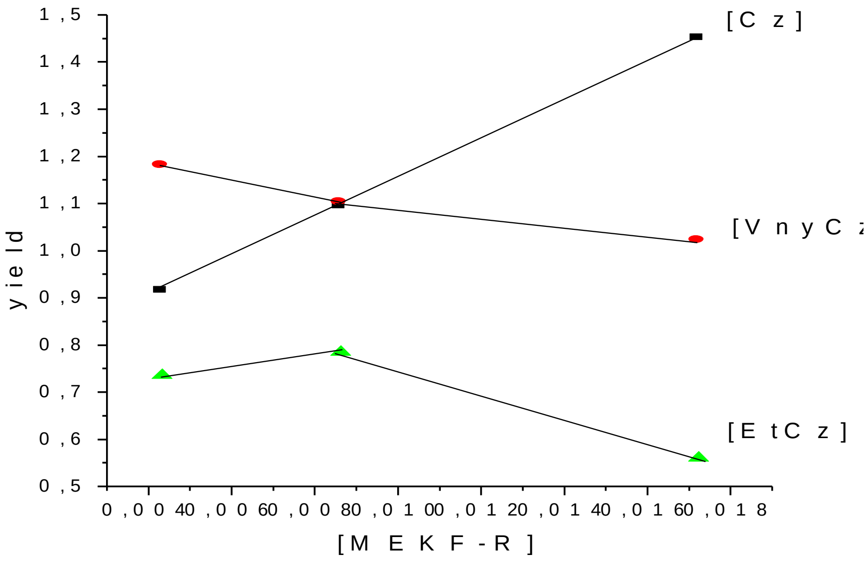


Figure 3a. The role of MEKF-R concentration on yield of precipitate I for Cz, NVCz and Ecz copolymers.

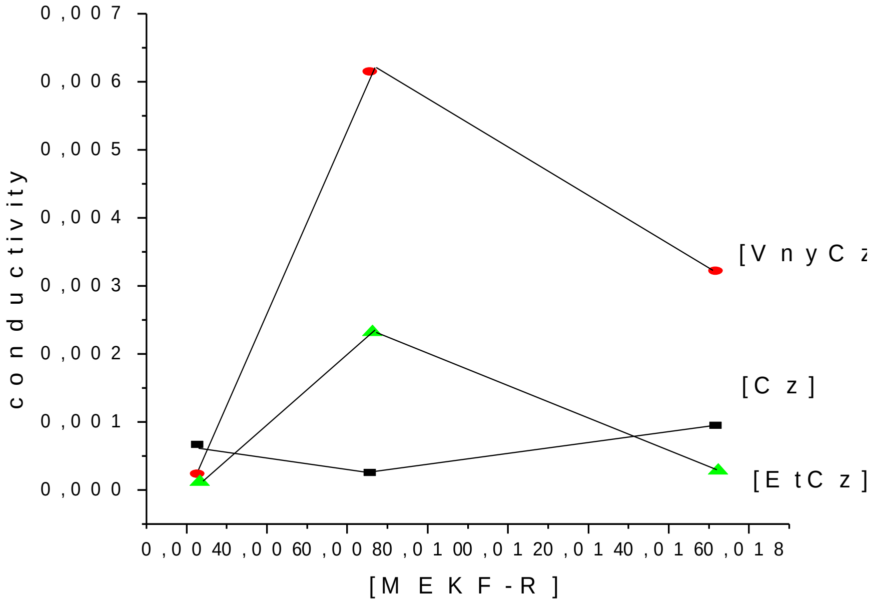


Figure 3b. The role of MEKF-R concentration on conductivity of precipitate I for Cz, NVCz, Ecz copolymers

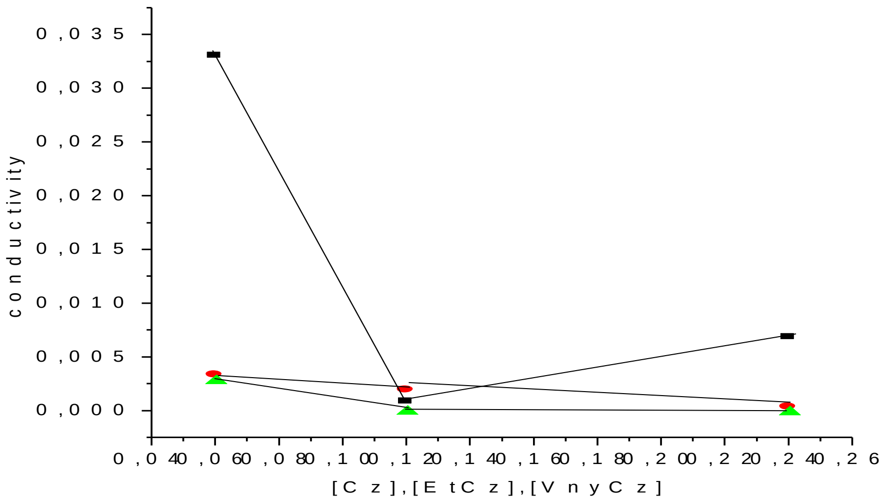


Figure 4a. The role of Cz, Ecz and NVCz concentrations on conductivity of precipitate I.

□ Cz ○ NVCz △ ECz

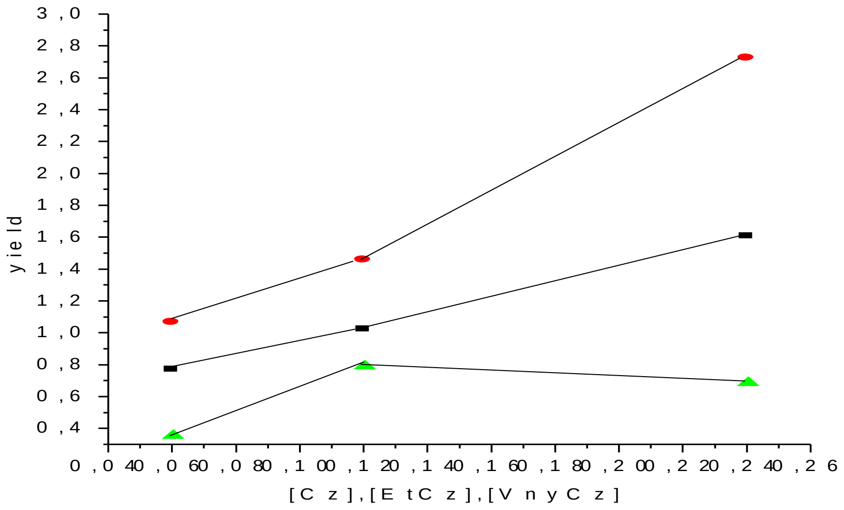


Figure 4b. The role of Cz, Ecz and NVCz concentrations on yield of precipitate I.

□ Cz ○ NVCz △ ECz

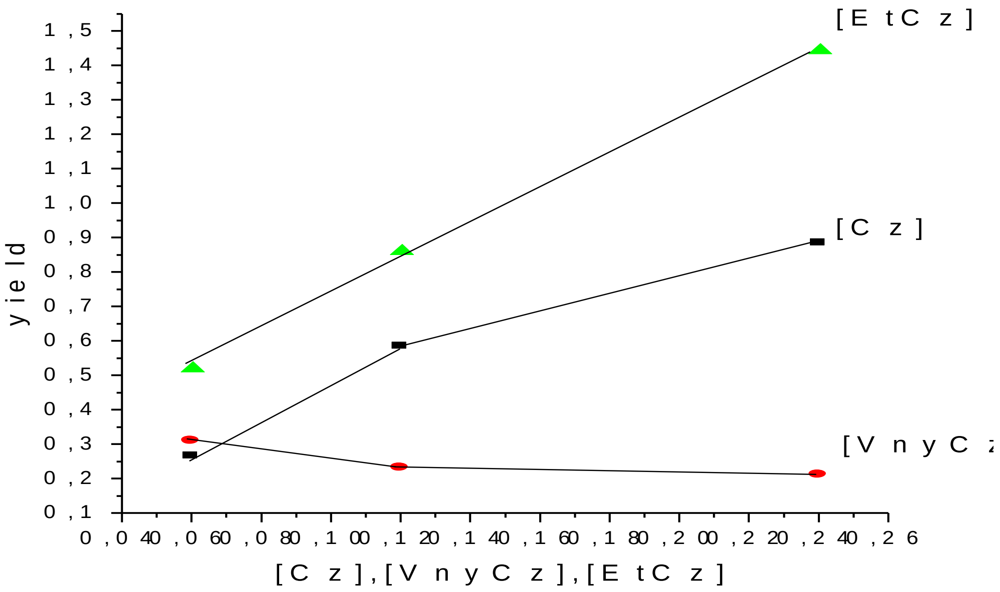


Figure 5a. The role of Cz, Ecz and NVCz concentrations on the yield of precipitate II

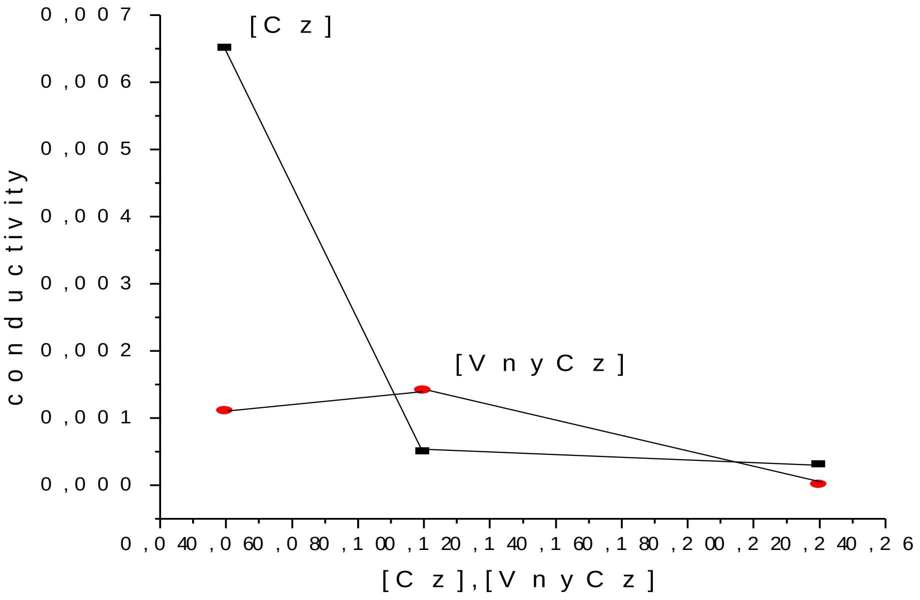


Figure 5b. The role of Cz and NVCz concentrations on the conductivity of precipitate II.

4.5. UV-Visible Analyses

The advantage of solubility of all copolymers UV-Visible measurements were done with DMF solution of products. The characteristic peak for polymer was observed at 260 nm. The change in absorbance values of precipitate I and precipitate II by increasing the monomer concentrations were given in Figure 6a, 6b, 6c and 7a, 7b, 7c. In all cases the absorbance values of precipitate I in DMF slightly increase by increasing monomer concentration and then decrease or stay constant. It means that the CAN concentration is not enough for polymerization of monomer after 0.12 M, regardless the substitution of Cz ring (8a and 8b). In addition to that, in the case of Cz the solution of precipitate II in DMF has an additional absorbance at 369 nm due to the Cz oligomers. This may be because of the reactivity ratio between Cz and its derivatives.

Figure 6a. The absorbance values of Cz copolymers solved in DMF (precipitate I).
0) PCz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

Figure 6(b). The absorbance values of Ecz copolymers solved in DMF (precipitate II)
0) PECz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

Figure 6(c). The absorbance value of NVCz copolymers solved in DMF (precipitate I) 0) PNVCz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

Absorbance values of precipitate II at 260 nm decrease slightly in the case of NVCz and ECz, but increases in the case of Cz. (Figure 7a, 7b, 7c)

Figure 7a. The absorbance value of Cz copolymers solved in DMF (precipitate II)
0) PCz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

Figure 7b. The absorbance value of Ecz copolymers solved in DMF (precipitate II)
0) PECz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

Figure 7 (c). The absorbance value of NVCz copolymers solved in DMF (precipitate II) 0) PNVCz 1) 0.06 M 2) 0.12 M 3) 0.24 M 4) MEKF-R

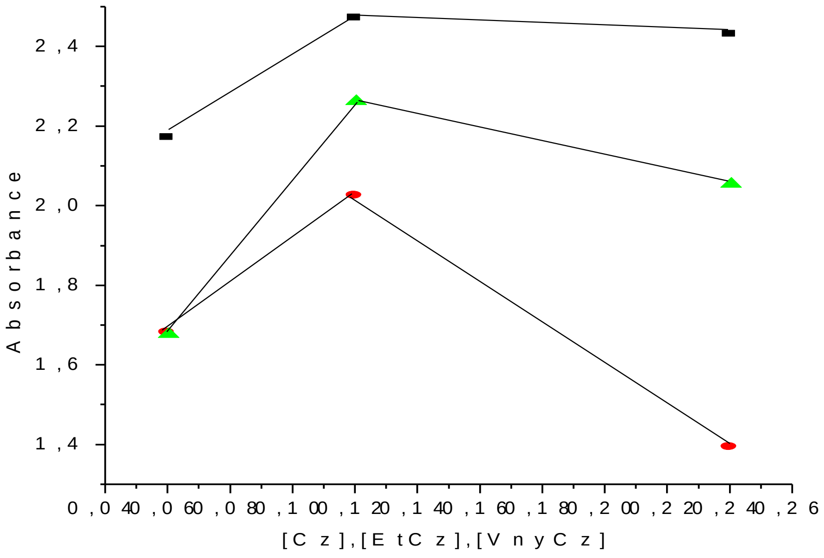


Figure 8 (a). The absorbance values versus Cz, Ecz and NVCz concentrations

○ NVCz □ Cz △ ECz

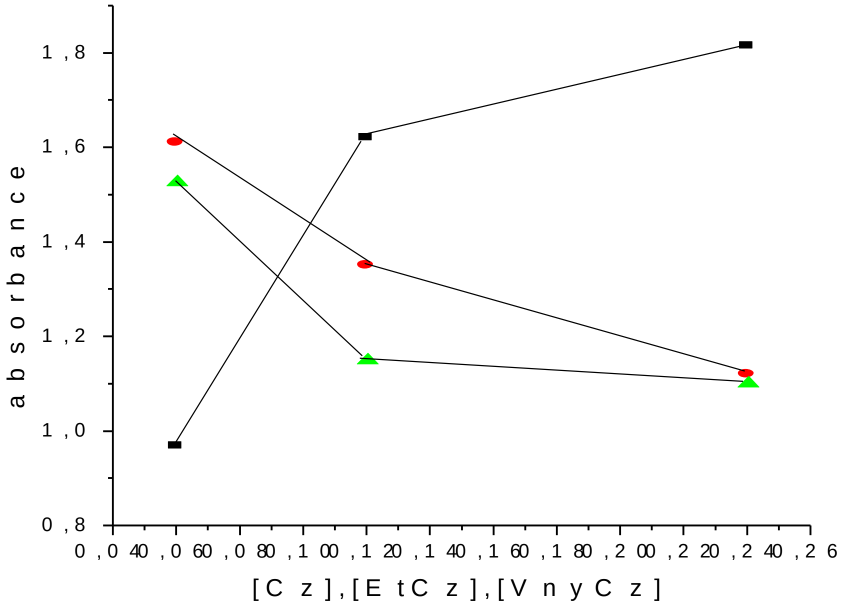


Figure 8 (b). The absorbance values versus Cz, Ecz and NVCz concentrations

○ NVCz ☐ Cz △ ECz

4.6. Viscosity Measurements

To understand the effect of Cz concentration on the chain length of copolymer, the viscosity of solutions obtained by dissolving precipitate I and precipitate II of samples in DMF which were polymerized by different Cz concentrations in DMF. The results are listed in Table 4.6.1 .

MEKF-R viscosity alone in DMF was 0.4 dl/gr and PCz was 0.56 dl/gr respectively. The similar viscosity values of precipitate I for all Cz concentrations indicates that the reaction rates of Cz monomer and MEKF-R are similar and the amount of MEKF-R in precipitate I is less than Cz. The structure of precipitate I and II indicates both Cz and MEKF-R, but precipitate II has a high amount of MEKF-R as expected from the other results. The lower viscosity value of precipitate II than the viscosity of PCz homopolymer, indicates the presence of Cz oligomers. A new peak at the UV Visible spectrum of Cz/MEKF-R copolymer solution in DMF also supports this idea (see Figure 6b). The inclusion of MEKF-R to the copolymer increases the viscosity of precipitate II.

Table 4.6.1. Viscosity differences of Cz copolymers obtained at different concentrations of Cz.

Concentration	η (dl/gr) Precipitate I	η (dl/gr) Precipitate II
0.06 M	0.27	0.04
0.12 M	0.28	0.17
0.24 M	0.29	1.03

Table 4.6.2. Viscosity differences of homopolymers and copolymers in insulator (white) and conductive (green) forms in toluene.

Polymer	Color	η (dl/gr)
PNVCz	White	0.04
PNVCz/MEKF-R	White	0.02
PNVCz	Green	0.05
PNVCz/MEKF-R	green	0.09

As it can be seen from Table 4.6.2, inclusion of MEKF-R to the chain via the vinyl group polymerization, slightly decreases the molecular weight of copolymer while the conductive form obtained by further addition of CAN to the white copolymer gradually converted into a green polymer due to the further oxidation of the carbazole rings.

4.7. Conductivity of Solutions

Increasing concentration values of Cz, Ecz and NVCz copolymers were taken and dissolved in DMF to measure the conductivity of the solution. The conductivity results support our conclusion for copolymerization of Cz, Ecz, NVCz with MEKF-R. As it can be seen from Figure 9a, increasing the monomer concentrations first cause a decrease in conductivity in solutions in the case of precipitate I. After 0.12 M monomer concentration, conductivities stay almost constant. This may be due to the termination of Cz radicals with MEKF-R radicals in the polymerization medium.

For precipitate II, solution conductivities of NVCz and ECz copolymer solution stay constant while Cz copolymer solutions increases (figure 9b). This result is parallel with absorbance values of precipitate II of Cz copolymers. This shows tha ability of releasing non-bonding electrons of N on the Cz ring in the absence of vinyl and ethyl groups which have both e- withdrawing and steric hindrance properties.

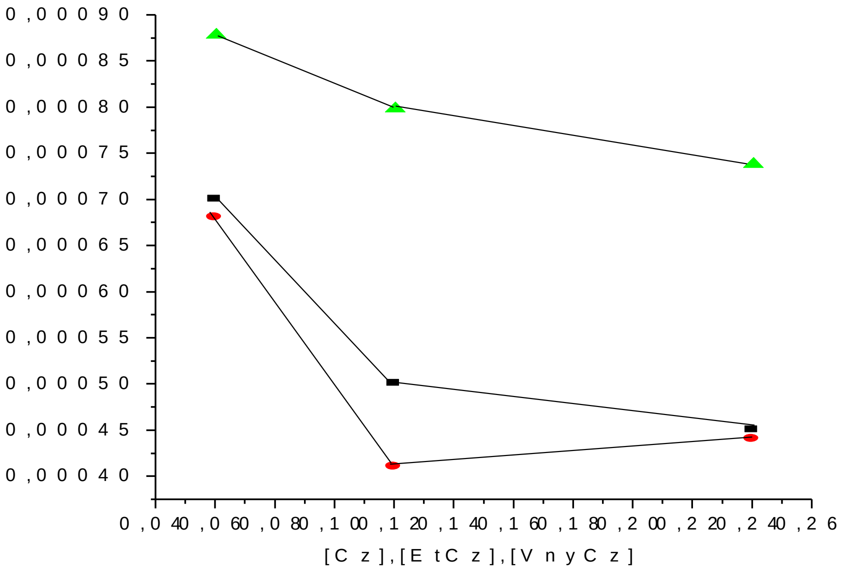


Figure 9a. The solution conductivities of Cz, Ecz and NVCz copolymers dissolved in DMF

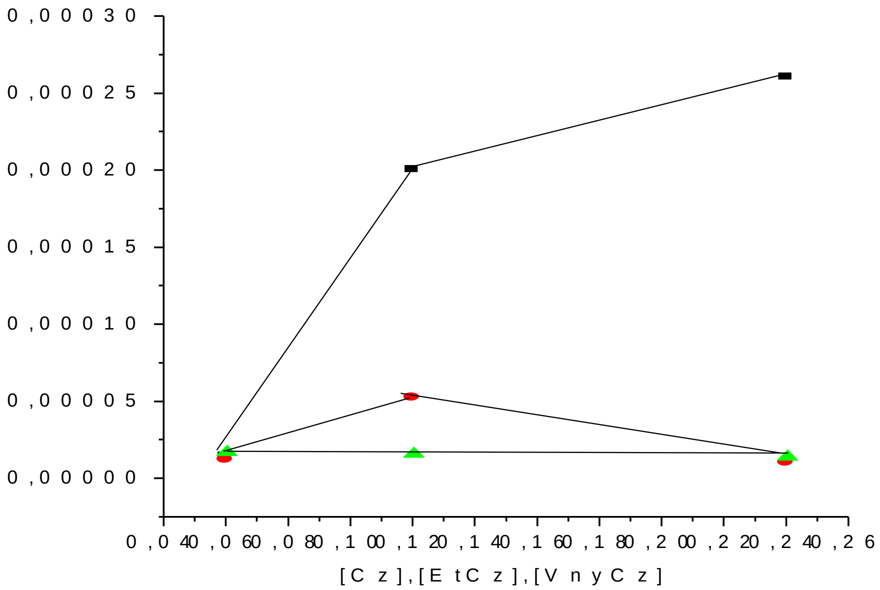


Figure 9b. The solution conductivities of Cz, Ecz and NVCz copolymers dissolved in DMF.

□ Cz ○ NVCz △ Ecz

4.8.Thermal Analyses

The DSC scan of PCz and PECz show no glass transition temperature (Tg) which is a characteristic property of conducting polymers. On the other hand it is known that PNVCz which is polymerized via the vinyl group has Tg at 227 ^{0}C. MEKF-R shows Tg at 131^{0}C and Tm at 92 ^{0}C (Figure 10). Precipitate I of all copolymers has Tm at 80 ^{0}C and Tg at 155 ^{0}C for NVCz copolymer (Figure 11a, 12a, 13a), this decrease in tg value in the case of copolymer with MEKF-R is not surprising. Because of higher MEKF-R content of precipitate II than precipitate I, Tg values of precipitate II for all case are lower than precipitate I (110 ^{0}C) (Figure 11b, 12b, 13b). Copolymer has a Tm still homopolymers have no Tm and inclusion of MEKF-R decrease the Tg supports the copolymerization.

Tm value of copolymer obtained electrochemically , at the highest n_{MEKF-R}/n_{Cz} ratio, was found as 90^0C. This result with the conductivity changes support the electrocopolymerization of Cz and MEKF-R.

Figure 10. DSC scan of MEKF-R

Figure 11a. DSC scan for precipitate I of Cz

Figure 11b. DSC scan for precipitate II of Cz

Figure 12a. DSC scan for precipitate I of NVCz

Figure 12b. DSC scan for precipitate II of NVCz

Figure 13a. DSC scan for precipitate I of ECz

Figure 13b. DSC scan for precipitate II of ECz

4.9. Electrochemical Polymerization

First, the colorless insulator form of PNVCz homopolymer and copolymer obtained from the polymerization of NVCz through only the vinyl group was prepared (Table 2.1). The white powder was solved in dichlorometan and was converted into green using TBAP as an electrolyte (Table 4.9.2.). Next, to compare the conductivity and solubility of Cz, Ecz and NVCz were polymerized electrochemically in the presence of MEKF-R and absence of MEKF-R in ACN using $NAClO_4$ as an electrolyte with the same concentrations of chemically method. (Table 4.9.1)

Chemical polymerization by can gives the advantages of obtaining PECz with high conductivities although tha anodic oxidation of Ecz does not produce films on the electrode in acetonitrile except on Au and glassy carbon electrodes in aqueous $HClO^4$ with conductivities of between 10^{-8} and 10^{-4} S/cm .

To discuss the amount of MEKF-R in copolymer and compare the conductivity results, MEKF-R concentration increases while Cz concentration is constant. The conductivity results are listed in Table 4.9.3.

To obtain a film of Ecz/MEKF-R copolymer on the stain steel prove the copolymerization. The decrease in conductivities of Cz and NVCz electropolymerized products support the inclusion of MEKF-R.

Table 4.9.1. Comparasion of conductivities of chemically and electrochemically prepared copolymers of Cz, Ecz and NVCz.

Cz Mol/lt	Ecz Mol/lt	NVCz Mol/lt	MEKF-R Mol/lt	Conductivity (S/cm)	
				Electrochemical	Chemically
0.12	-	-	$8.6x10^{-3}$	$8.5x10^{-4}$	$8.8x10^{-4}$
-	0.12	-	$8.6x10^{-3}$	-	$2.0x10^{-5}$
-	-	0.12	$8.6x10^{-3}$	$5x10^{-5}$	$1.91x10^{-3}$
0.12	-	-	-	$6.2 x10^{-2}$	$4.4x10^{-3}$
-	0.12	-	-	-	$1.8x10^{-4}$
-	-	0.12	-	$4.2x10^{-4}$	$2.2x10^{-3}$
$1.55x10^{-2}$	-	-	$3.1x10^{-3}$	$2.18x10^{-4}$	-
-	$1.55x10^{-2}$	-	$3.1x10^{-3}$	-	-
-	-	$1.55x10^{-2}$	$3.1x10^{-3}$	$1.2x10^{-4}$	-
-	$1.55x10^{-2}$	-	$1.63x10^{-2}$	$2.6x10^{-6}$	

Table 4.9.2.Conductivity differences of NVCz products due to the polymerization route.

Polymer	Chemical	Electrochemical	Colour	Conductivity (S/cm)
PNVCz	+		white	-
		+	Green	2.7x10^{-4}
NVCz/MEKF-R	+		White	-
	+		Green	1.91x10^{-3}
NVCz/MEKF-R		+	Green	5.1x10^{-5}
		+	Green	1.2x10^{-4}

Table 4.9.3. The role MEKF-R on the conductivity of electrochemically prepared copolymers of Cz

Carbazole (mol/lt)	MEKF-R (mol/lt)	Conductivity (S/cm)
1.55x10^{-2}	-	2.2x10^{-3}
1.55x10^{-2}	1.55x10^{-3}	5.0x10^{-4}
1.55x10^{-2}	3.10x10^{-3}	2.1x10^{-4}
1.55x10^{-2}	6.20x10^{-3}	4.0x10^{-5}
1.55x10^{-2}	1.63x10^{-2}	8.8x10^{-6}

4.10. Spectral Analyses

FT-IR Spectra of chemically prepared PCz by CAN and Cz/MEKF-R copolymer (precipitate I and precipitate II) are shown in Figure 15 in line I,II,III. Since n_{MEKF-R}/n_{Cz} ratio is very low (0.07), the peaks due to C=O stretching at about 1700 cm^{-1} appear not much clearly in the spectra of precipitate I. The presence of peak at this wavenumber shows the high enough MEKF-R inclusion to PCz chain in precipitate II. The similar results were observed in the case of NVCz and Ecz used as monomer (Figure 16 and Figure 17).

After polymerization of NVCz, the vinyl bands of monomer 860 and 960 cm^{-1}, are not present in the spectrum of colourless form of PNVCz, indicating that polymerization of NVCz monomer via the vinyl group (18). The lack of the peaks at the same wavenumbers in the spectra of colourless NVCz/MEKF-R copolymer shows the similar vinyl polymerization (Figure 18 line III).

The spectra also indicates Ce(III) and NO_3 ligands incorporated into the polymer. For the copolymerization of Cz with MEKF-R by using CAN, peak intensity at 1380 cm^{-1} due to N-O stretching of the nitro group increases with increasing metal ion concentration (Figure 19, lines I,II,III). However, there were no peaks at this wavenumber for both courless PNVCz homopolymer (Figure 18, line II) and colourless NVCz/MEKF-R copolymer (Figure 18 line III). This results show that if the CAN concentration high enough, it may be incorporated into the polymer.

In order to investigate the complexation possibility of carbonyl groups of resin with Ce(IV) and Cz, next experiment was performed. Sample 4 (Table 1) was obtained at the same monomer and resin concentration but the reaction time was 15 and 30 minute in this time instead of 1 hour. The same amount of MEKF-R was also reacted with CAN for 15 minutes in the absence of Cz monomer (blank experiment). The carbonyl peaks were clear only in the spectrum of blank experiment (Figure 20). The lack of carbonyl peaks in 15 minute in the presence of Cz shows the complex formation occurs between carbonyl groups of MEKF-R, metal and Cz. AAS results also support this idea which shows the presence of Me in the precipitate I and precipitate II (Table 7).

Since it is known that the characteristic peak of MEKF-R is about at 1700 cm^{-1} and except PNVCz, Cz and Ecz homopolymers do not have remarkable peaks at this wavenumber.

^{1}H-NMR and C^{13} NMR spectra of copolymers were given in Figure 21, 22 and 23. Similarly with FT-IR spectra, carbonyl peaks could not be seen.

In the ^{1}H –NMR spectra of Cz copolymer for precipitate I, chemically prepared with CAN, CH_3 protons relating to MEKF-R is obtained at 1 ppm surroundings. 6 items of aromatic H of CH related to PCZ is between at 6 ppm - 9 ppm (Figure 21).

In the case of 1H-NMR of NVCz copolymer polymerized with CAN, the peaks between 0.9 ppm and 2 ppm are related to both MEKF-R's CH_3 and CH and CH_2, CH of the vinyl groups of PNVCz. The peaks between 6-8 ppm are aromatic CH (Figure 22). In C^{13} NMR of NVCz copolymer for precipitate I, at 205 ppm carbon of C=O relating to MEKF-R is seen. Aromatic carbons are between 105-139 ppm and at 20 ppm CH_3's C of MEKF-R is obtained (Figure 18b).

In the case of ECz copolymer polymerized with CAN, the peak at 1.3 ppm is the aliphatic CH_3 proton of ethyl. 4.5 ppm is the aliphatic CH_2 bound to N and aromatic ring peaks are seen between 6.9 and 8.5 ppm. The ketonic resin is seen at 1 ppm (Figure 23).

^{1}HNMR and C^{13}NMR of MEKF-R is given in Figure 24 and 25. In C^{13} NMR the peak at 20 ppm is the carbon related to CH_3. 74 ppm means the methylol carbon and the carbonyl is obtained at 214 ppm. In ^{1}HNMR, protons of $CH_3$3 is at 1 ppm, protons of CH-CH_2 are at 1.6-2.1 and the protons of methylol group is between 3.1-3.4 ppm.

1^1HNMR of Ecz copolymer oxidized with $Cu(NO_3)_2$ shows a peak at 1 ppm of MEKF-R’s CH_3, methyl protons of Ecz at 1.3 ppm and at 4.4 ppm protons of CH_2 of Ecz. (Figure 26)

In the 1^1HNMR of Cz copolymer polymerized by Cu $(NO)_3$, peaks at 1 ppm and 2 ppm owns to aliphatic CH protons of MEKF-R and the aromatic ring peaks of Cz are observed at 7.1 and 8 ppm. (Figure 27)

4.11.Atomic Absorption Results

The metal contents of the insoluble part of copolymerization products (precipitate I), obtained by using different metals which have different oxidation potentials, were determined by Atomic Absorption Spectroscopy. The results were given in Table 7. The Fe(III) has the highest oxidation potential among the metal ions used in this study (0.77 V versus hydrogen electrode). Metal contents in insoluble parts (precipitate I) of Cz and Ecz copolymers oxidized by Fe(III) are higher than other products polymerized with Cu(II), Ni(II) and Zn (II) . Since Ce(IV) has higher oxidation potential than Fe(III), so similar results can be expected for Ce(IV). Thia result supports the idea of possibility of the complex formation between Ecz/ Cz-Metal amd MEKF-R.

Table 4.11.1. The effect of oxidation potential of metal used for oxidative copolymerization of Cz, Ecz and NVCz with MEKF-R

(Me)	Ox.Pot. (V)versus St.H_2 electrode	Monomer	MEKF-R	İnitial amount of Me (mEg)	Metal content in soluble part	Metal content in insoluble part
Fe(III)	0.77	Cz	-	0.410	0.363	0.047
			+	0.138	0.099	0.038
		Ecz	-	0.218	0.178	0.040
			+	0.254	0.185	0.068
Cu(II)	0.34	Cz	-	0.519	0.432	0.087
			+	0.161	0.125	0.035
		Ecz	-	0.200	0.151	0.048
			+	0.228	0.193	0.03
Ni(II)	-0.25	Cz	-	0.562	0.461	0.100
			+	0.061	0.04	0.021
		Ecz	-	0.370	0.157	0.212
			+	0.370	0.314	0.055
Zn(II)	-0.76	Cz	-	0.504	0.343	0.161
			+	0.156	0.039	0.116
		Ecz	-	0.126	0.084	0.041
			+	0.156	0.136	0.019

4.12. Elemental Analysis

Tablo 12.1. Elemental Analyses of electrocopolymerized Cz and MEKF-R

[Cz]	[MEKF-R]	% Oxygen
1.55×10^{-2}	-	33.23
1.55×10^{-2}	1.55×10^{-3}	28.54
1.55×10^{-2}	3.1×10^{-3}	30.65
1.55×10^{-2}	6.2×10^{-3}	31.31
1.55×10^{-2}	1.63×10^{-2}	30.65

Since the increase in MEKF-R resin, % O don’t increase. Because the amount of MEKF-R added to chain is very low.

Figure 15. FT-IR Spectra of chemically prepared PCz (I) by CAN and Cz/MEKF-R copolymer precipitate I (II) and precipitate II (III).

Figure 16. FT-IR Spectra of chemically prepared PNVCz (I) by CAN and NVCz/MEKF-R copolymer precipitate I (II) and precipitate II (III).

Figure 17. FT-IR Spectra of chemically prepared PECz (I) by CAN and ECz/MEKF-R copolymer precipitate I (II) and precipitate II (III).

Figure 18. FT-IR spectra of NVCz monomer (I), chemically prepared white PNVCz (II), chemically prepared white NVCz/MEKF-R copolymer (III)

Figure 19. FT-IR spectra of chemically prepared Cz/MEKF-R copolymer by inreasing CAN concentration I) 0.06 M II) 0.12 M III) 0.24 M

Figure 20. FT-IR spectra of chemically prepared Cz/MEKF-R copolymer with different reaction time I) 15 minute II) 30 minute III) 1 hour

Figure 21. ^{1}HNMR of Cz copolymer for precipitate I, chemically prepared with CAN

Figure 22. ^{1}HNMR of NVCz copolymer for precipitate I, chemically prepared with CAN

Figure 23. ^{1}HNMR of ECz copolymer for precipitate I, chemically prepared with CAN

Figure 24. ^{1}HNMR of MEKF-R

Figure 25. C^{13} NMR of MEKF-R

Figure 26. ^{1}HNMR of Ecz copolymer oxidized with Cu(NO)$_3$

Figure 27. C^{13} NMR of Cz copolymer polymerized with $Cu(NO)_3$

4.13.Mechanism

The initial step in the electropolymerization of NVCz is thought to be formation of NVCz radical cations at the anode surface [56]. The same mechanism has reported for Cz also .Since Ecz could not obtain on the electrode surface as homopolymer mechanism could be given for polymerization of Ecz . Polymerization in the solution can also be produced by oxidation of NVCz by Ce(IV) to form radical cations which can dimerize with the expulsion of H+ in the manner proposed for electrochemical synthesizes. The initial rate of NVCz cation radical formation in the chemical polymerization was reported in the presence of PEG [111].

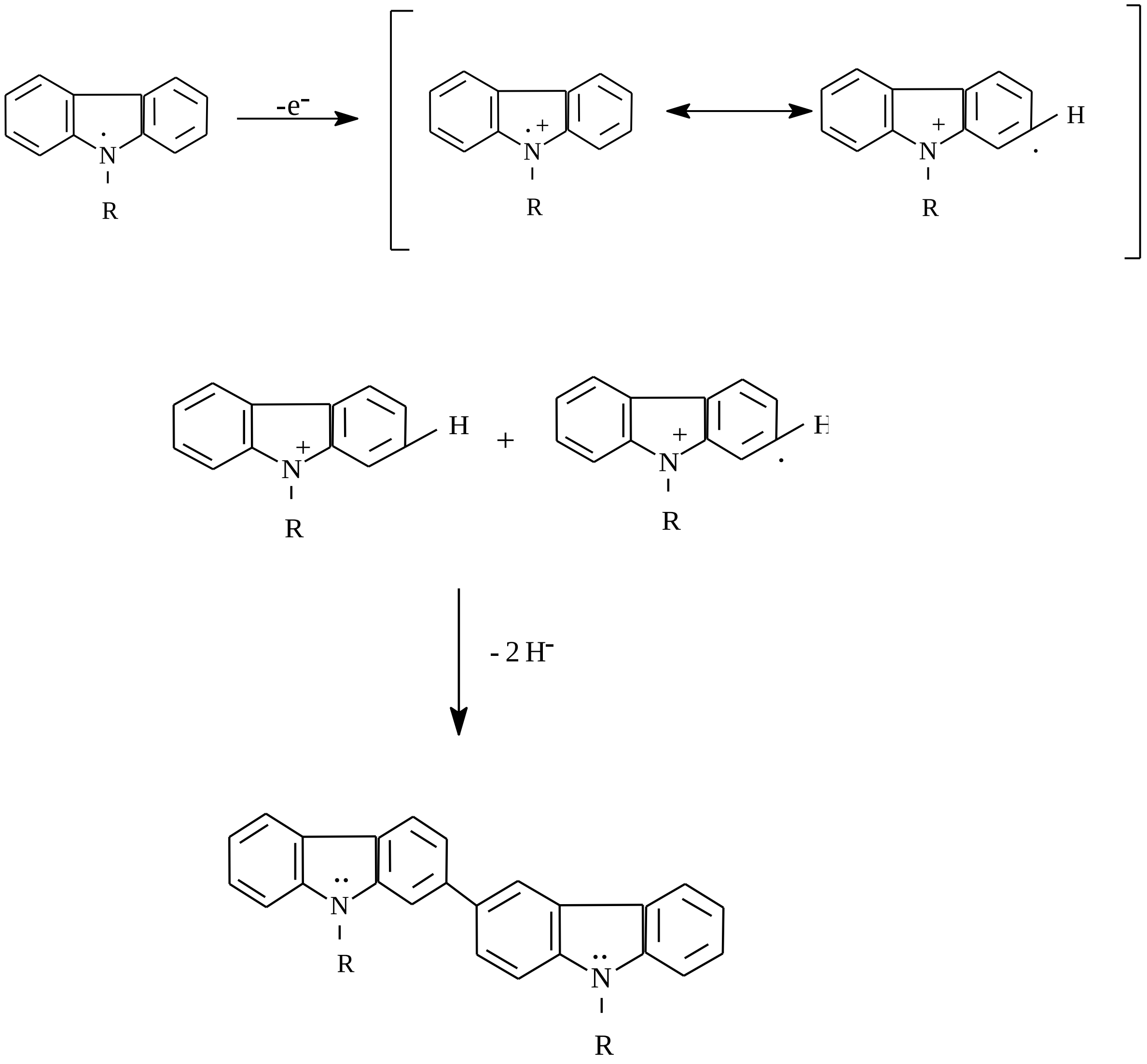
The second mechanistic possibility for the polymerization is proton loss of radical cation in the initiation step, to form radical that attacks another monomer molecule. Py can be copolymerized by MEKF-R and Si Tegomer by this mechanism [112].

On the other hand, formation of MEKF-R radical by Ce(IV) was proposed reported [113]. By using the addition order of MEKF-R, CAN and Cz, MEKF-R can find time to interact with Ce(IV) first. Thus, MEKF-R radicals and Ce (III)-MEKF-R and Cz/Ecz/NVCz-Ce(IV)-MEKF-R complexes are always present in the media.

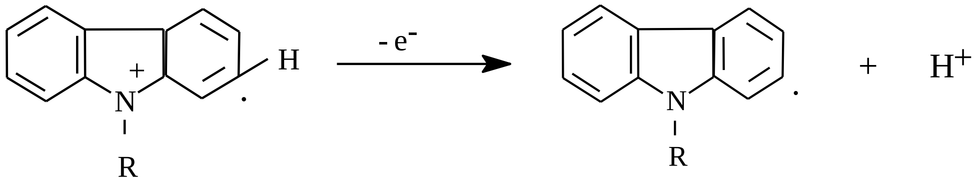
In the termination step, growing Cz, Ecz and NVCz radicals may combine with MEKF-R radicals to produce Cz-MEKF-R, Ecz-MEKF-R or NVCz-MEKF-R copolymers.

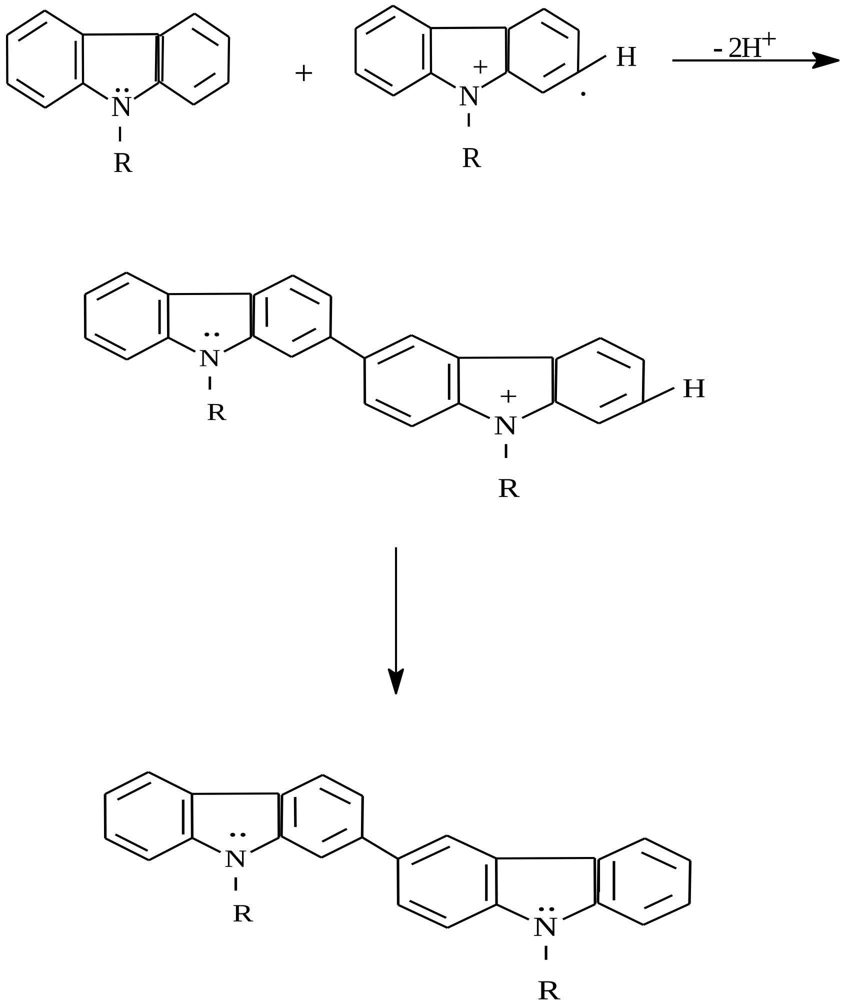
MECHANISM

Initiation:

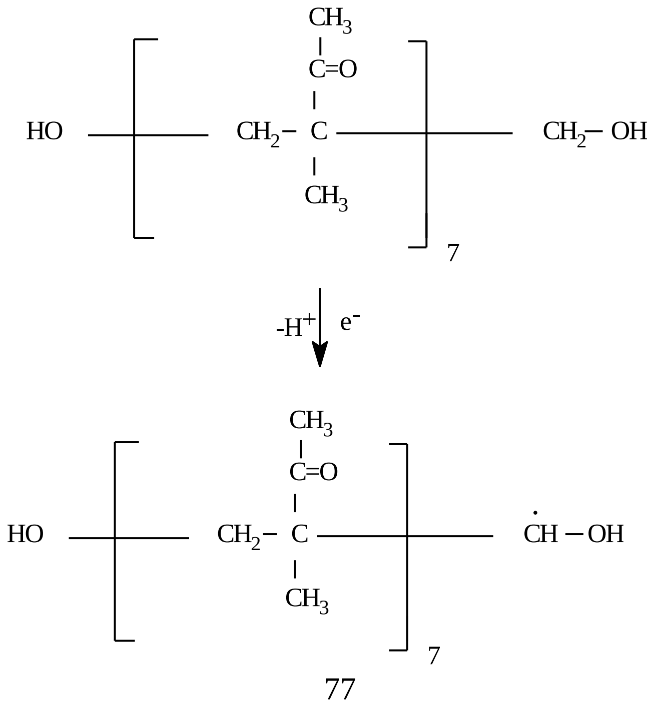


Dimer



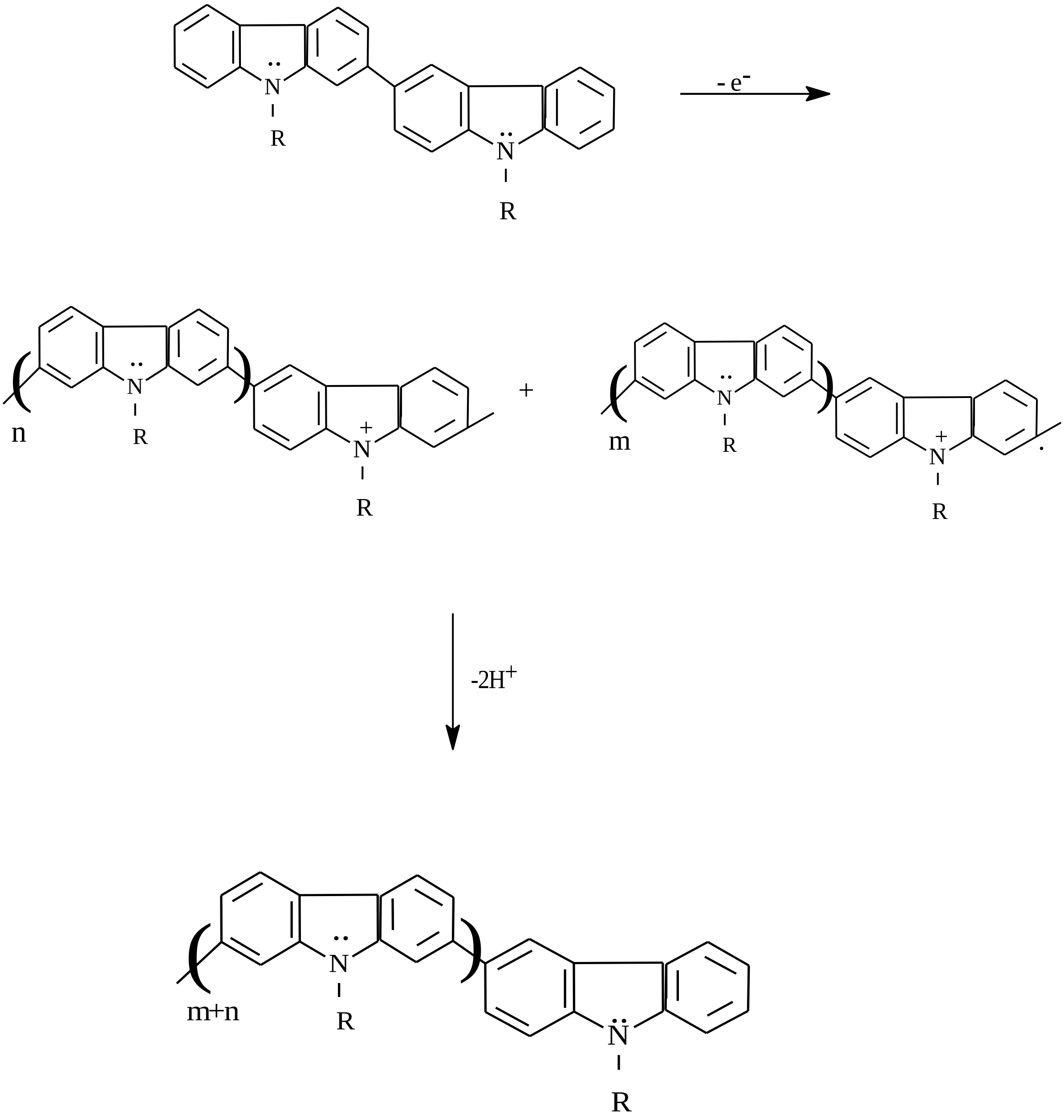


dimer

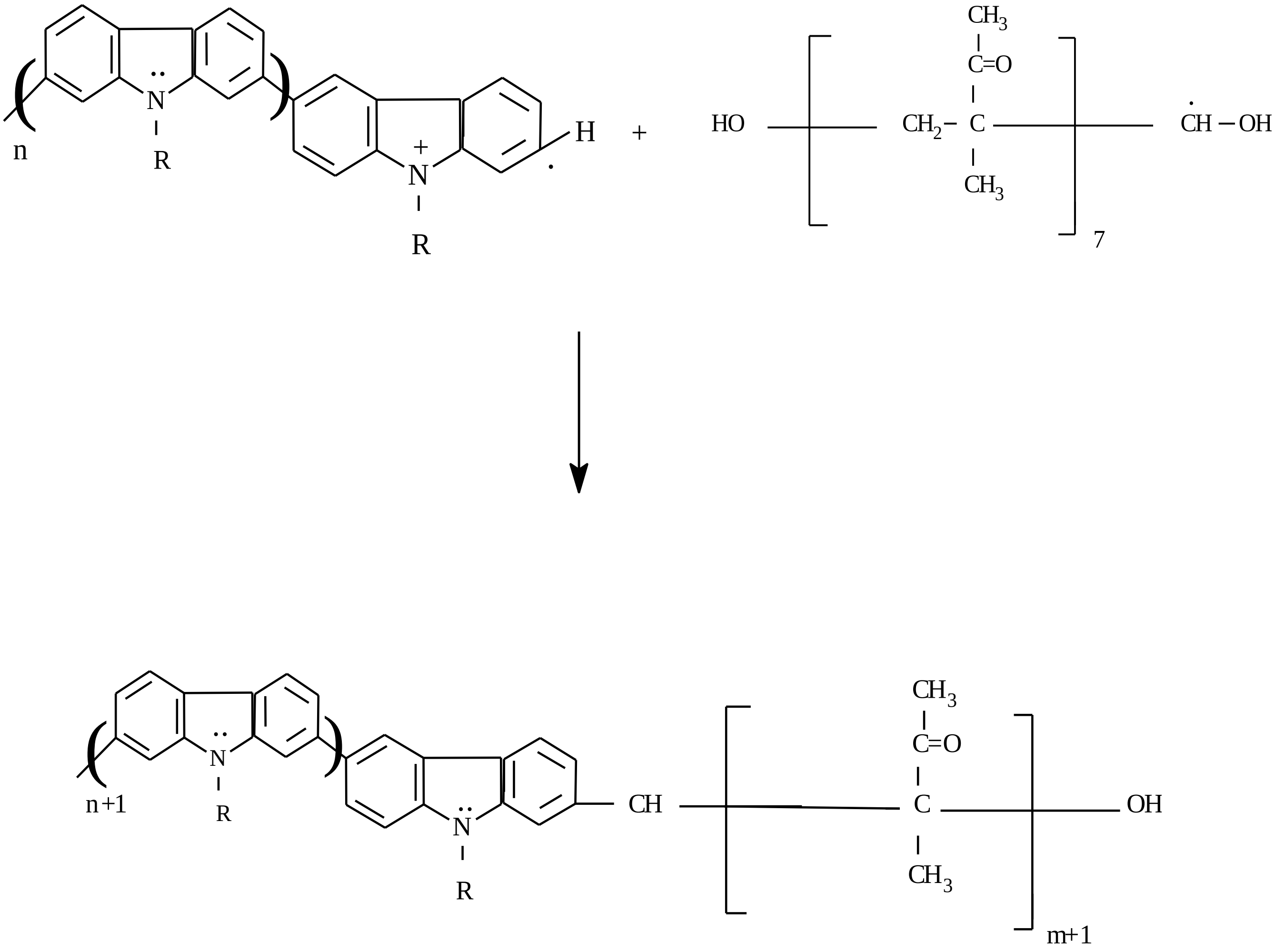


$$\mathrm{HO}\left[\mathrm{CH_2}-\overset{\overset{\displaystyle\mathrm{CH_3}}{|}}{\underset{\underset{\displaystyle\mathrm{CH_3}}{|}}{\overset{\displaystyle\mathrm{C{=}O}}{\overset{|}{\mathrm{C}}}}}\right]_7\mathrm{CH_2-OH}\xrightarrow{-\mathrm{H^+}\;\;e^-}\mathrm{HO}\left[\mathrm{CH_2}-\overset{\overset{\displaystyle\mathrm{CH_3}}{|}}{\underset{\underset{\displaystyle\mathrm{CH_3}}{|}}{\overset{\displaystyle\mathrm{C{=}O}}{\overset{|}{\mathrm{C}}}}}\right]_7\dot{\mathrm{C}}\mathrm{H-OH}$$

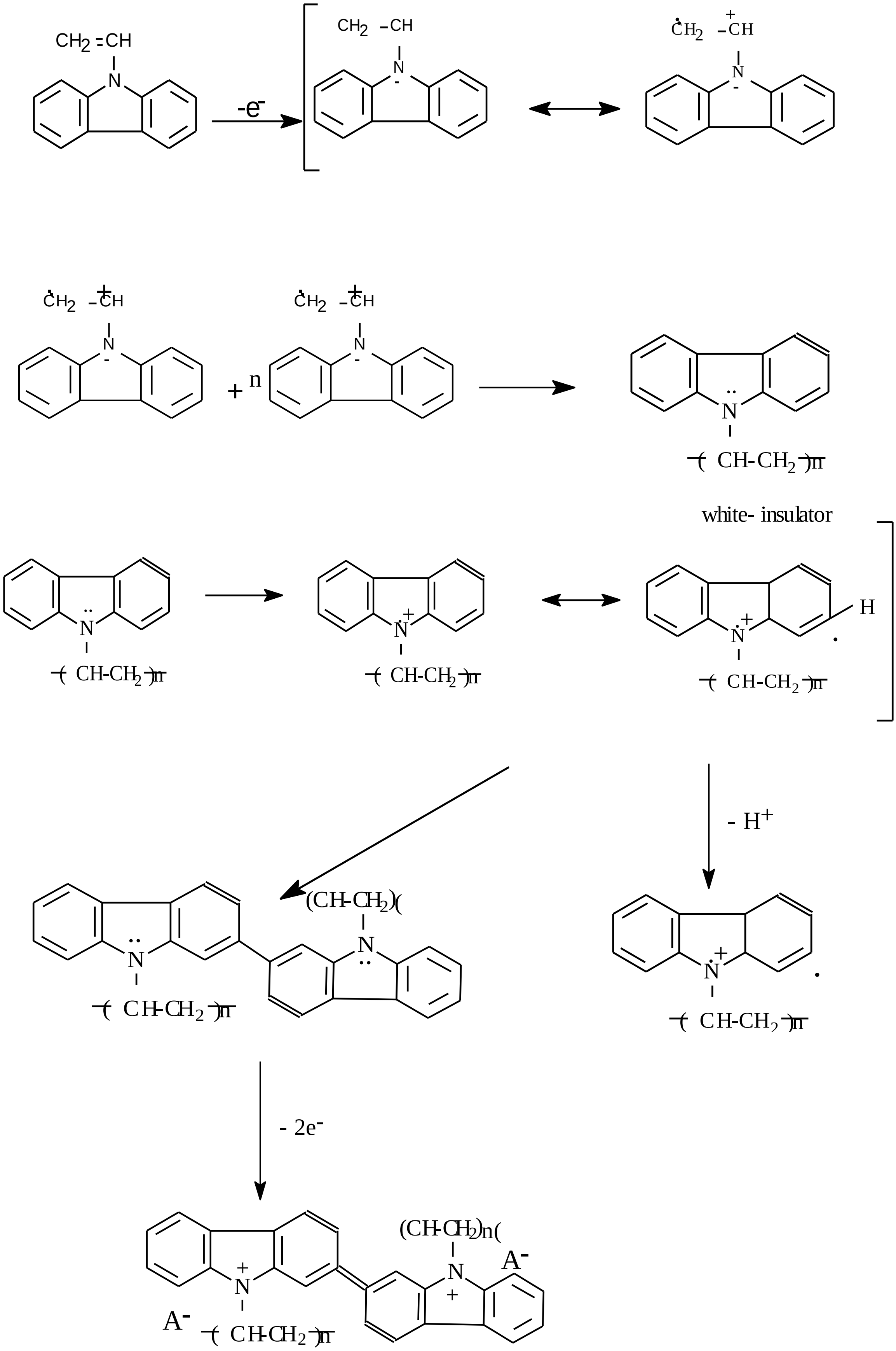
Propagation:



Termination:



R = H, CH_2CH_2



R = CH-CH$_2$

5. CONCLUSIONS

A new class of soluble and conductive Cz /Ecz/NVCz-MEKF-R copolymers were synthesized for the first time by oxidative and electrochemical polymerization routes. Both soluble and insoluble products were obtained according to the MEKF-R, oxidant and monomer concentrations.

Since PCz and derivatives are slightly soluble in DMF, inclusion of MEKF-R to the polymer chain was proved by obtaining totally soluble polymers. The decrease in conductivities of polymers also supports this inclusion. Although no experiments were done to obtain the reactivity ratio of monomer and resin, the similar conductivities of polymers, both soluble and insoluble parts in ACN proved the similar reactivities of monomer and resin. This idea is supported by UV-Visible results. UV-Visible and solution conductivity results show the steric effect of e-withdrawing (ethyl and vinyl) groups reduce the ability of releasing e- of nonbonding nitrogen electron, so absorbance and solution conductivity values of Cz copolymer found higher than the substitue monomers.

Because of the small ratio of n MEKF-R /nCz characteristic peak of resin could not be obtained clearly for insoluble products in ACN. Carbonyl peak of resin could be obtained only at C^{13} NMR spectrum of NVCz copolymer due to the copolymerization of NVCz with MEKF-R both via the vinyl group and carbazole ring. FT-IR results in different reaction time and the presence of Me in copolymers show together a complex between monomer-metal and resin.

The presence of Tm and Tg values at DSC measurements of polymers also support the copolymerization clearly. Since it is known that conducting polymers have no Tm and Tg value, except PNVCz (white and insulator).

Decrease in conductivity of copolymers and obtaining ECz-MEKF-R copolymer synthesized by electrochemically is the best prove of inclusion MEKF-R to the PECz chain since PECz gives no product alone by this route.

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