# Introduction

1.1 Polymer:

A polymer is a substance composed of molecules of large molecular mass composed of repeating structural units called monomers connected by covalent chemical bonds.Well known examples of polymers are plastics,DNA and protiens atc. The process by which the monomer molecules are linked to form a big polymer molecule is called polymeruzation.In chemical compounds polymerization occurs via different mechnisms which vary in complexity due to functional groups present in reacting compounds and their inherent steric effects.

Polymerization are of two types:

1.Addition polymerization

2.Condensation polmerization

Addition polymerisation, also called polyaddition or chain growth polymerization, is a polymerisation technique where unsaturated monomer molecules add on to a growing polymerchain one at a time. It can be represented with the chemical equation:

$$n\text{M (monomer)} \rightarrow \text{-(-M-)}_n\text{- (polymer)}$$
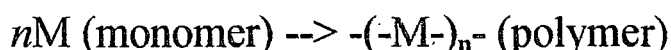
In this polymerization the monomer species retains its structaral identitywhen it gets converted into polymer.

Condensation polymerization, a form of step-growth polymerization, is a process by which two molecules join together, with the loss of a small molecule which is often water. The type of end product resulting from a condensation polymerization is dependent on the number of functional end groups of the monomer which can react. Monomers with only one reactive group terminate a growing chain, and thus give end products with a lower

molecular weight. Linear polymers are created using monomers with two reactive end groups and monomers with more than two end groups give three dimensional polymers which are crosslinked.

Most polymer research may be categorized as polymer science, a sub-discipline of materials science which includes researchers in chemistry, physics, and engineering. Polymer science may be roughly divided into two subdisciplines:

- Polymer chemistry or macromolecular chemistry, concerned with the chemical synthesis and chemical properties of polymers.

- Polymer physics, concerned with the bulk properties of polymer materials and engineering applications.

1.2 Properties and morphology of polymers:

Polymers do not have a perfectly ordered crystal lattice formation and not completely crystalline. X-ray diffraction analysis shows that polymer contain both crystalline and amorphous regions.
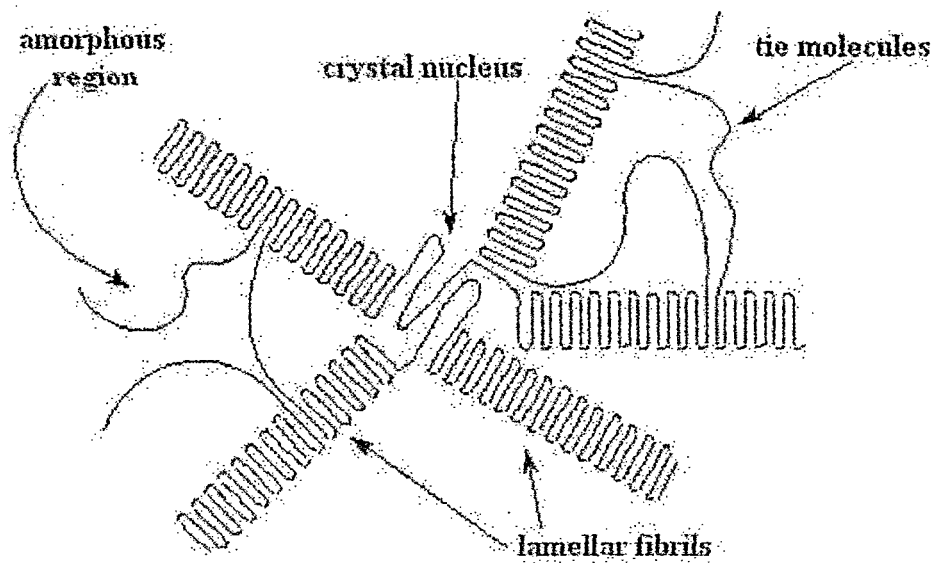
Figure 1.1: arrangement of polymer chains forming crystalline and amorphous regions in polymers

The crystalline and amorphous components influence polymerr properties in as much as the molecularb weight of a polymer is influenced by that of the various fractions which make the polymer. As we see in the fig the crystalline portion is in the lamellae, and the amorphous potion is outside the lamellae. In between the crystalline lamellae, there are regions where there is no order to the arrangement of the polymer chains. These disordered regions are the amorphous regions we were talking about. Thus a polymer shows mixed morphology.

Any polymer higher than its melting temperature (T_m) or freezing temperature (T_f) is in the form of a viscous melt. The melt is in a liquid phase where polymer chains exist in a completely disordered manner.

Monomer arrangement in copolymers

Monomers within a copolymer may be organized along the backbone in a variety of ways.

- Alternating copolymers possess regularly alternating monomer residues

- Periodic copolymers have monomer residue types arranged in a repeating sequence

- Random copolymers have a random sequence of monomer residue types

- Statistical copolymers have monomer residues arranged according to a known statistical rule

- Block copolymers have two or more homopolymer subunits linked by covalent bonds. Block copolymers with two or three distinct blocks are called diblock copolymers and triblock copolymers, respectively

Chain linearity

The simplest form of polymer molecule is a straight chain or linear polymer, composed of a single main chain. The flexibility of an unbranched chain polymer is characterized by its persistence length. A branched polymer molecule is composed of a main chain with one or more substituent side chains or branches. Special types of branched polymers include star polymers, comb polymers, and brush polymers. If the polymer contains a side chain that has a different composition or configuration than the main chain, the polymer is called a graft or grafted polymer. A cross-link suggests a branch point from which four or more distinct chains emanate. A polymer molecule with a high degree of crosslinking is referred to as a polymer network. Sufficiently high crosslink concentrations may lead to the formation of an 'infinite network', also known as a

'gel', in which networks of chains are of unlimited extend - there is essentially all chains have linked into one molecule.

Chain size

Polymer bulk properties may be strongly dependent on the size of the polymer chain. Like any molecule, a polymer molecule's size may be described in terms of molecularweightor mass. In polymers, however, the molecular mass may be expressed in terms of degree of polymerization, essentially the number of monomer units which comprise the polymer. For synthetic polymers, the molecular weight is expressed statistically to describe the distribution of molecular weights in the sample. This is because of the fact that almost all industrial processes produce a distribution of polymer chain sizes. Examples of such statistics include the number average molecular weight and weight average molecular weight. The ratio of these two values is the polydispersity index, commonly used to express the "width" of the molecular weight.

The space occupied by a polymer molecule is generally expressed in terms of radius of gyrationor excluded volume.

Chain length

Increasing chain length tends to decrease chain mobility, increase strength and toughness, and increase the glass transition temperature (Tg). This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length. These interactions tend to fix the individual chains more strongly in position and resist deformations and matrix breakup, both at higher stresses and higher temperatures.

Branching

Branching of polymer chains also affect the bulk properties of polymers. Long chain branches may increase polymer strength, toughness, and Tg due to an increase in the number of entanglements per chain. Random length and atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization. Short side chains may likewise reduce crystallinity due to disruption of the crystal structure. Reduced crystallinity may also be associated with increased transparency due to light scattering by small crystalline regions. A good example of this effect is related to the range of physical attributes of polyethylene. High density polyethylene (HDPE) has a very low degree of branching, is quite stiff, and is used in applications such as milk jugs. Low density polyethylene (LDPE), on the other hand, has significant numbers of short branches, is quite flexible, and is used in applications such as plastic films. The branching indexof the polymer is a parameter that characterizes the effect of long-chain branches on the size of a branched macromolecule in solution

Degree of crystallinity

Increasing degree of crystallinity tends to make a polymer more rigid. It can also lead to greater brittlness. Polymers with degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline / glassy regions

1.3 Electrolyte:

The substance which allows electricity to pass through its aqueous solution or in the fused state is called an electrolyte.An electrolyte is an ionic conductor and electronic insulator.Electrolytes are the medium through which ionic conduction takes place. Because they generally consist of ions in solution, electrolytes are also known as ionic solutions, but molten electrolytes and solid electrolytesare also possible.Depending upon

the phase we can classify the electrolytes into four types as follows:

1. Solid electrolyte

2. Liquid electrolyte

3. Polymer electrolyte

4. Composite electrolyte

1.4 Polymer electrolyte:

Polymer electrolytes may be considered as solutions of ionic salts in a polymer matrix that acts as an 'immobile solvent',unlike classical solid electrolytes ,both the anions and cations are mobile. The cations are coordinated to lone pairs on the hetero atoms of the polymer chain.

Another feature of polymer electrolytes is their propensity to attract moisture and retain solvent.Another aspect of polymer electrolyte behavior for certain systems,especially for those based on Rb salts.is phase separation of the crystalline salt at higher temperatures.The appearance of the salt crystal on the surface of some polymer electrolyte films at elevated temperatures suggests that these salt-polymer solutions exhibit lower critical solution temperature behavior.

Various attempts have been made to modify the structure of polymer electrolytes in order to enhance electrical and mechanical properties.The plasticization of polymer electrolyte using diethyle-carbonate,propelyne carbonate etc. greatly improve electrical conductivity. The plasticizers dissolve enough charge carriers and provide more mobile medeum for the ions to enhance conducting behaviour.

Another process to improve conductivity is the crosslinking of polymers.If the interaction between cation and polymer chain is strong then chemical cross linking occurs and

the cations become immobilized so that ionic conductivity is solely due to anions.

We can also increase conductivity by blending.A wide range of polymers have been blended using blend mixing processess.

1.5 Classification of polymer electrolytes:

1.5.1 Polymer salt complexes:

Solvent free polymer electrolytes such as poly(ethylene oxide)peo, poly(propylene oxide)ppo or their blend complex with suitable salts.Salts dissolve only in those polymers for which exothermic ion polymer inetractions compensate for lattice energy of the salt so as to reduce then free energy of the system

1.5.2 Plasicized polymer electrolyte

In these types of electrolyte small amount of low molar mass polar liquids are added to first type of electrolytes.Plasticized polymer electrolytes represent a compromise between polymer and liquid electrolytes.

1.5.3 Rubbery electrolytes

In these electrlytes high molar mass polymers are dissolved in low temperature molten salt mixtures forming a rubbery matarial. These polymers have glass transition low enough to remain rubbery at room temperature.

1.5.4 Composite polymer electrolytes

In these type of electrolytes nano to micron size inorganic particles are introduced in to a polymer electrolyte. In addition to

improvements in the ionic conductivity, the mechanical strenght and intrfacial stability are also enhanced in composites.Enhancement of conductuvity in this type of eletrolyte is attributed to reduction of crystallinity and polymer ceramic grain bounderies with high defect concentration that may allow better ion transport.

1.5.5 Gel polymer electrlytes

These electrolytes are prepsred by immobilizing a non aqueous electrolyte solution within an inactive structural polymer matrix or by increasing the viscosity of a liquid electrolyte by adding a suitable polymer .

1.6 Mechanism of ion conduction in poly(ehylene oxide):

Ionic solids dissolve in heteropolymers such as PEO because the lone pair electrons on the polymer oxygen coordinate with the cation.An indivitual cation is linked to several heteroatoms at any instant of time,old coordination links breaking and formation of new links take place as the ion moves in the polymer chain.The Li ions which move along the PEOchannel via the types of step illustrated in Fig. 1.2 Li-ion displacement to create an ion pair leaves behind a vacancy and an uncoordinated Oet atom (Fig. 1.2a). This vacancy is subsequently occupied by a Li-ion (Fig. 1.2b), and the ion pair finally breaks (Fig. 1.2c). In this way, a sequence of Li-ions moves along the channel. The picture is shown in the next page.
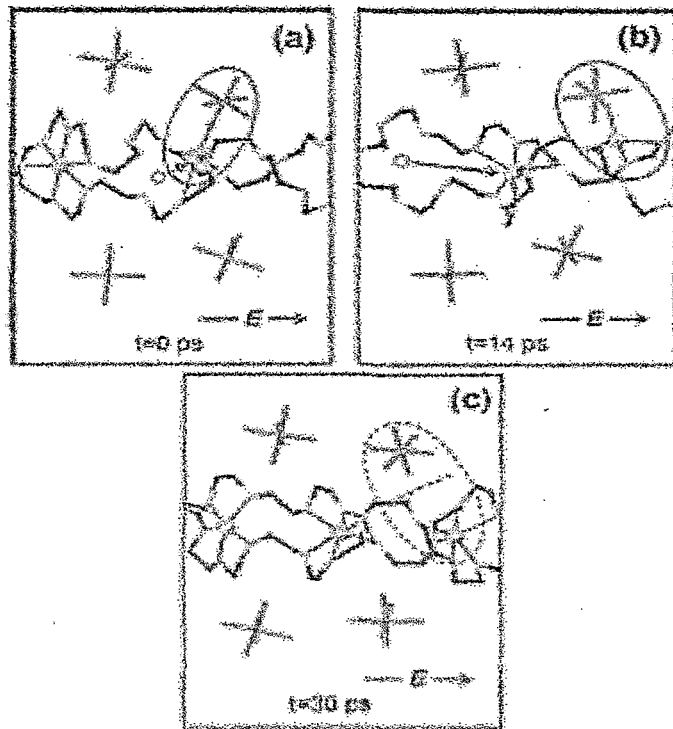
Fig   1.2:An
anion-mediated Li-ion-conduction mechanism inside a
PEO channel: (a) ion-pair formation; followed by (b) ion-pair
migration and simultaneous Li-occupation of the vacancy site left
as a result of the pair formation; and finally (c) ion-pair breaking
and Li-occupation of an available vacancy site.

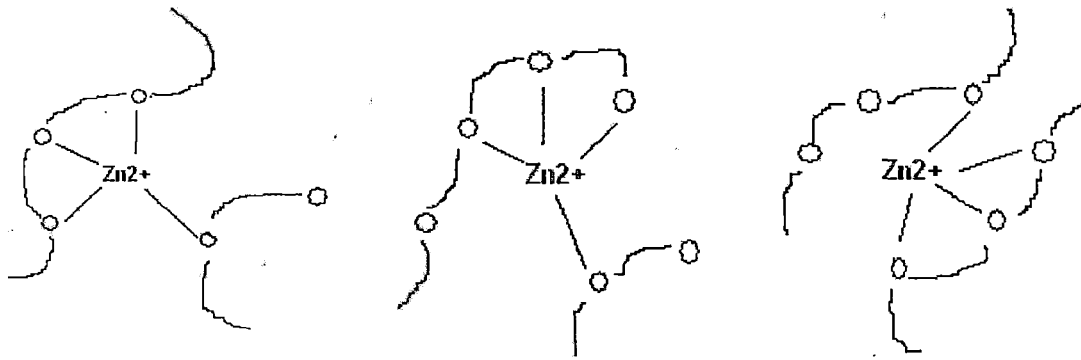A clearer picture of ion conduction in PEO taking Zn^{2+} as an
example is shown in figure in next page

Fig 1.3: Schematic representation of a Zn^{2+} ion moving along PEO that are themselves flexing.

The hetero atoms to which the cat ions are coordinated may well belong to more than one polymer chain .Such chins are therefore temporarily linked together by their common bonding to an individual cation.Such indirectly connected chains cannot display their normal unfettered long chain segmental motion. This can be disadvantageous for ionic conductivity as there is some degree of coupling between polymer flexibility and ionic motion.

1.7 Ion-matrix interactions, salvation and ion sites:

The cationic transport process in polymer electrolyte can be envisaged as a "roll on" mechanism in which the cat ion is initially coordinated to several oxygen atoms; the linkages to one or more of the polymer segments that lie behind the direction of motion of the cat ion break and new linkages are formed in the forward direction .The cat ion motion is facilitated by the flexing of polymer chain segments which allows old links to be broken and new attachments to be made. The unique type of ion matrix interaction that is found in polymer electrolytes produces a strong coupling between the segmented motions of the polymer and the

transport of the ion , the study of which has formed the basis of a considerable body of work .

1.8 Copolymer:

A heteropolymer or copolymer is a polymer derived from two (or more) monomeric species, as opposed to a homopolymer where only one monomer is used. Copolymerization refers to methods used to chemically synthesize a copolymer.

Since a copolymer consists of at least two types of constitutional units (not structural units), copolymers can be classified based on how these units are arranged along the chain. These include:

- **Alternating copolymers** with regular alternating A and B units (2)

- **Periodic copolymers** with A and B units arranged in a repeating sequence (e.g. $(A-B-A-B-B-A-A-A-A-B-B-B)_n$

- **Random copolymers** with random sequences of monomer A and B (3)

- **Statistical copolymers** in which the ordering of the distinct monomers within the polymer sequence obeys known statistical rules

- **Block copolymers** comprised of two or more homopolymer subunits linked by covalent bonds (4). The union of the homopolymer subunits may require an intermediate non-repeating subunit, known as a **junction block**. Block copolymers with two or three distinct blocks are called **diblock copolymers and triblock copolymers**, respectively.
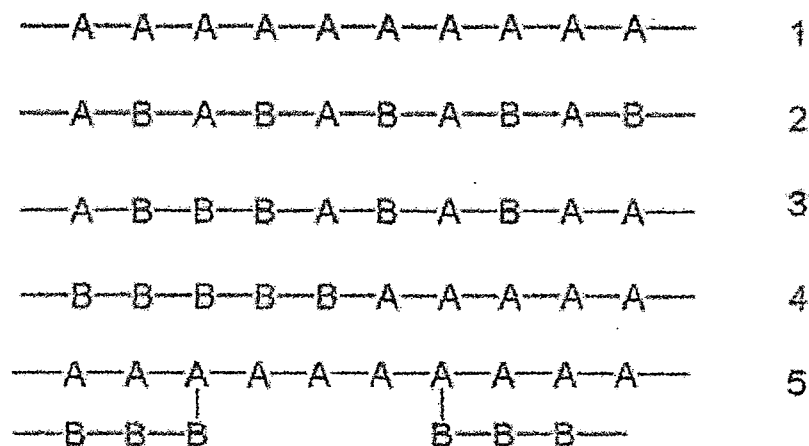
The figure is shown in the next page

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——A——A——A——A——A——A——A——A——A——A——        1

——A——B——A——B——A——B——A——B——A——B——        2

——A——B——B——B——A——B——A——B——A——A——        3

——B——B——B——B——B——A——A——A——A——A——        4

——A——A——A——A——A——A——A——A——A——A——        5
——B——B——B          B——B——B——
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Fig 1.4: Different copolymers

1.9 Polymer blends:

A macroscopically homogeneous mixture of two or more different species of *polymer*.

1. In most cases, blends are homogeneous on scales smaller than several times visual optical wavelengths.

2. For polymer blends, no account is taken of the miscibility or *immiscibility of the constituent polymers*, i.e. *no assumption is made regarding the number of phases present*.

A few polymer pairs mix. Most don't. But there are also polymer pairs that sometimes mix and sometimes don't. The variables that one can control to make them mix or not mix are usually temperature and composition. A lot of polymer pairs are only miscible when there is a lot more of one polymer than of the other. There will be a range of compositions for which the two polymers won't mix. For example, let's say we have two polymers, polymer A and polymer B. Let's also say they are miscible when we have less than 30% polymer B, that they are miscible when there is more than 70% polymer B. But between 30 and 70%

polymer B, the blend phase-separates into two phases. Here's a graph for those who of you who like that sort of thing:

miscible	immiscible	miscible

0   30   70   100
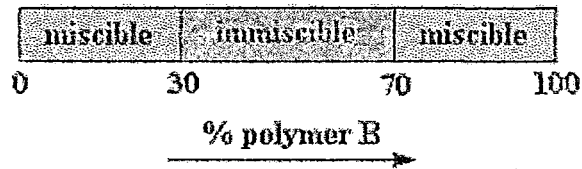
% polymer B →

Interestingly, one phase will have 30% polymer B and the other will have 70% polymer B. There's a reason for this. If we look at a plot of free energy versus composition, we'll see that these two compositions are lower in energy than any other compositions.
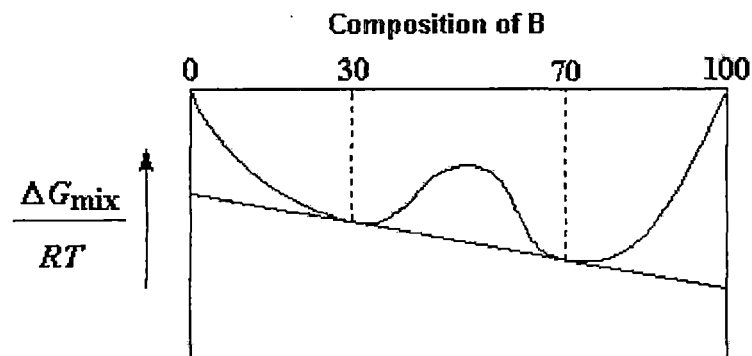
Composition of B

0   30   70   100

$$\frac{\Delta G_{mix}}{RT}$$

Fig 1.5: Energy versus composit6ion of polymer b curve

So these are the most stable compositions possible, and any mixture between 30 and 70 % polymer B will phase separate into a 30% polymer B phase and a 70 % polymer B phase.

1.10Polyaniline Nano fibers:

Polyaniline is unique among the family of conjugated polymers since its doping level can be readily controlled through an acid doping /base dedoping process. Due to its conducting properties it has potential application including light weight battery electrodes, anticorrosion coating, tissue scaffold and sensors. Nanostructures polyaniline (nanofibers/ rods) offers the possibility of enhanced performance wherever a high interfacial area between polyaniline nanofibers and environment is important. For example, in sensor application and biological application. Such materials are till now not used sufficiently, likely due to facile and reliable method for making high quality nanofibers .In the present work polyaniline nanofibers are synthesized by a gentle interfacial polymerization route, which do not require any template and are not dependant on any complex do pants. The synthesis can be carried out in a single pot with a wide choice of solvent pairs, acid do pants, and reagent concentration over a broad range of temperature.
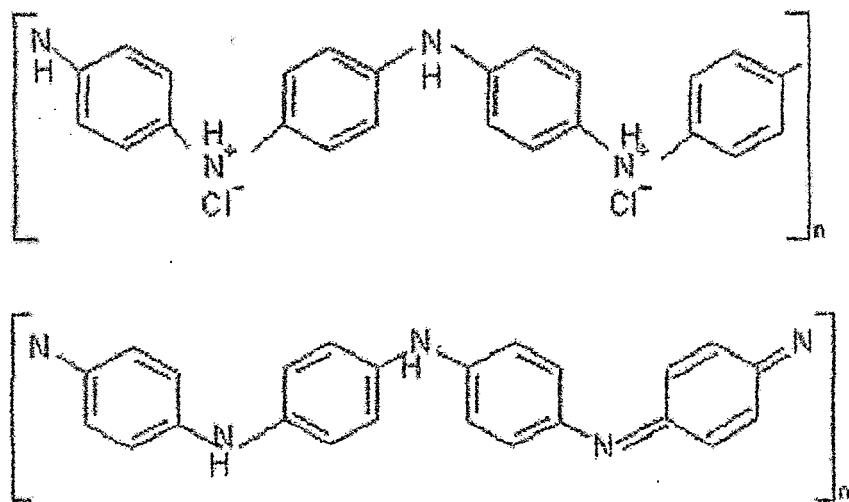
Figure1.6: Schematic of HCl doped conducting form of polyaniline and undoped form of polyaniline

1.11 Formation mechanism of Polyaniline nanofibers:

It has been known from the early years of conducting polymer research that polyaniline fibers of approx. 100nm in diameter can form naturally during electrochemical polymerization on the surface of the electrodes. The basic morphological unit for chemically synthesized polyaniline also appears to be nanofibers with diameter of tens of nanometers. Through careful observations, a small amount of nanofibers can be found among the irregularly shaped particulates in conventionally synthesized polyaniline. This gives the idea of synthesis of polyaniline nanofibers without any structural directing agent. A transition from pure, well defined nanofibers, to irregularly shaped, micron scale particulates was observed during the polymerization reaction. The overgrowth of polyaniline on the initially formed nanofibers scaffolds seems to be responsible for the final agglomerates in the product. This reaction mechanism is based on the principle of suppressation of secondary growth.

In this method, the reaction is placed in a heterogeneous biphasic system, where the polymerization occurs prime rally at the interface. Since the as-made polyaniline product is synthesized in its hydrophilic Emeraldine salt form, it diffuses away from the reactive interface into the water layer. In this way, the nanofibers formed at the interface are collected in the water layer without severe secondary growth.
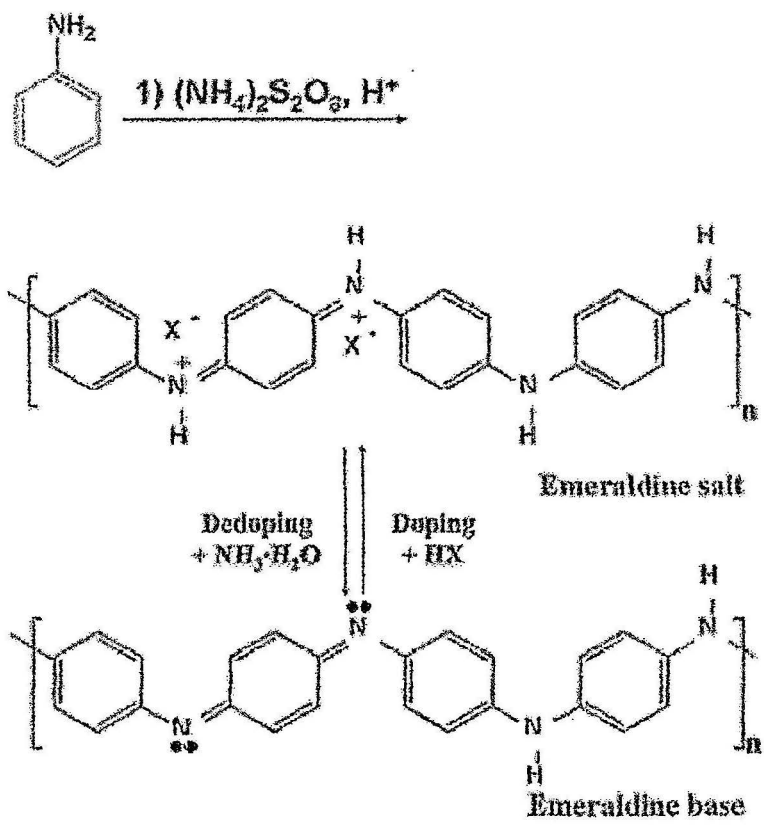
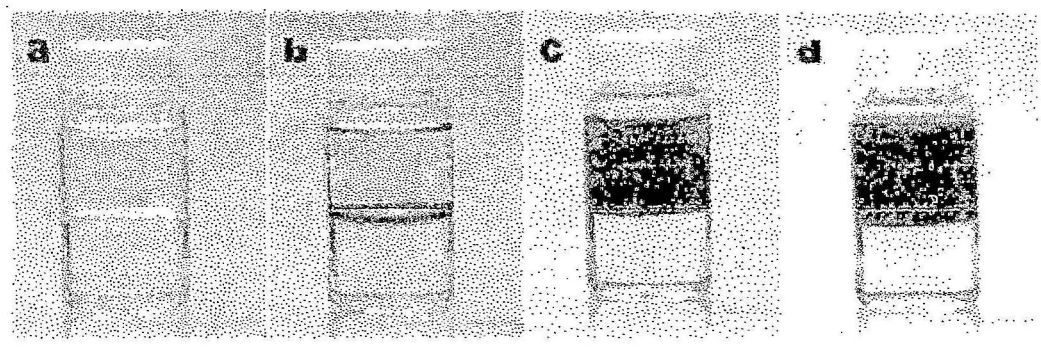Figure1.7: The oxidative polymerization reaction carried out in an acid solution.

Figure1.8: (a) An aqueous solution of acid and oxidant and an organic solution of aniline are brought together to form an interface (b) Polyaniline first forms at the interface and then (c) Diffusion in to the water layer (d) Complete diffusion in the water layer.

Chapter Two
Experimental Details

2.1 Parent Materials:

Poly(ethylene oxide) PEO (Mw=400000) and Poly(vinylidene fluoride-co-hexafluoropropylene) (Mw=400000) polymers were procured from Aldrich Chemicals Inc.(USA).Organic solvent acetonitrile was procured from E-Merck (Germany)
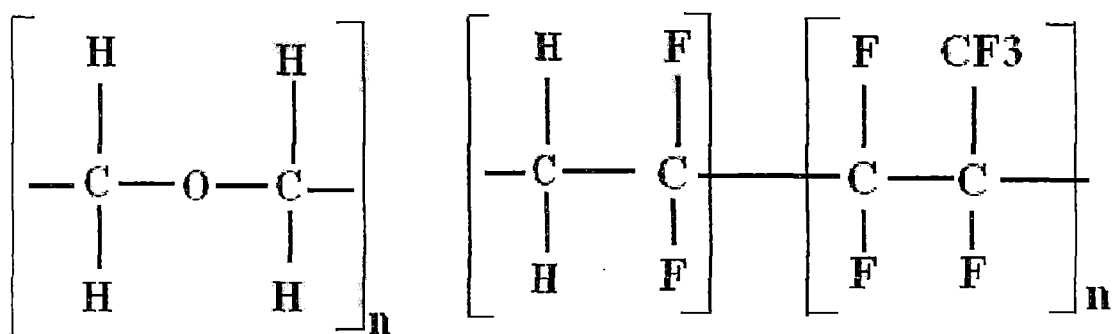
PEO   P(VDF-HFP)

Figure 2.1 shows the structure of two polymers that was used in my work.

Table 2.1 shows some basic physical properties of the two polymers

Polymers	Glass transition temperature Tg(°C)	Melting point (°C)	Tensile strength (N/mm^2)	Dielectric constant at 1MHz	Density (gm/cm^3)	Water absorption @ 24 hrs
PEO					1.13	
P(VDF-HFP)	-100-(-90)	140	28-41	7.5		1.78

2.2 Method of synthesis:

The mixing of polymer and salt make the polymer electrolyte and then the prepared polyaniline nano fiber is added while stirring and thin film of that sample is made by solution casting technique. I have taken P(VDF-HFP) at 40% weight of PEO and I have made five samples taking different weight percentage of polyaniline nanofiber.

Polymer electrolyte films were synthesized by so9lution casting technique involving the following steps.

1. PEO polymer was dissolved in acetonitrile solvent.

2. P(VDF-HFP) was dissolved in acetone

3. The salt $LiCl_4$ was dissolved in acetonitrile

4. Firstly PEO and the salt were mixed together in a beaker and magnetically stirred during continuous heating for 7-8 hours at 50°c .

5. P(VDF-HFP) was added to the polymer salt when it became a little viscous and allowed to stir.

6. The dedoped polyaniline nano fiber prepared previously was then added while stirring is allowed for 7-8 hours until it became complete viscous.

7. The above viscous solution was then cast on glass-plate and allowed to dry.

I have chosen 40 weight percentage of P(VDF-HFP) because at this percentage the conductivity of PEO-P(VDF-HFP) becomes maximum. The Polyaniline nano fiber was prepared by interfacial polymerization and then dedoped by sodium hydroxide. I have taken different weight percentage of the nano fiber in PEO-P(VDF-HFP) starting from 5 up to 25 at regular intervals of five . I have prepared 5 samples. The preparation technique for Polyaniline nano fiber is given in the next page.
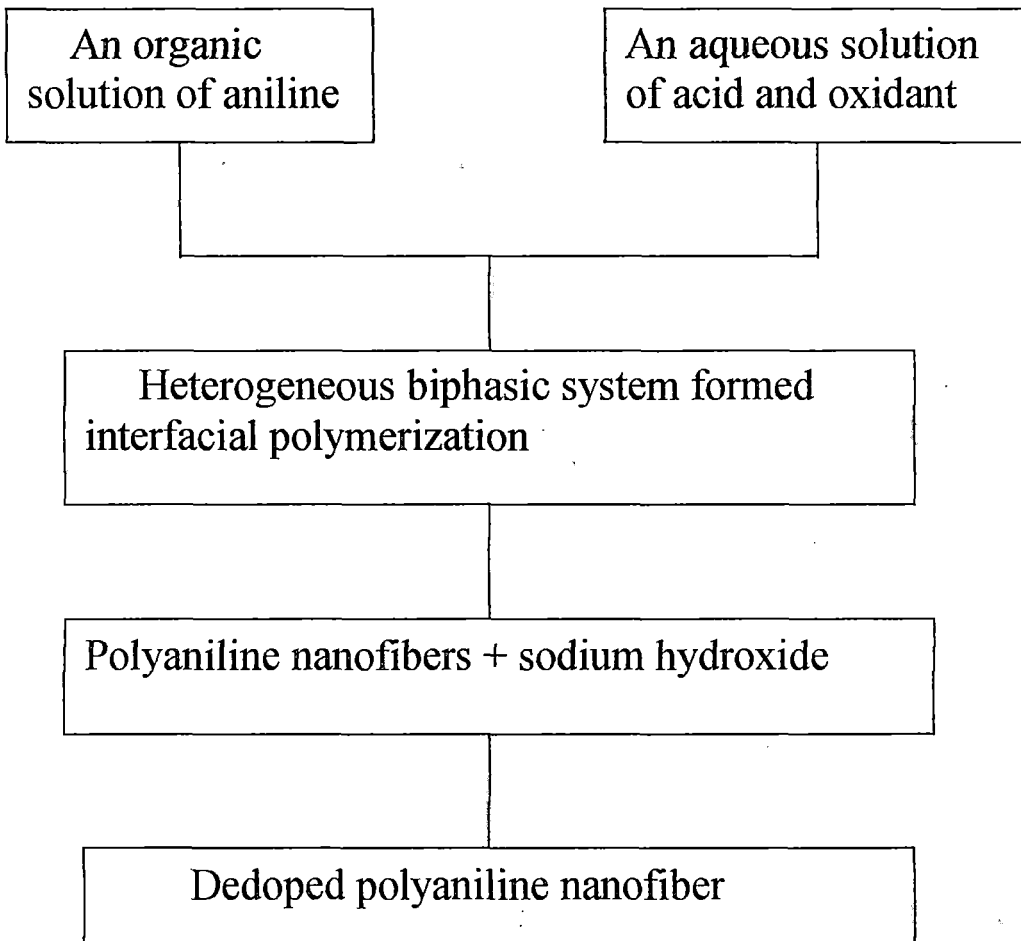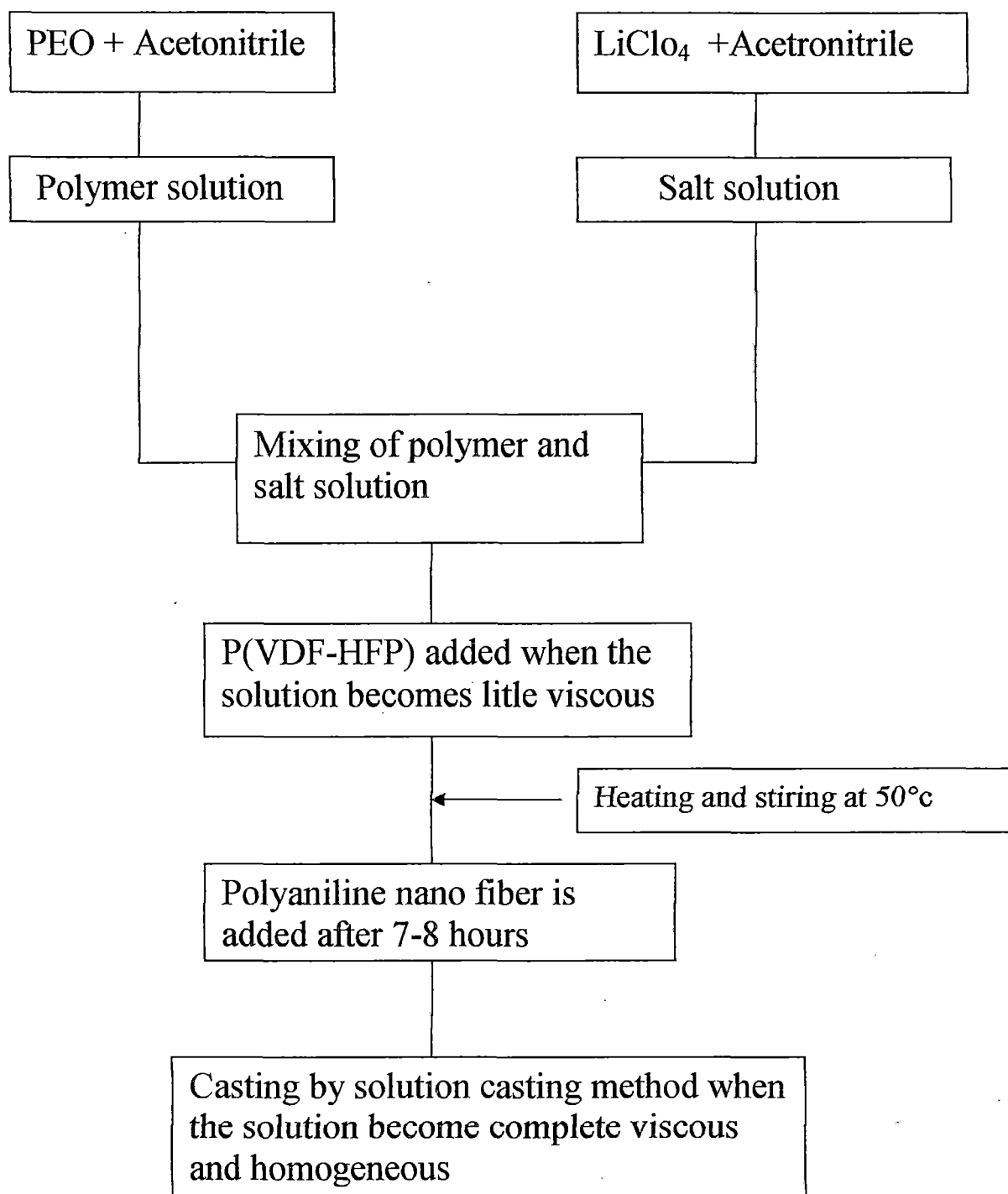
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┌─────────────────────┐        ┌─────────────────────┐
│   An organic        │        │  An aqueous solution│
│ solution of aniline │        │  of acid and oxidant│
└─────────────────────┘        └─────────────────────┘
           │                              │
           └──────────────┬───────────────┘
                          │
          ┌───────────────────────────────────────────┐
          │  Heterogeneous biphasic system formed      │
          │ interfacial polymerization                 │
          └───────────────────────────────────────────┘
                          │
                          │
          ┌───────────────────────────────────────────┐
          │ Polyaniline nanofibers + sodium hydroxide  │
          └───────────────────────────────────────────┘
                          │
                          │
          ┌───────────────────────────────────────────┐
          │      Dedoped polyaniline nanofiber         │
          └───────────────────────────────────────────┘
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Figure2.2: Block diagram of Interfacial Polymerization of polyaniline nanofibers

The block diagram for the preparation of PEO P(VDF-HFP) polyaniline nnofiber thin film is shown below

PEO + Acetonitrile		LiClo₄ +Acetronitrile

Polymer solution		Salt solution

Mixing of polymer and
salt solution

P(VDF-HFP) added when the
solution becomes litle viscous

Heating and stiring at 50°c

Polyaniline nano fiber is
added after 7-8 hours

Casting by solution casting method when
the solution become complete viscous
and homogeneous

The mount of plymer and salt that were taken for different samples were given below:

1. For the first sample :

      PEO =2 gm

      $LiClO_4$ = 0.605 gm

      P(VDF-HFP) =1.042 gm (40% weight of PEO)

      Nano fiber =0.18235 gm (5% of PEO-P(VDF-HFP)

2. For the second sample:

      PEO =2 gm

      $LiClO_4$ = 0.605 gm

      P(VDF-HFP) =1.042 gm (40% weight of PEO)

      Nano fiber =0.3647gm (10% of PEO-P(VDF-HFP)

3. For the third sample:

      PEO =2 gm

      $LiClO_4$ = 0.605 gm

      P(VDF-HFP) =1.042 gm (40% weight of PEO)

      Nano fiber =0.547gm (15% of PEO-P(VDF-HFP)

4.For the fourth sample:

    PEO =2 gm

    $LiClO_4$ = 0.605 gm

    P(VDF-HFP) =1.042 gm (40% weight of PEO)

    Nano fiber =0.7294gm (20% of PEO-P(VDF-HFP)

5.For the fifth sample:

    PEO =2 gm

    $LiClO_4$ = 0.605 gm

    P(VDF-HFP) =1.042 gm (40% weight of PEO)

    Nano fiber =0.9117gm (25% of PEO-P(VDF-HFP)

2.3 Characterisation techniques :

1. Conductivity measurement
2. X-ray diffraction nalysis
3. Scaning electron misroscopy

2.4 Conductivity measurement :

Hioki 3532-50 LCR HiTester has been empolyed for complex impedence (mod Z and phase angle θ) measurements. The instrument is interfaced with a computer to collect the data. It has a built in frequency synthesizer and has frequency range from 42 Hz to 5 MHz.

The ionic conductivity is obtained from the relation

$$\sigma = (L / R_b A)$$

where L is the thickness and A is the cross sectional area the poly6mer electrolyte sample. R_b is the bulk resistance obtained from the complex impedence plot.

Complex impedence analysis:

Simple dc measurement can not yield the dc resistance of the samples because of the choice of electrodes and polarization at the electrode/ electrolyte interface. The process however can be represented by n equivlent circuit involving resistors, capacitors. inductors etc.

The complex impedence spectroscopy is a technique to separate the contributions from various processes such as electrode reactions at the electrode/electrlyte interfaceand the migration of

charge carrier species through the grain nd acros the grain bounderies.

If we consider the series combination of resistance and capcitors the impednce is given by

$$Z_{Tot} = Z_1 + Z_2 + Z_3$$

$$Z_{Tot} = R - j/\omega c$$

$$= R + 1/j\omega C$$

$$= Z' - jZ''$$

For a resistance R and capacitor c in parrallel the complex impedence Z is given by

$$Z = R(I/j\omega C)/(R + 1/j\omega C)$$

Or $$Z = R/1 + \omega^2 C^2 R^2 + j(-R^2\omega C)/1 + \omega^2 C^2 R^2$$

Thus the real and imaginary parts of Z are

$$Z' = R/1 + \omega^2 C^2 R^2$$

$$Z'' = (-R^2\omega C)/1 + \omega^2 C^2 R^2$$

Eleminaing ω from these equtions we get

$$(Z' - R/2)^2 + Z''^2 = R^2/4$$

which is the equation of a circle with radias R/2 and center at (R/2, 0)

The various impedance behaviour observed in polymer electrolytes is shown below:
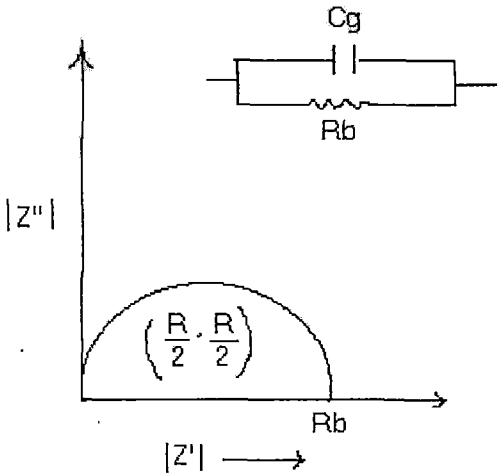
Fig 2.3 a
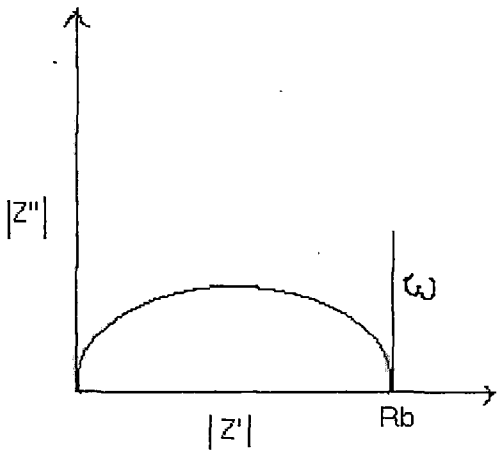
Fig 2.3 b
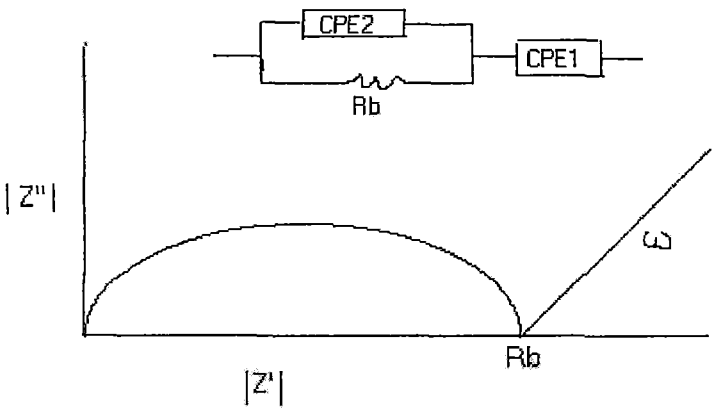
Fig 2.3 c

The value obtained at the intersection of the flattened semicircle and the tilted spike is the bulk resistance,Rb of the electrolyte.This is related to the conductivity σ by

$$\sigma = GL/A = L/\ RbA$$

where G is the conductance , L is thickness and A is the cross sectional rea of the sample.

2.5 X-ray diffraction analysis:

X-ray diffraction pattern gives information about different crystal parameters crystalline size , d-spacing,phases and lattice constans atc.In case of polymer the xrd is used to measyre the he degree of crystallinity of the sample.

The degree of crystallity measures how much the sample is crystalline in percantage and it can be measured by x-ray diffraction. Depening upon its degree of crystallinityx-ray diffractogram of polymer sample has sharp peaks superimposed on broad amorphous hump.The amount of crystallinity in a polymer depends on the following parameters:

1.The secondary valance bonds which can be formed.

2.The structure of polymer chain

3.The physical treatment of the polymer

4.The thermal history of the polymer

5.The moleculer weight of the polymer

2.6 Scaning electron microscopy:

Scaning electron microscopy or SEM is used for analysis of microstructural and morphological features of solid objects.Each specimen was gold coated using sputtering unit before taking the micrographs. The micrographs were taken at 30 kv accelerating voltage.

Scaning process:

In a typical SEM, electrons are thermionicaly emitted from a tungsten or lanthanum (LaB_6) cathode and are accelerated towards an anode alternatively, electrons can be emitted via field emission (FE). Tungsten is used because it has the highest melting point and lowest vapor pressure of all metals, thereby allowing it to be heated for electron emission. The electron beam, which typically has an energy ranging from a few hundred eV to 100 kV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 0.4 nm to 5 nm. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron optical column, typically in the objective lens which deflect the beam horizontally and vertically so that it scans in a raster fashion over a rectangular area of the sample surface. When the primary electron beam interacts with the sample, the electrons lose energy by repeated scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electrons' landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the emission of electrons and electromagnetic radiation, which can be detected to produce an image, as described below.

as fixed as need.

Chapter three
Results and disscussion

3.1 Ionic conductivity of different smples:

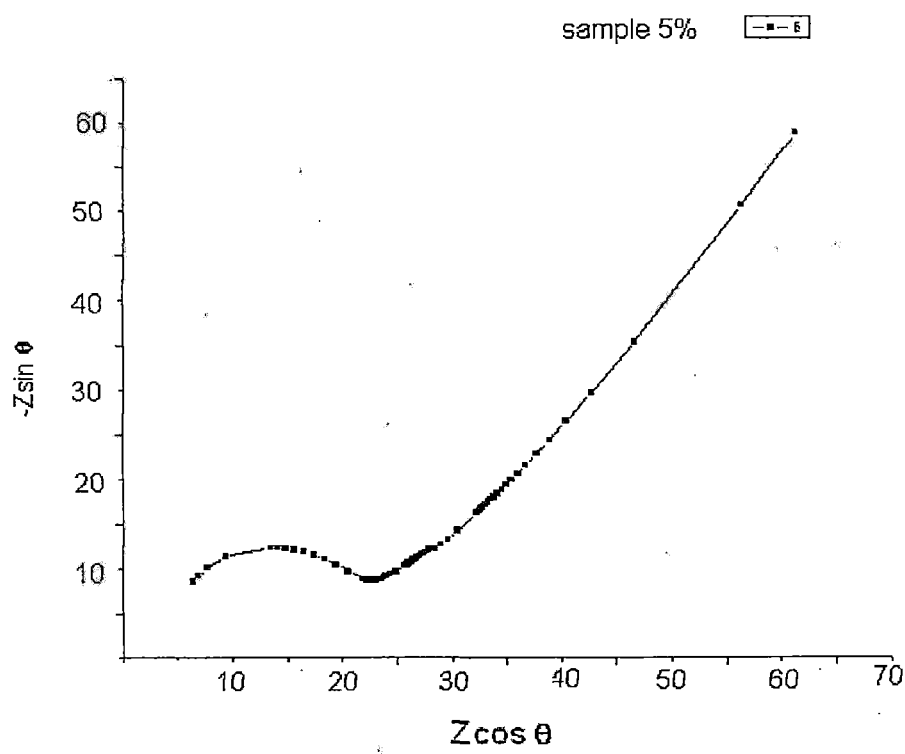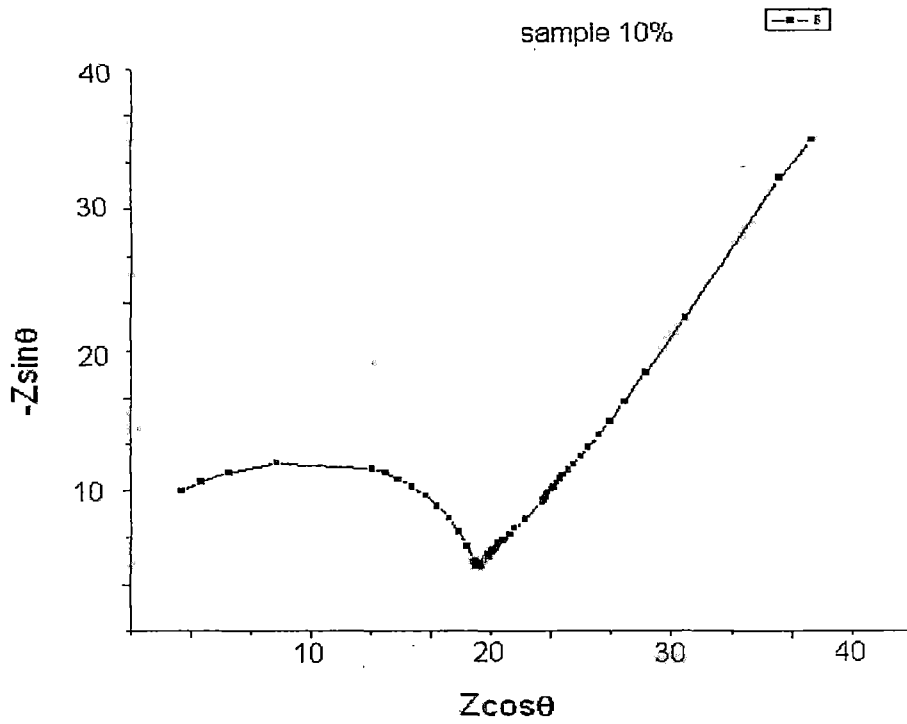1. The ionic conductivity curve of PEO-LiClO$_4$-P(VDF-HFP) (40weigth%) is shown below:
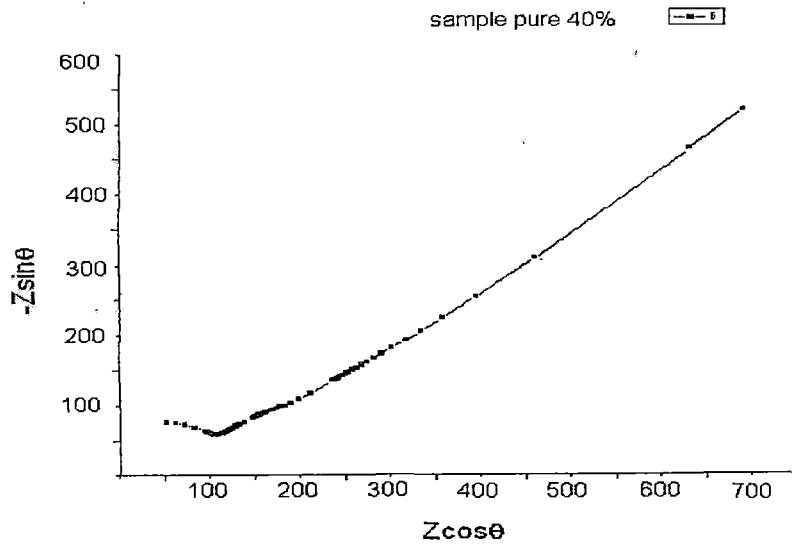
Fig 3.1: The complex impedance spectra of PEO-P(VDF-HFP)

From figure;

Bulk resistance of the sample =150 Ω

Thickness of the sample is = 0.1 cm

Radius of the sample =0.5 cm

So the resistivity will be

$$\rho = R_b \, A / t$$

$$A = \pi r^2$$

So the resistivity is $\rho = (150 * \pi r^2 / 0.)$ Ωcm

$$= 11775 * 10^4 \ \Omega\text{cm}$$

Hence the conductivity $\sigma = 1/\rho$

$$= 8.5 * 10^{-4} \ \Omega^{-1}\text{cm}^{-1}$$

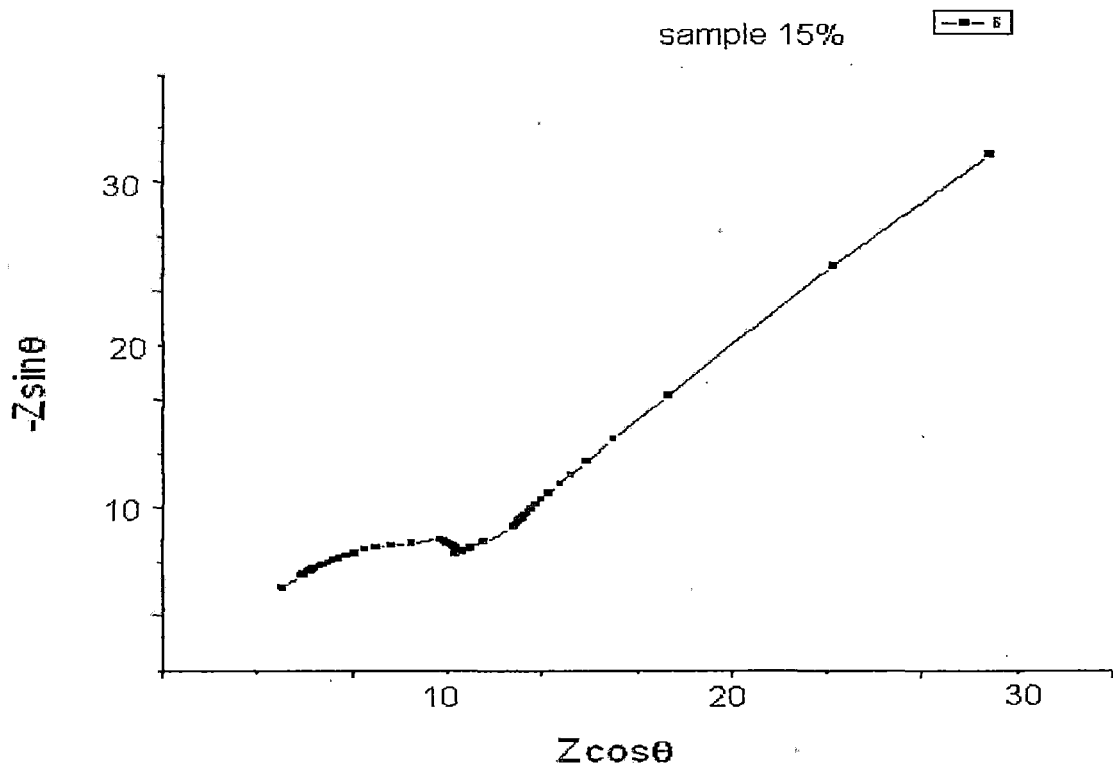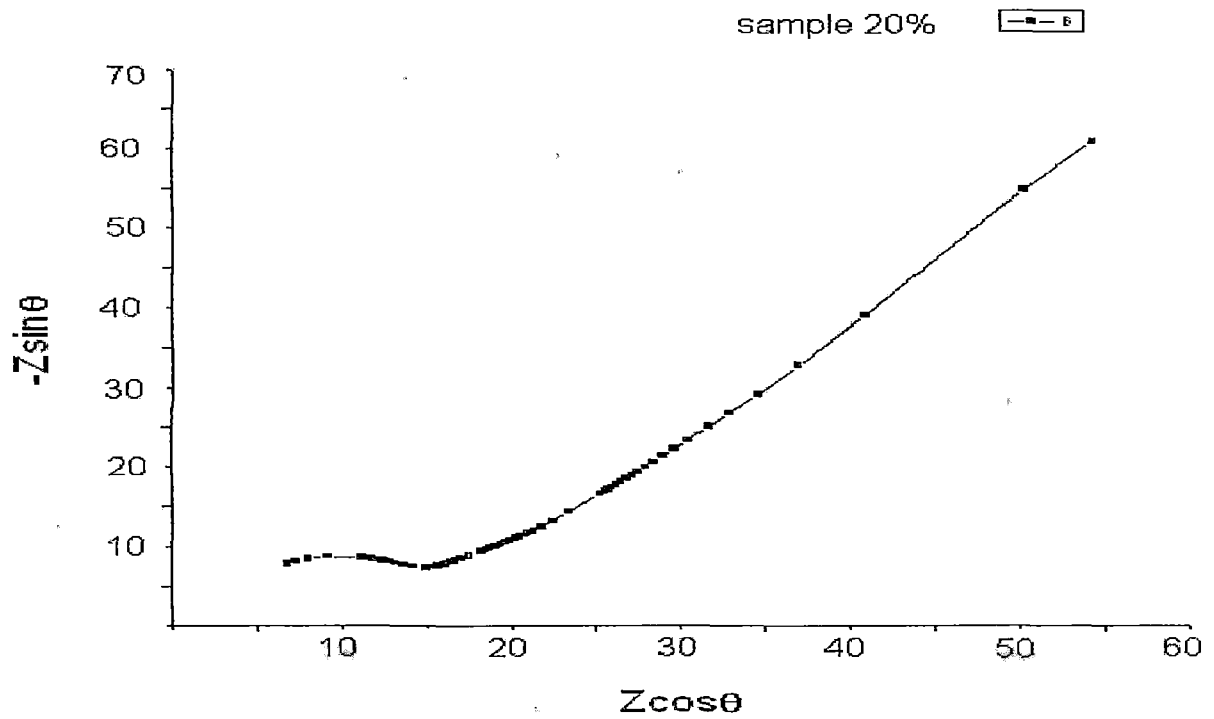2. The ionic conductivity spectra of PEO-P(VDF-HFP) +Nano fiber (5 weight %) is shown below:

Fig 3.2: The complex impedance spectra of PEO-P(VDF-HFP) + 5% nano fiber

From figure;

Bulk resistance of the sample $= 25$ Ω

Thickness of the sample is $= 0.1$ cm

Radius of the sample $= 0.5$ cm

So the resistivity will be

$\rho = Rb.A /t$

$A = \pi r^2$

So the resistivity is $\rho = (25 * \pi r^2 / 0.1)$ Ωcm

$= 196.25 \Omega$cm

Hence the conductivity $\sigma = 1/\rho$

$= 5.1 * 10^{-3}$ Ω^{-1}cm^{-1}

3. The ionic conductivity spectra of PEO-P(VDF-HFP) +Nano fiber (10 weight %) is shown below:

Fig 3.3: The complex impedance spectra of PEO-P(VDF-HFP) + 10% nano fiber

From figure;

Bulk resistance of the sample $= 20\ \Omega$

Thickness of the sample is $= 0.1$ cm

Radius of the sample $= 0.5$ cm

So the resistivity will be

$$\rho = Rb.A\ /t$$

$$A = \pi r^2$$

So the resistivity is $\rho = (20 * \pi r^2 / 0.1)\ \Omega cm$

$$= 157 \Omega cm$$

Hence the conductivity $\sigma = 1/\rho$

$$= 6.4 * 10^{-3}\ \Omega^{-1} cm^{-1}$$

4. The ionic conductivity spectra of PEO-P(VDF-HFP) +Nano
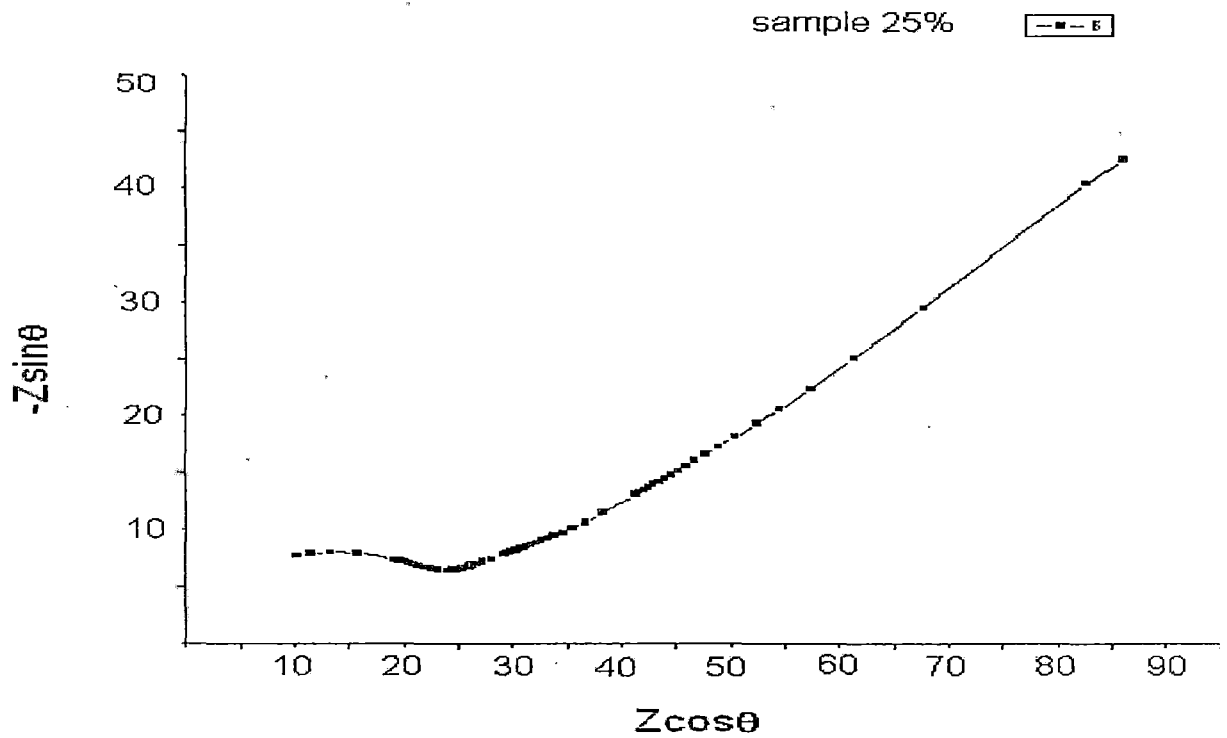fiber (15 weight %) is shown below:

Fig 3.4: The complex impedance spectra of PEO-P(VDF-HFP) + 15% nano fiber

From figure;

Bulk resistance of the sample $= 15 \, \Omega$

Thickness of the sample is $= 0.1$ cm

Radius of the sample $= 0.5$ cm

So the resistivity will be

$\rho = R_b . A / t$

$A = \pi r^2$

So the resistivity is $\rho = (15 * \pi r^2 / 0.1) \, \Omega cm$

$= 117.75 \Omega cm$

Hence the conductivity $\sigma = 1/\rho$

$= 8.5 * 10^{-3} \, \Omega^{-1} cm^{-1}$

5. The ionic conductivity spectra of PEO-P(VDF-HFP) +Nano fiber (20 weight %) is shown below:

Fig 3.5: The complex impedance spectra of PEO-P(VDF-HFP) + 20% nano fiber

From figure;

Bulk resistance of the sample $= 18 \ \Omega$

Thickness of the sample is $= 0.1$ cm

Radius of the sample $= 0.5$ cm

So the resistivity will be

$\rho = Rb.A / t$

$A = \pi r^2$

So the resistivity is $\rho = (18 * \pi r^2 / 0.1) \ \Omega cm$

$= 141.3 \Omega cm$

Hence the conductivity $\sigma = 1/\rho$

$= 7.1 * 10^{-3} \ \Omega^{-1} cm^{-1}$

6. The ionic conductivity spectra of PEO-P(VDF-HFP) +Nano fiber (25 weight %) is shown below:

Fig 3.6: The complex impedance spectra of PEO-P(VDF-HFP) + 25% nano fiber

From figure;

Bulk resistance of the sample $= 29\Omega$

Thickness of the sample is $= 0.1$ cm

Radius of the sample $= 0.5$ cm

So the resistivity will be

$\rho = Rb.A / t$

$A = \pi r^2$

So the resistivity is $\rho = (29 * \pi r^2 / 0.1)\ \Omega cm$

$= 227.65\Omega cm$

Hence the conductivity $\sigma = 1/\rho$

$= 4.39 * 10^{-3}\ \Omega^{-1}cm^{-1}$

3.2 Conductivity versus weight percentage curve:

CONDUCTIVITY vs WEIGHT%
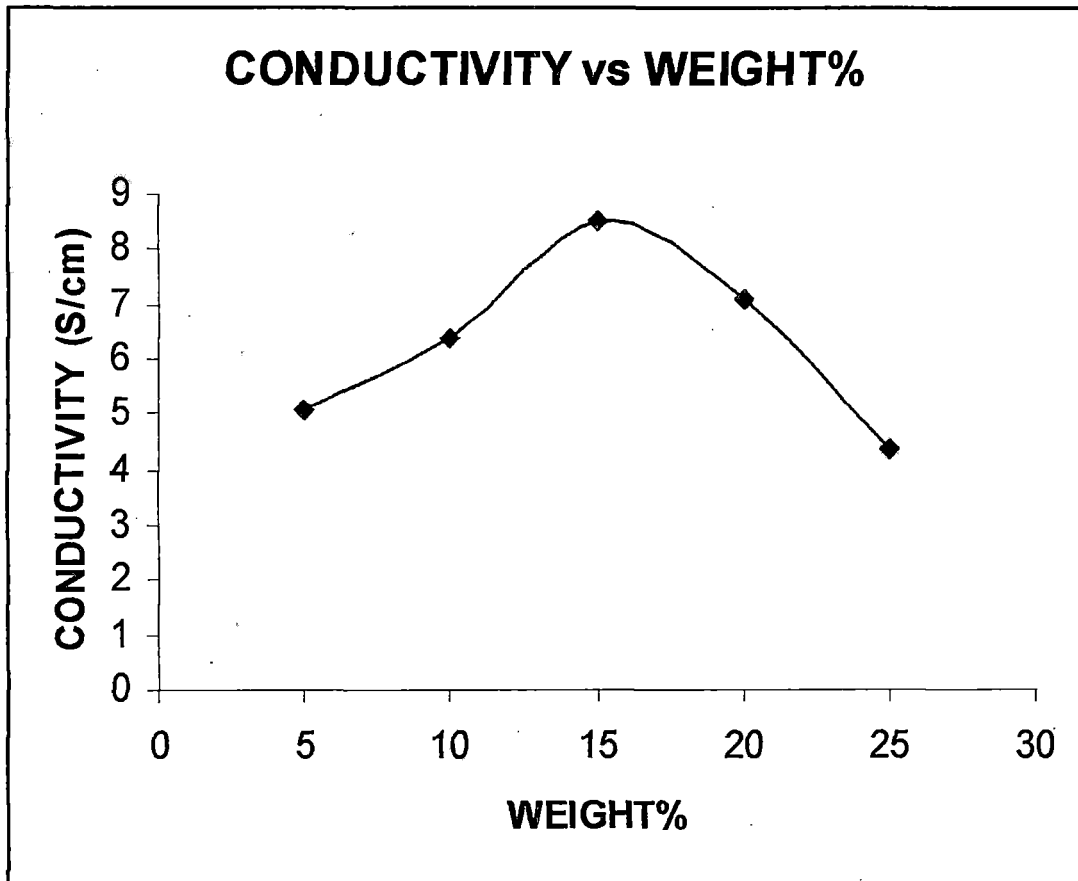
The graph shows that the conductivity is maximum at 15 weight %

3.3 X-ray diffraction plot of different samples:

1. X-ray diffraction of PEO-P(VDFHFP) (40weight %)
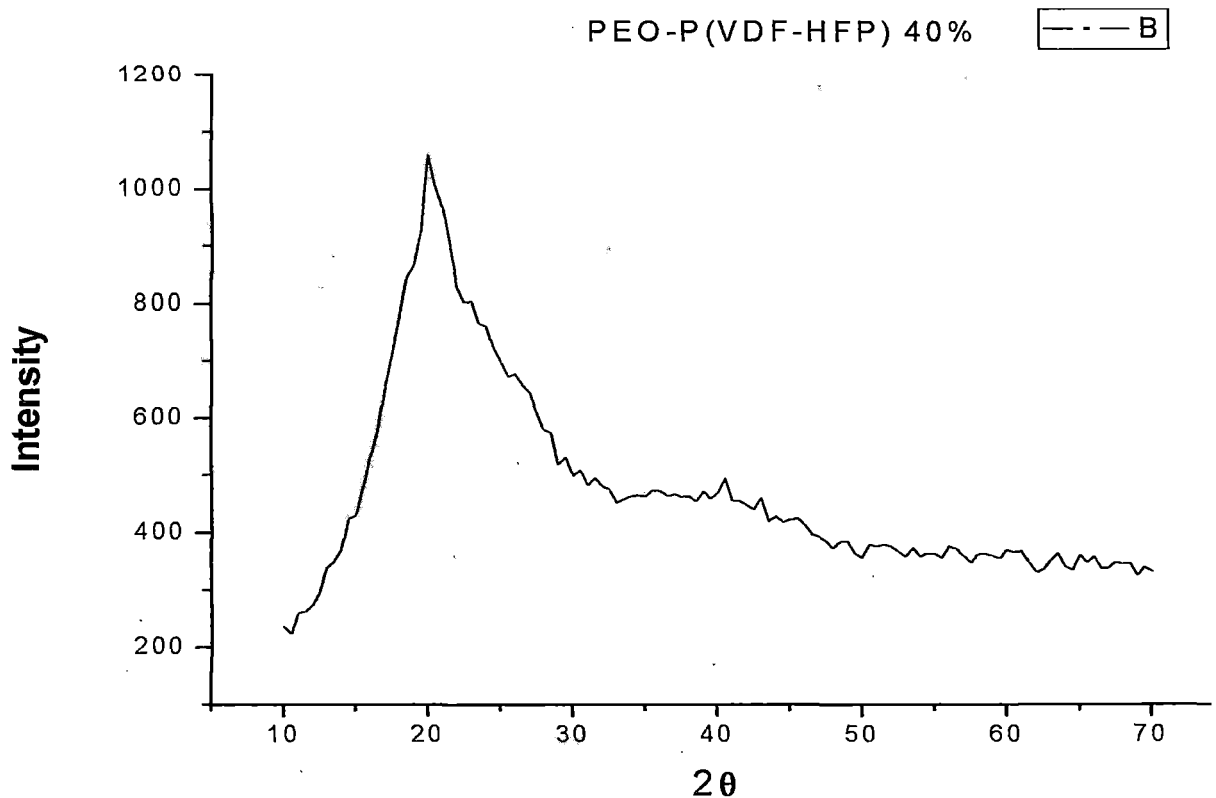
Fig 3.7:Xrd spectra of PEO-P(VDF-HFP) (40 weight %)

The degree of crystallinity (K) is

$$K = (S / S_0) * 100\%$$

Where S is the sum of areas of all crystalline peaks and S_0 is the sum of all crystalline peaks and amorphous hump i.e. total area under the diffractogram.

$$K = 39/127 \ x100\%$$

$$=30.7\%$$

2. X-ray diffraction of PEO-P(VDFHFP)+nanofiber(10weight %)
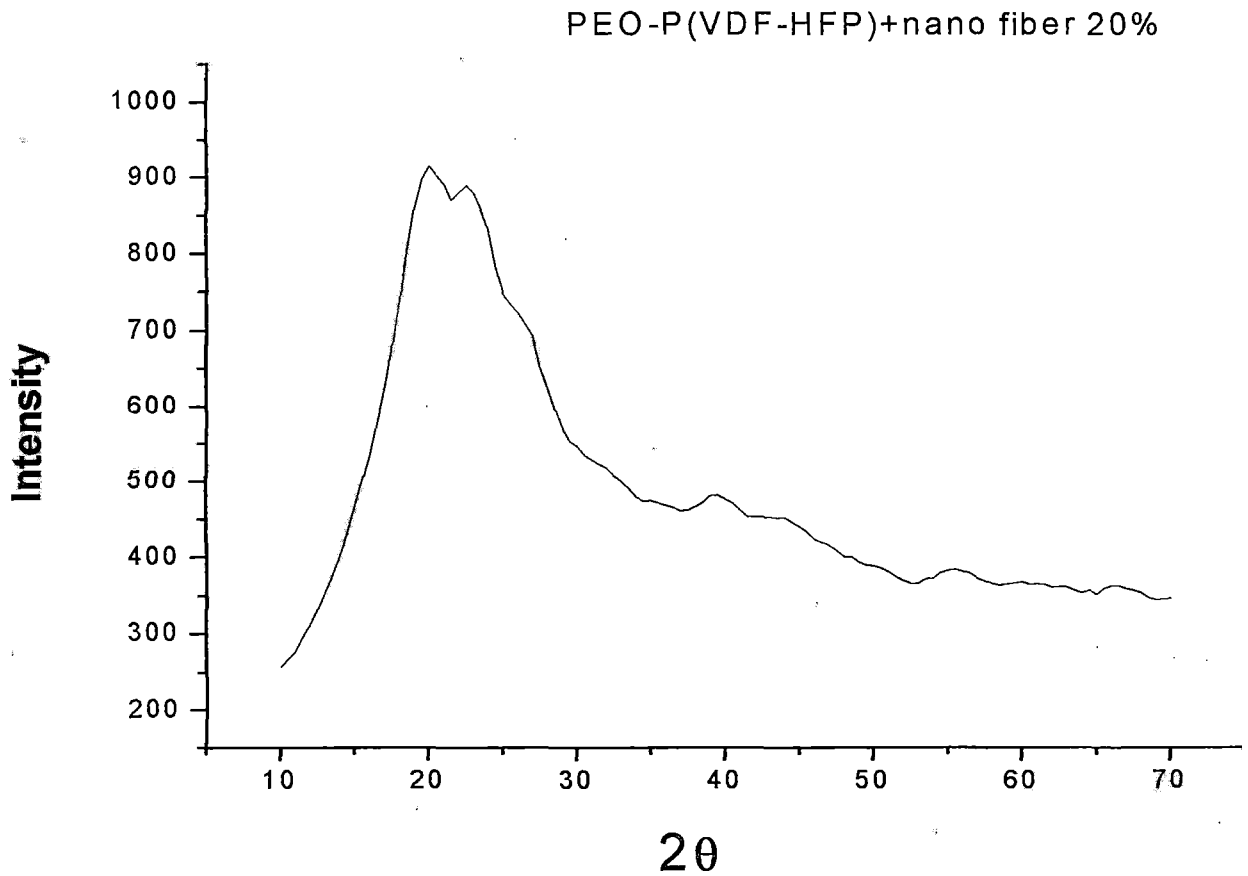
PEO-P(VDF-HFP)+nano fiber 10%
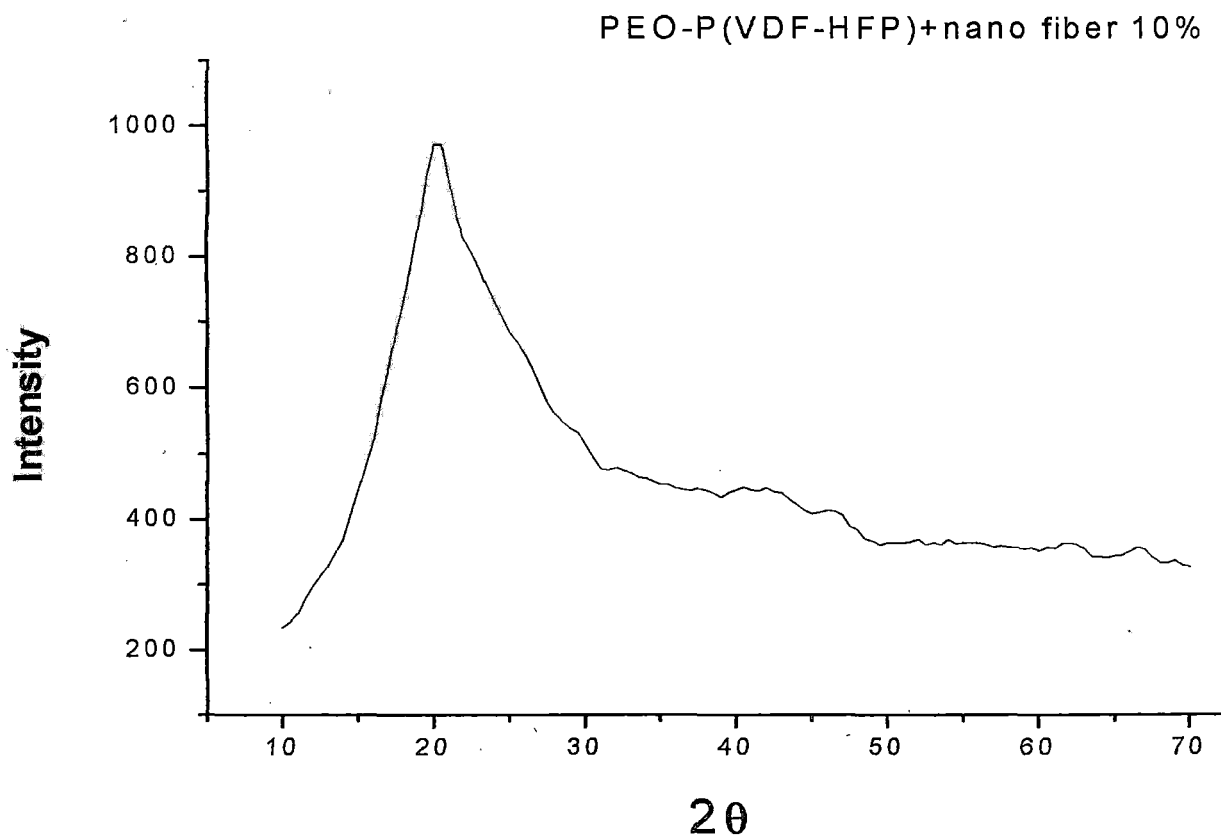
Fig 3.8:Xrd spectra of PEO-P(VDF-HFP)+nano fiber (10weight %)

Degree of crystallinity(K)

$$K = 32/127 \times 100\%$$

$$= 25.2\%$$

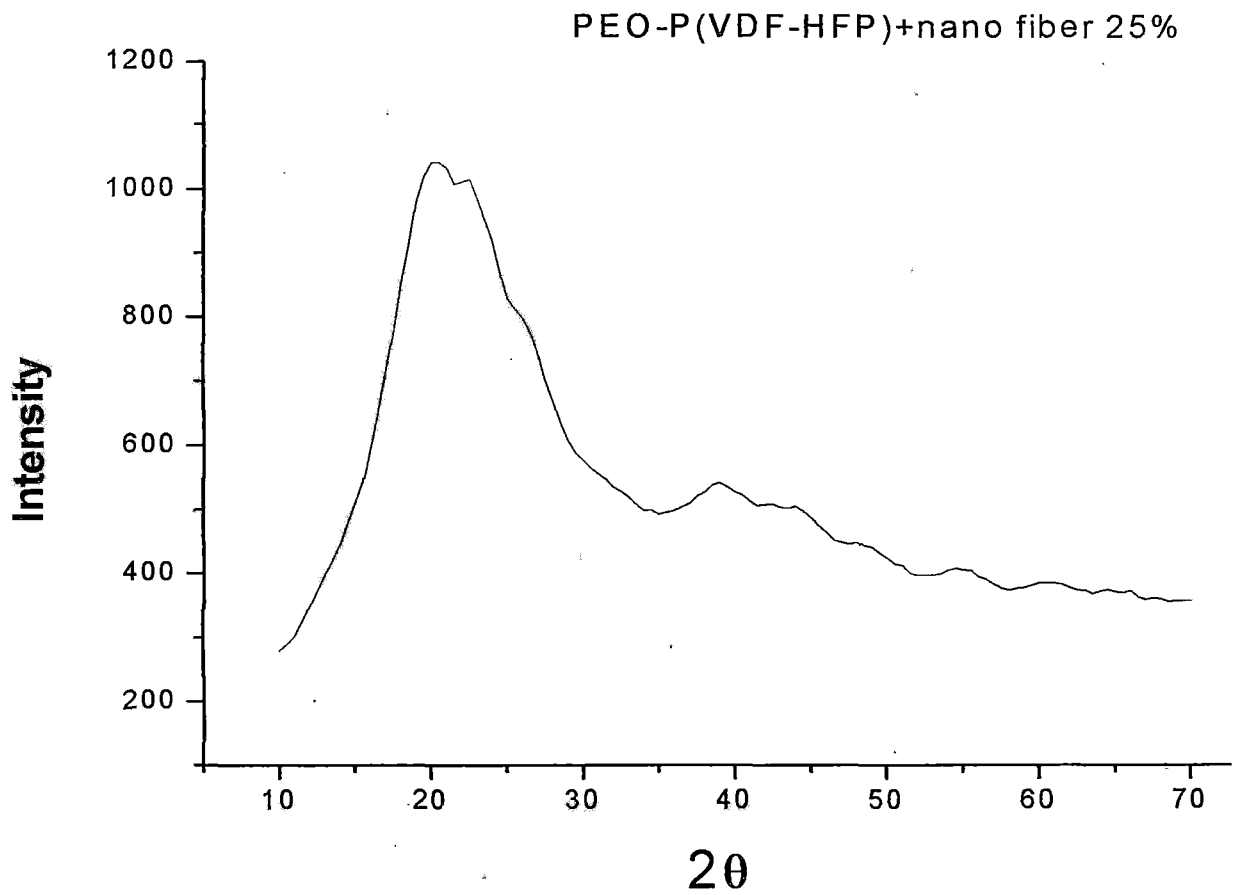## 3. X-ray diffraction of PEO-P(VDFHFP)+nanofiber(15weight %)

PEO-P(VDF-HFP)+nano fiber 15%
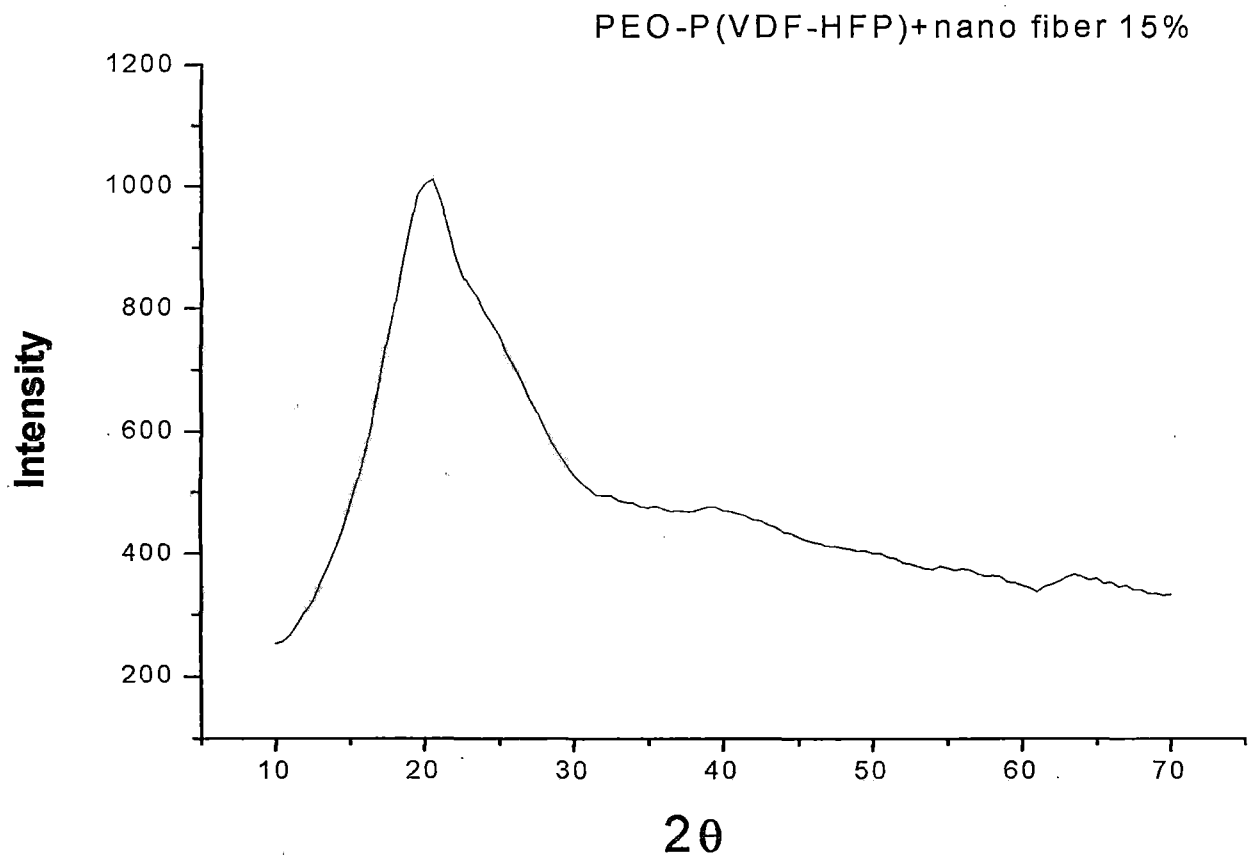
Fig 3.9: Xrd spectra of PEO-P(VDF-HFP)+nano fiber (15weight %)

Degree of crystallinity(K)

$$K = 18/127 \times 100\%$$

$$= 14.2\%$$

4. X-ray diffraction of PEO-P(VDFHFP)+nanofiber(20weight %)

Fig 3.10: Xrd spectra of PEO-P(VDF-HFP)+nano fiber (20weight %)

Degree of crystallinity (K)

$$K = 32/127 \times 100\%$$

$$= 25.2\%$$

5. X-ray diffraction of PEO-P(VDFHFP)+nanofiber(25weight %)

PEO-P(VDF-HFP)+nano fiber 25%

Fig 3.10: Xrd spectra of PEO-P(VDF-HFP)+nano fiber (20weight %)

Degree of crystallinity (K)

$$K = 35/127 \times 100\%$$
$$= 28\%$$

3.4 scanning electron microscopy :

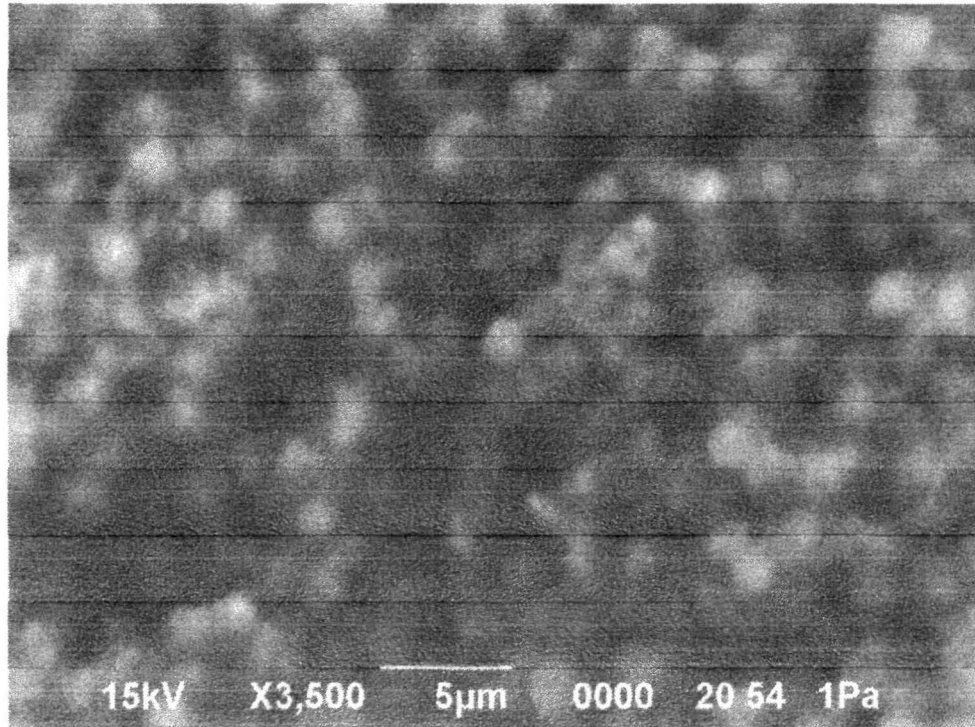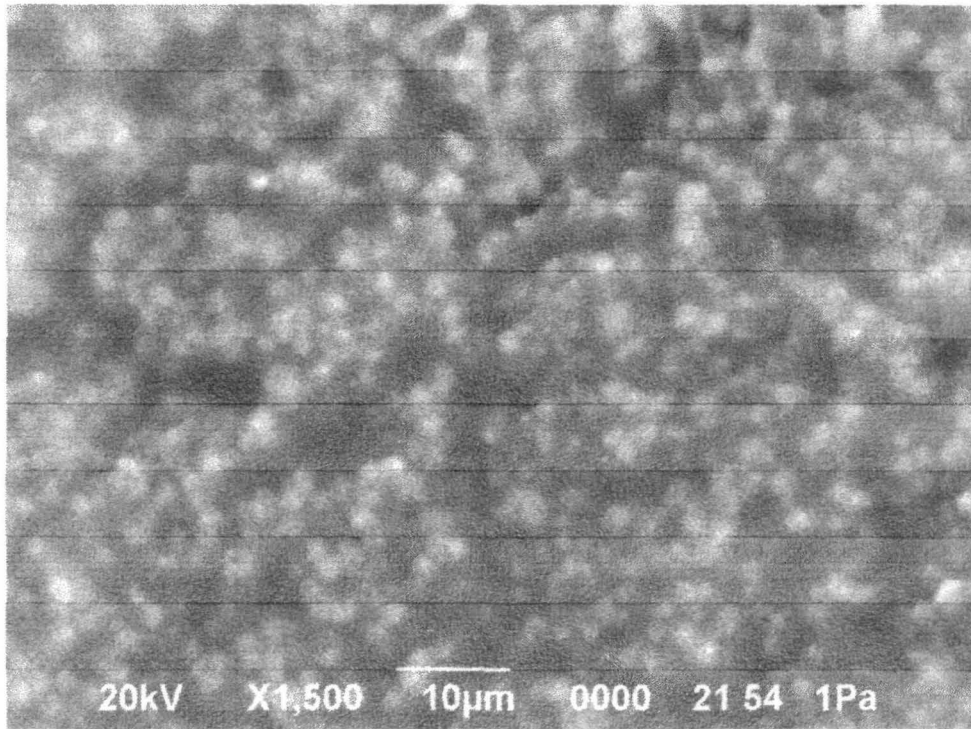1. SEM picture of PEO-P(VDF-HFP)+nano fiber (5weight%):
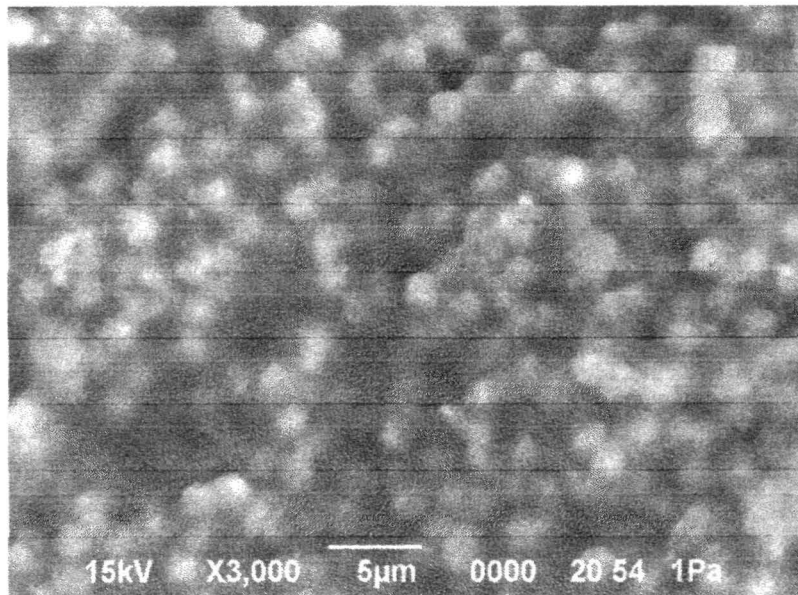
Fig 3.11: SEM of PEO-P(VDF-HPF)+Nano fiber (5weight%)
at 15 kV and 3000x magnification
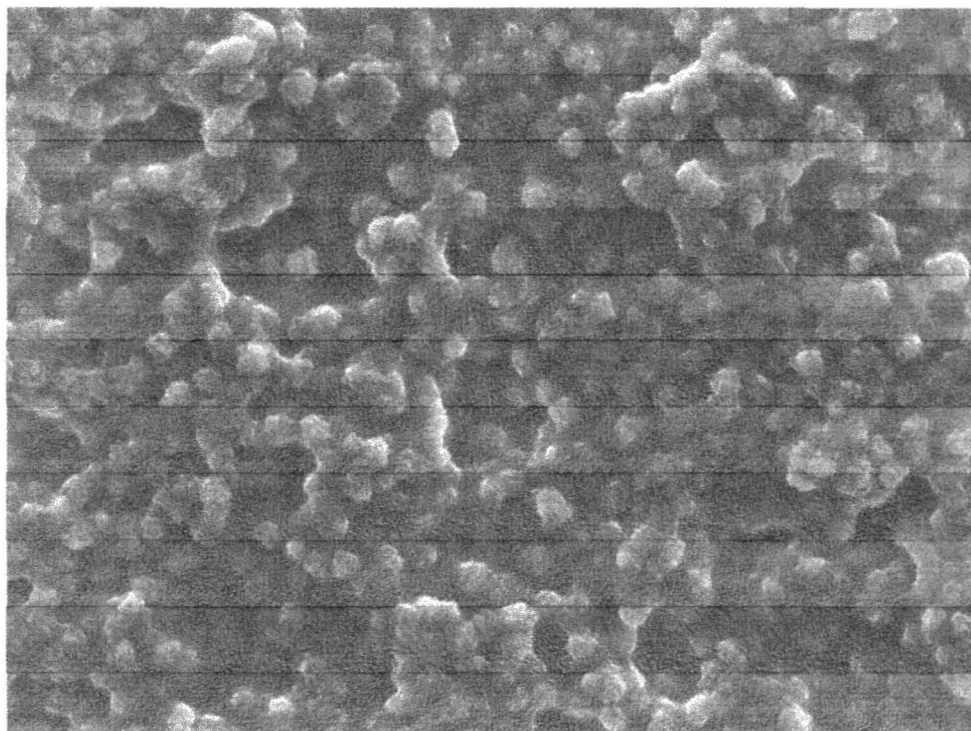
2. SEM picture of PEO-P(VDF-HFP)+nano fiber (5weight%):

Fig 3.12: SEM of PEO-P(VDF-HPF)+Nano fiber (5weight%)
at 15 kV and 3500x magnification

3. SEM picture of PEO-P(VDF-HFP)+nano fiber (5weight%):

Fig 3.13: SEM of PEO-P(VDF-HPF)+Nano fiber (5weight%)
at 20 kV and 1500x magnification

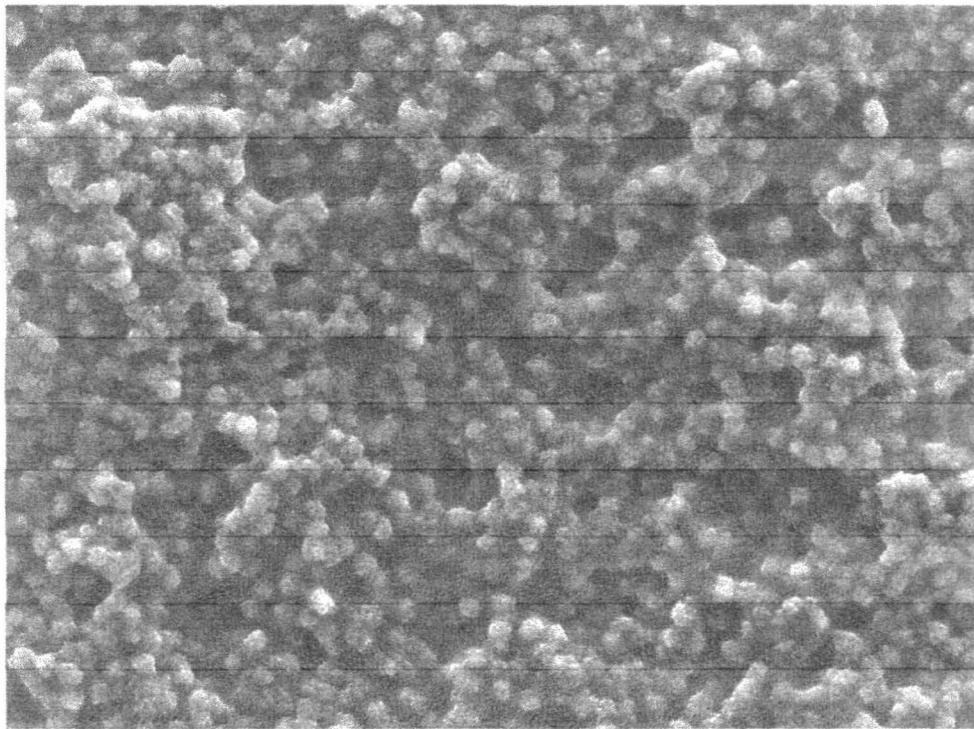4. SEM picture of PEO-P(VDF-HFP)+nano fiber (10weight%):

20 kV   X 3000   10μ m

Fig 3.14 SEM of PEO-P(VDF-HPF)+Nano fiber (10weight)
at 20 kV and 3000x magnification

5. SEM picture of PEO-P(VDF-HFP)+nano fiber (5weight%):

20 kV   X 3000   10μ m

Fig 3.15 SEM of PEO-P(VDF-HPF)+Nano fiber (10weight)
at 20 kV and 3000x magnification

3.5 Conclusion:

The following conclusions can be drawn about my project:

1. The conductivity of PEO-P(DF-HFP) increases greatly on addition of polyaniline nano fiber. The maximum conductivity obtained is 8.5 x 10^{-3} at 15 weight % of the fiber.

2.The XRD analysis also reveals that crystallinity decreases from weight % 5 to 15 .But after that crystallinity increases as also conductivity decreases .

3.The SEM pictures clearly shows the polymer chains. But due to smaller magnification nano fibers are not visible.

4.The aim of my project which is to increase the conductivity is obtained.

3.6 Future prospects:

There is vast scope for further development of high ion conducting polymer electrolytes materials such as lithium ion batteries , superconductors etc.Movements of anions in polymer electrolytes deteriorates the capacity of devices so cationic transport should be increased. There is a vast future prospect in this field.

3.7 References:

1.Bruno Scrosati and Robin J .Neat,Lithium polymer batteries.

2.Ashok Kumar and D.Saikia, Ion Conducying Polymers.

3.W.Chen,Q.Xu,R.Z. Yuan,The influence of polymer state on the electrical properties of polymer/layered –silicate nanocomposites.

4.Mary Kurian,Mary E.Galvin,Patrick E Trapa,Donald Sadoway,Anne M.Mayes ;Single-ion conducting polymer-silicate nanocomposite electrolytes for lithium battery applications.

5.Chun-Guey Wu,Ming-I.Lu,Chung-Chih Tsai,Huey-JanChuang, PVDF-HFP/metal oxide nanocomposites:The matrices for high-conducting , low-leakage porous polymer electrolytes