SYNTHESIS OF GEL POLYMER ELECTROLYTES FOR POLYMER SOLAR CELLS

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Dedicated to my
Loving Parents
& family

ABSTRACT

The aim of this work is to sensitize an electrolyte from the copolymer of Acrylonitrile and Methylmethacrylate to replace the liquid electrolyte in die sensitized solar cells. A copolymer, Acrylonitrile–Methylmethacrylate (AN–MMA) was synthesized by emulsion polymerization from acrylonitrile (AN) and methylmethacrylate (MMA) as monomers. The performances of the copolymer were characterized by FTIR, SEM, and TGA. The copolymer contains CH_2, CN and CO bonds, and shows its thermal stability up to 350 °C. Porous membranes based on Acrylonitrile-Methylmethacrylate (AN-MMA) copolymer were prepared by phase-inversion method. Microstructures of the porous membranes were controlled through the variation of the evaporation drying time before immersion in a nonsolvent (water) bath. The polymer membrane has a porous structure with an average pore diameter of about 0.5 μm. Gel polymer electrolytes were prepared from these porous membranes via soaking them in an organic electrolyte solution. They encapsulated the electrolyte solution well without solvent leakage and maintained good mechanical properties that allowed the preparation of thin films (≈40μm thickness).The ionic conductivities of thin films were calculated by Hall Effect apparatus. These systems showed acceptable ionic conductivity values up to (1.87×10^{-4} S $(cm)^{-1}$) at room temperature. From these results and analysis we can consider these gel polymer electrolytes for utilization in dye sensitized solar cells as a hole conducting material instead of liquid electrolytes which have many draw backs like their sensitivity towards environmental conditions etc.

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INTRODUCTION TO GEL POLYMER ELECTOLYTES

1.1 IMPORTANCE

During the last years there was a lot of effort done on the electrochemical preparation of gel polymer electrolytes. These materials are often used as electrolytes in lithium batteries, super capacitors and eletrochromic components. Even when these materials are known for a longer time already, studies of their properties are being accomplished as late as in the recent years. The easiest way to create a polymer gel electrolyte is by polymerizing polymethylmethacrylate (PMMA) with addition of electrolyte. For real application of polymer gel electrolyte its parameters have to be known. Most important parameter in this case is electrical resistance or electrical conductivity, capacity or real and imaginary part of impedance [1].

1.2 ION CONDUCTORS

The reason of ion conductivity is mobility of ions in crystals. It is caused by the existence of cavities, tunnels or other empty spaces in the matrix. In gel polymer electrolytes however, the ions migrate in the liquid phase which is immobilized by the polymer macromolecules.

In the absence of electrical field ions in crystal are doing random thermal movement. As soon as there are electrodes in contact with the electrolyte and an external voltage is connected to them, the electric field will cause orientation of the movement of ions. Positive ions will move to the negative electrode and negative ions will move to the positive electrode. Electric current will pass through the electrolyte. At the start it will be small current but it will disappear soon. Permanent current will be emerged after breaking an electric boundary V_r called decomposition voltage. For voltage V bigger than the decomposition voltage V_r the current is approximately linear, so it is:

$$V = Vr + R \times I$$

Where I is current Vr is decomposition voltage and R is a constant with stable temperature and it is called an electrolyte resistance [2].

1.3 ELECTROLYTES

By the dissolution of electrolyte (usually a salt able to carry the electric current) in the proper solvent, liquid electrolyte is formed. In the common language is "electrolyte" often used in meaning of "liquid electrolyte". Under the category electrolyte we include those conducting systems where electric current is joined with material transporting. The layer of ionic conductor is used as ion source for implementing them to the active layer or as a base for their subtracting. That's why electrolyte must be able of fast ion transport between layers or between electrodes. High conductivity is required for electrolytes in practical applications (it should be somewhere above 10^{-12} S.cm^{-1}). Ratio of cations and/or anions on the whole charge Q in the liquid of electrolyte is different and it is expressed by transference numbers defined by equations:

$$Tc = Qc/Q$$

$$Ta = Qa/Q$$

Where Tc and Ta are transference numbers, Qc and Qa is charge transferred by positive and negative ions and Q is total charge transferred during the process [3].

1.3.1 SOLID ELECTROLYTES

These electrolytes involve solid polymers (often used polypropylen or polyethylene), lithium salts (lithium perchlorate) and ceramic oxides. Cation transference number depends on the amount of added ceramic. By experiments it was found that size of Al_2O_3 have to be smaller than 0.3 μm to build a material with high transference numbers, but it is hard to create as thin layers because they are very unstable when left in places with higher air humidity. It is also possible to use dielectric or insulator cellular layer to absorb humidity from the air When the layer is embedded between two electrodes and electric voltage is higher than 1.3 V, water is decomposed on H_2 and O_2 [4].

1.3.2 LIQUID ELECTROLYTES

Materials conducting electric current are divided into two groups that are ionofors and ionogens. Ionofor is a material compact from ions only. Conductivity of ionofor depends on concentration, dielectric constant and viscosity of dissolver. Ionogen is a material which crystals are compounded from molecules creating ions while being affected by dissolver [5]. By other words, inofors contains ions while to make ions from ionogen material we have to use dissolver.

1.3.3 GEL ELECTROLYTES

Gel electrolytes are electrolytes with polymer addition with balanced ratio so polymerization will produce gel structure. Often used materials to create gel polymers we can find polymers – polypropylene, polyethylene oxide (PEO), polymethyl methacrylate (PMMA), polyvinylpyrrolidone and polyvinylpyridine (PVP), polypropyleglycol-methylmethacrylate (PPG-PMMA) etc and AN-MMA copolymer which we have prepared.

1.4 POLYMER GEL ELECTROLYTES

Polymer electrolytes are defined as solid ion conductors formed with dissolving salt in polymer having fitting high molecular weight. Based on the method of holding ions in the polymer they can be divided into two groups:

- Poly electrolytes
- Gel electrolytes

1.4.1 GELATION

During the research of second polymer electrolyte type it was found that one of most important things is increasing conductivity of electrolytes at room temperature. Principe of this is holding liquid polymer with high dielectric constant involving dissolved alkali salt in the chemical or electrochemical polymer inert matrix in the base polymer. Target is using good properties of inert form and size stability and liquid electrolyte with high conductivity. Basically it is thickening up (or immobilization) of liquid electrolyte by appropriate polymer material. Ions of alkali salts are moving in the gaps between macromolecular chains. These electrolytes are called gel electrolytes [6]. They can be prepared by three methods:

- Thermal formation (polymerization)
- Formation by light (polymerization)
- Chemical forming (polymerization)

1.4.2 PROPERTIES AND USABILITY OF GEL POLYMER ELECTROLYTES

Polymer gel electrolytes are very progressive materials. They can be prepared in semisolid or solid form, which is a cheap and reliable process when they are manufactured. Requirement for wide usability of gel electrolytes is high conductivity.

Polymer electrolytes and in recent days especially gel polymer electrolytes can be used in several different cases. In solar cells they can be utilized instead of liquid electrolytes, in accumulators and super capacitors they can replace liquid electrolytes, as they are more stable in the meaning of chemical and electric stability and also in electro chromic displays and devices as they are very handful to prevent devices from drying out or leaking electrolyte [5].

1.5 POLYMER ELECTROLYTES FOR DYE SENSITIZED SOLAR CELLS

The first report on a new type of dye-sensitized solar cell (DSSC) was published by O'Regan and Gratzel. By improving TiO_2 electrodes they attained an overall energy conversion efficiency of 10% in simulated solar light. Since then, DSSCs have been intensively studied and have attracted an ever growing interest from many researchers of different disciplines. DSSCs are one of the promising candidates for the next generation of solar cells because of their simple structure with relatively high conversion efficiencies, inexpensive fabrication procedures in contrast with amorphous silicon solar cells and the 500 W DSSC showcase outdoor application is running successfully for more than 2 years, which gives a picture of the prospective industrial application in the near future [7].

A typical DSSC consists of a dye-coated mesoporous TiO_2 nanoparticle film sandwiched between two conductive transparent electrodes and a liquid electrolyte traditionally containing the iodide/tri-iodide redox couple to fill the pores of the film and contact the nanoparticles. The photovoltaic effect in a DSSC originates from the interface between a redox electrolyte containing iodide and tri-iodide ($I-/I_3-$) ions and a dye-adsorbed TiO_2 electrode. The electrolyte, as one of the key ingredients, provides internal electric conductivity by diffusing within the mesoporous TiO_2 layer and is an important factor in determining the cell performance. Light-to-electrical energy conversion efficiencies of the DSSCs based on liquid electrolytes using organic compounds such as acetonitrile (ACN), propylene carbonate (PC) and ethylene carbonate (EC) as solvents and iodide/tri-iodide ($I-/I_3-$) redox couple as an electrolyte have reached 10–11%. Despite the high conversion efficiencies obtained for the DSSCs with liquid electrolytes, potential problems caused by liquid electrolytes, such as leakage and volatilization of the liquid, possible desorption and photo degradation of the attached dyes, and the corrosion of the counter electrode, have brought about difficulties in cell fabrication and limited the long term performance and practical use of these DSSCs [8].

To prevent or reduce electrolyte leakage, several methods have been introduced. One strategy is to replace the volatile solvents with ionic liquids and Secondly, p-type semiconductors and inorganic hole transport materials, organic hole transport materials and polymer/redox couples blends have been introduced as substitutes for traditional liquid electrolyte in all-solid-state DSSC configurations. Furthermore nanocomposites , polymer gels and solid-state or quasi-solid-state materials have been introduced to replace the organic liquid electrolytes.

Among them, polymer electrolytes stand out because of their excellent properties such as easy fabrication, low cost and good stability so that they have obtained growing interests from the point of practical applications. Polymer electrolytes comprise metal salts of low lattice energy dissolved in a polymer matrix containing polar moieties such as ether, ester or amide linkages. Metal salts can dissolve into such polymer matrixes by virtue of the coordinative interaction between the metal ion and the polar groups. The conductive properties of polymer electrolytes have led them to be intensively studied for potential applications in lithium polymer batteries and electrochromic devices, especially for the DSSCs. According to their states, the polymer electrolytes can be divided into two types, including solid polymer electrolytes and gel polymer electrolytes (GPEs) [9].

1.5.1 GEL POLYMER ELECTROLYTES (GPES)

Compared to other kinds of charge transport materials, GPEs are constructed by trapping liquid electrolytes, which usually contain organic solvents and inorganic salts such as PC, EC or ACN, lithium iodide (LiI), sodium iodide (NaI) and potassium iodide (KI). Compared to the corresponding parameters of the DSSC based on liquid electrolytes, after gelation the decrease of Jsc (short-circuit density) due to the comparatively lower conductivity and the increase of Voc (open-circuit voltage) because of the suppression of dark current by polymer chains covering the surface of TiO_2 electrode result in the almost same efficiency for the DSSCs with GPEs and with liquid electrolytes [10].

1.5.2 THE ADVANTAGES OF GPE

GPEs have some advantages, such as low vapor pressure, excellent contacting and filling properties between the nanostructured electrode and counter electrode, higher ionic conductivity compared to the conventional polymer electrolytes and excellent thermal stability. Thus the DSSCs based on GPE have outstanding long-term stability. Therefore, GPEs have been attracting intensive attentions and these advantages lead to broad applications in the DSSCs [10].

1.5.3 HIGHER IONIC CONDUCTIVITY

To pursue high conversion efficiency of the DSSCs, it is necessary to enhance the ionic conductivities of these GPEs. However, conventional polymer electrolytes exhibit very low ambient ionic conductivity because of the severe crystallinity of polymers. In this aspect, most of the recent studies have been directed to the preparation and characterization of GPEs that have higher ionic conductivity at ambient temperature. It is known that room-temperature ionic liquids (RTILs) have wide liquid-phase range, non-flammability and very low vapor pressure at room temperature, wide electrochemical windows, high ionic conductivity and excellent thermal and chemical stability. One of the interesting developments in the field of RTILs is the combination of RTILs and polymers to form gel-like composites for the application in DSSCs, where the RTILs are both ionic sources and the plasticizers. On the other hand, to increase the ionic conductivity to a practical level (at least 1 mS cm^{-1}), highly conductive polymer gels composed of polymer matrix, plasticizer and redox couple salts have been widely tested. Wang prepared a series of quasi-solid-state DSSCs by adding 5 wt% of poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) in methoxypropionitrile (MPN)-based gel electrolytes [11]. The conductivities of these polymer gels exceeded 10 mS cm^{-1} and the cell efficiencies were over 6% but the sealing problem remained. Cheng previously developed a PVDF-based polymer gel system distributed in polyethylene glycol dimethacrylate (PEGDMA) cross-linking reinforced network, showing fairly good ionic conductivity and mechanical ruggedness [12].

1.5.4 EXCELLENT THERMAL STABILITY

GPEs possess excellent thermal stability and the DSSCs based on them exhibit outstanding stability to heat treatments. There was negligible loss in weight at temperatures $\leqslant$200 °C for ionic liquid-based electrolytes of poly(1-oligo (ethylene glycol) methacrylate-3-methyl-imidazolium chloride) (P(MOEMImCl), the effect of heat treatments on performance of the DSSC based on this GPE indicated drops in the conversion efficiency of about 2.1% and 3.9% after heat treatments at 100 °C for 30 and 120 min, respectively, compared to the optimal efficiency of 6.1% at 30 °C for 5 min [13]. This degradation during heat treatment resulted from the evaporation of iodine at elevated temperature which can be confirmed by detecting the evaporated iodine during the heat treatment at 100 °C in an analyzer using a wet starch paper. Additionally, it was speculated that dye desorption could also be a cause of the decrease in cell performance at elevated temperature. The dye adsorption on TiO_2 surface is in equilibrium with dye desorption and this adsorption/desorption equilibrium shifts depending on the temperature [14].

1.6 FACTORS INFLUENCING THE IONIC CONDUCTIVITY OF GPE AND THE PHOTOVOLTAIC PERFORMANCE OF THEIR DSSCS

The ionic conductivity of GPE depends on charge carrier transfer and diffusion efficiency of the redox couple resulting from its own ingredients such as various types of polymer, the concentration of polymers with various molecular weights and conductivities, and the concentration and property of iodide salts. External factors also influence the conductivity to a certain extent, such as the organic solvents and temperature. All the factors above further decide the photovoltaic performance of the DSSCs based on GPE.

1.6.1 POLYMER CONCENTRATION

The ionic conductivity of GPE decreases with an increase of the polymer concentration because the polymer cages or pores trapping liquid electrolyte become smaller and hinder ionic movement. For the polyblend gel electrolytes based on polymers with different conductivities and viscosities, the ionic conductivity of GPE decreases with increasing amount of the component with lower conductivity and higher viscosity under the same salt concentration. For instance, the conductivity of P(MMA-co-MAA) [15].

1.6.2 DIFFERENT TYPES OF POLYMERS

Up to the present, several types of gel electrolytes based on different kinds of polymers have already been used in the DSSCs, such as poly(acrolynitrile), poly(ethylene glycol), poly(oligoethylene glycol methacrylate), poly(butylacrylate), the copolymers such as poly(siloxane-co-ethylene oxide) with different plasticizers, and the composites. GPE with different polymer compositions have different ionic conductivities and their DSSCs exhibit various photovoltaic performances [16].

1.6.3 ORGANIC SOLVENTS

The swelling of polymer mainly depends on Lewis acidic–basic interaction between polymer matrix and organic solvents so that solvents or mixed solvents with different donor numbers affect the liquid electrolyte absorbency of the hybrid, which determines the ionic conductivity of GPE and further influences the photovoltaic performance of quasi-solid-state DSSCs. The photovoltaic performance of the quasi-solid-state DSSCs such as Voc, Jsc, FF (fill factor) changes with a change of donor number of mixed solvents, but the change tendencies are not as regular as that of liquid-electrolyte-based DSSCs due to the more complicated affecting factors in quasi-solid-state DSSCs.

A polymer gel electrolyte with ionic conductivity of 4.45 mS cm^{-1} was obtained by using poly(acrylic acid)-oligo-(ethylene glycol) as polymer matrix, and absorbing 30 vol% N-methyl pyrrolidone and 70 vol% γ-butyrolactone with 0.5 M NaI and 0.05 M I2. By using this GPE coupling with 0.4 M pyridine additive, a quasi-solid-state DSSC with conversion efficiency of 4.74% was obtained under irradiation of 100 mW cm^{-2} [17].

1.6.4 TEMPERATURE

The ionic conductivity of GPE increases with an increase of temperature, which abides by the Arrhenius conductivity–temperature behavior $\sigma_{(T)}=A^{[-Ea/RT]}$ (where Ea is the activation energy, R the molar gas constant, A is Arrhenius constant and T is the absolute temperature) because the conductivity depends on the thermal hopping frequency of ions when an ionic transport process involves intermolecular ion hopping.

The following reasons can be used to explain the temperature dependence of the ionic conductivity for GPE. It is said that the polymer matrix is amorphous and has large amounts of free-volume cages or pores. These free-volume cages increase with an increase in temperature and these results in an increase in more movable ions and a higher ambient ionic conductivity of GPE [18].

1.7 STRATEGIES TO IMPROVE THE PROPERTIES OF GPE AND THEIR DSSC

Although the stability of DSSCs was improved by using quasi-solid-state electrolyte, it is found that the photovoltaic performance of GPE-based quasi-solid-state DSSCs is lower than those of the corresponding liquid-electrolyte-based DSSCs. Although polymers of some kinds can gelate liquid electrolytes effectively, they exert a negative influence on the photovoltaic performance and stability of the DSSCs. For instance, the gel network may hinder charge transport in the gel electrolyte to a certain extent and also there is a possibility that the gelators may react with components of electrolytes. Several effective strategies as follows have been taken to improve the ionic conductivity of GPE and thus the performance of GPE-based DSSCs.

1.7.1 GPE MEMBRANE WITH POROUS STRUCTURE

GPE membrane with porous structure possesses numerous advantages such as a free-standing framework, high ionic conductivity and ease of cell fabrication and very recently this kind of gel polymer membrane has been employed to fabricate the quasi-solid-state DSSCs. Pores closely interconnected to each other make the ion transportation in polymer membrane similar to the behavior in liquid electrolytes so that the porous structure can improve the ionic conductivity of GPE membranes. Moreover, it is advantageous to hold liquid electrolytes and improve the contact property between electrolyte and electrode, resulting in an enhancement of the photovoltaic performance of the DSSCs. GPE membrane with porous structure can be fabricated by the conventional phase inversion method of immersing porous polymer membrane in liquid electrolytes, in a novel way to use water as plasticizer and by controlling the solvent evaporation of GPE in other polymer networks.

1.7.2 THE PHASE INVERSION METHOD

GPE membrane with porous structure can be prepared by the conventional phase inversion method of immersing dry porous polymer membrane in liquid electrolyte. Quasi-solid-state DSSCs assembled with this kind of GPE exhibited energy conversion efficiencies of 2.4% moreover, long-term stability of these cells was superior to those assembled with organic liquid electrolyte. The largest obstacle for the wide application of this membrane is probably its complicated production process and lower energy conversion efficiency [19].

1.7.3 A NOVEL WAY TO USE WATER AS PLASTICIZER

A novel method of using water as plasticizer was applied to fabricate the polymer porous membrane with outstanding capacity of liquid up taking and good mechanical strength. This preparation method is environmentally friendly and dramatically simplifies the fabrication of dry porous polymer membrane as well as assembly of solar cells. Moreover, this technology makes the fabrication of quasi-solid-state DSSCs with different shapes.

These porous electrolyte membranes serve as a separator in solar cells to prevent the DSSCs from short circuiting. The porous structure of the polymer membrane permits close contact of the surface of TiO_2 particle with organic electrolyte in the pores of the membrane, which is advantageous to charge transfer on the surface of semiconductor particle. The polymer acts only as a framework in this system. It may be evidently predicted that the working mechanism of solar cells fabricated with this kind of electrolyte should be similar to those employing liquid electrolyte. The cell efficiency with this kind of GPE should parallel those using liquid electrolyte but displays better long-term stability than those with liquid electrolyte, indicating that the liquid reserving ability of porous polymer framework is extremely high [20].

1.7.4 CONTROLLING THE SOLVENT EVAPORATION OF GPE IN OTHER POLYMER NETWORKS

GPE membrane with porous structure can be fabricated by distributing GPE in cross-linked polymer films and controlling the solvent evaporation to make porous structure in the membrane. This cross-linked feature may lead to lower ohmic loss in GPE, easier cell assembly and may possess potential for flexible DSSC configuration. Furthermore, the micrometer-level pores created by controlling the evaporations of casting solvents can soak liquid electrolytes as channels for fast transport of iodides and tri-iodides, rendering high conductivity over 1 mS cm^{-1}. In contrast, films without pore structure have to deliver ions by sluggish chain swing. The DSSC using this polymer electrolyte notably exhibited higher Voc than the DSSC using liquid electrolyte and its conversion efficiency can be significantly improved to 5.14% [21].

1.7.5 INCORPORATION OF PROTON DONORS

Polymer electrolytes doped with proton donors have recently attracted much attention due to their high proton conductivity, chemical and electrochemical stability, and easier processing of polymer matrices. The proton donor can effectively enhance the ionic conductivity of GPE, resulting in an increase of the I^-/I_3^- mobility and increase in the open-circuit voltage, short-circuit current density, stability and energy conversion efficiency of the DSSCs. As one of the most attractive inorganic proton donors, heteropolyacids (HPAs) have been demonstrated to be highly conductive and structurally stable [22].

1.8 SUMMARY

The electrolytes used for dye-sensitized solar cells are usually liquids and contain electrolytes, ionic liquid oligomer electrolytes and polymer electrolytes. The best photovoltaic performance was achieved for DSSCs based on liquid electrolytes, however, the leakage and volatilization of the solvent have caused difficulties in fabrication, reduced the long-term stability and limited practical applications. Polymer electrolytes are alternatives to liquid electrolytes in order to improve the stability of electrolytes and thus that of their DSSCs. Polymer electrolytes, especially in the gel state, have been a research hotspot due to their high ionic conductivity, excellent thermal stability and long-term stability of the DSSCs based on them. The concentration of iodide salts significantly influences the ionic conductivity of GPE and the performance of the DSSCs because of viscosity and bond formation between the cation and atoms of polymer chains. Higher polymer concentration leads to a decrease in ionic conductivity due to smaller polymer cages or pores. Moreover, the ionic conductivity of GPE depends on temperature and exhibits Arrhenius conductivity–temperature behavior. However compared to the liquid electrolytes, the ionic conductivity of GPE and the photovoltaic performance such as in the enhancement of the DSSCs performance is lowered.

1.9 OBJECTIVE OF OUR WORK

Objective of our work was also to sensitize a GPE for DSSCs which will have a high thermal stability and good conductivity. First a copolymer was prepared from Acrylonitrile (AN) and Methylmathacrylate (MMA) and then porous membrane was sensitized. Membrane was immersed in organic electrolyte which made it more conductive.

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Chapter No.2

ANALYTICAL TECHNIQUES

Analysis and characterization is an important part in materials research. We also used some available analytical techniques for the analysis and characterization of the copolymer of acrylonitrile and methylemathacrylate and also for the study of porous membrane or thin film which we have sensitized from the copolymer. The details of these analytical techniques are given below.

2.1 FTIR

2.1.1 INTRODUCTION

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments.

2.1.2 QUALITATIVE ANALYSIS

FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. By interpreting the infrared absorption spectrum, the chemical bonds in a molecule can be determined. FTIR spectra of pure compounds are generally so unique that they are like a molecular "fingerprint". While organic compounds have very rich, detailed spectra, inorganic compounds are usually much simpler. For most common materials, the spectrum of an unknown can be identified by comparison to a library of known compounds. We have several infrared spectral libraries including on-line computer libraries. To identify less common materials, IR will need to be combined with nuclear magnetic resonance, mass spectrometry, emission spectroscopy, X-ray diffraction, and other techniques.

2.1.3 QUANTITATIVE ANALYSIS

Because the strength of the absorption is proportional to the concentration, FTIR can be used for some quantitative analyses. Usually these are rather simple types of tests in the concentration range of a few ppm up to the percent level.

2.1.4 PHYSICAL PRINCIPLES

Molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate. According to quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to cause the frequency of a molecular vibration to increase is to excite the bond by having it absorb light energy. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states [usually ground state (E_0) and the first excited state (E_1)].The energy corresponding to these transitions between molecular vibrational states is generally 1-10 kilocalories/mole which corresponds to the infrared portion of the electromagnetic spectrum.

Difference in Energy States = Energy of Light Absorbed

$E_1 – E_0 = hc / I$

Where h = Planks constant

c = Speed of Light

I = Wave length of light

2.1.5 SAMPLE PREPARATION

Samples for FTIR can be prepared in a number of ways. For liquid samples, the easiest is to place one drop of sample between two plates of sodium chloride (salt). Salt is transparent to infrared light. The drop forms a thin film between the plates. Solid samples can be milled with potassium bromide (KBr) to form a very fine powder. This powder is then compressed into a thin pellet which can be analyzed. KBr is also transparent in the IR. Alternatively, solid samples can be dissolved in a solvent such as methylene chloride, and the solution placed onto a single salt plate.

The solvent is then evaporated off, leaving a thin film of the original material on the plate. This is called a cast film, and is frequently used for polymer identification.

Solutions can also be analyzed in a liquid cell. This is a small container made from NaCl (or other IR-transparent material) which can be filled with liquid, such as the extract for EPA 418.1 analysis. This creates a longer path length for the sample, which leads to increased sensitivity. Sampling methods include making a mull of a powder with hydrocarbon oil (Nujol) or pyrolyzing insoluble polymers and using the distilled pyrolyzate to cast a film. Materials can be placed in an Attenuated Total Reflectance (ATR) cell and gases in gas cells.

2.1.6 FTIR-MICROSCOPE

For small samples or samples with surface contamination visible to the naked eye, a microscope attachment can be used to obtain reflectance or transmittance spectra on particles as small as 20 microns [1].

2.2 TG/DTA

Thermal analysis is basically an important branch of material sciences where the properties of materials are studied as they change with temperature. Several methods are commonly used. These are distinguished from one another by the property which is measured:

- Differential thermal analysis (DTA): temperature difference
- Differential scanning calorimetry (DSC): heat difference
- Thermo gravimetric (TGA): mass

Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of thermogravimetry (TGA) and Differential scanning calorimetry (DSC) to one and the same sample in a single instrument. The test conditions are perfectly identical for the TGA and DSC signals (same atmosphere, gas flow rate, vapor pressure of the sample, heating rate, thermal contact to the sample crucible and sensor, radiation effect, etc.).

2.2.1 THERMAL ANALYSIS OF POLYMERS

Polymers represent another large area in which thermal analysis finds strong applications. Thermoplastic polymers are commonly found in everyday packaging and household items, but for the analysis of the raw materials, effects of the many additive used (including stabilizers and colors) and fine-tuning of the molding or extrusion processing used can be achieved by using DSC. An example is oxidation induction time (OIT) by DSC which can determine the amount of oxidation stabilizer present in a thermoplastic (usually a polyolefin) polymer material. Compositional analysis is often made using TGA, which can separate fillers, polymer resin and other additives. TGA can also give an indication of thermal stability and the effects of additives such as flame retardants

Thermal analysis of composite materials, such as carbon fiber composites or glass epoxy composites are often carried out using DMA or DMTA, which can measure the stiffness of materials by determining the modulus and damping (energy absorbing) properties of the material. Aerospace companies often employ these analyzers in routine quality control to ensure that products being manufactured meet the required strength specifications. Formula 1 racing car manufacturers also have similar requirements! DSC is used to determine the curing properties of the resins used in composite materials, and can also confirm whether a resin can be cured and how much heat is evolved during that process. Application of predictive kinetics analysis can help to fine-tune manufacturing processes. Another example is that TGA can be used to measure the fiber content of composites by heating a sample to remove the resin by application of heat and then determining the mass remaining [2].

2.3 SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron- sample interactions reveal information about the sample including external morphology, chemical composition, crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1cm to 5microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample. This approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions [3].

2.3.1 FUNDAMENTAL PRINCIPLES OF SCANNING ELECTRON MICROSCOPY (SEM)

Accelerated electrons in an SEM carry significant amounts of kinetic energy. This energy is dissipated as a variety of signals produced by electron- sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons, photons (characteristic X-rays) that are used for elemental analysis and continuum X-rays), visible light cathode luminescence (CL), and heat. Secondary electrons and backscattered electrons are commonly used for imaging samples. Secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete shells of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive" that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly [4].

2.3.2 APPLICATIONS

The SEM is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical compositions acquiring elemental maps or spot. The SEM is also widely used to identify phases based on qualitative chemical analysis and crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Backscattered electron images (BSE) can be used for rapid discrimination of phases in multiphase samples. SEMs equipped with diffracted backscattered electron detectors (EBSD) can be used to examine micro fabric and crystallographic orientation in many materials [5].

2.4 HALL EFFECT APPARATUS

The importance and significance of the Hall Effect is supported by the requirements to find out accurately carrier concentration DC electrical resistivity, mobility, Hall coefficient and sheet magneto resistance in case of metals and semiconductors thin films, which account basically in electrical characterization of these thin surface coatings. Hall Effect is relatively very simple method for doing all these measurements.

2.4.1 HALL VOLTAGE

Suppose we have bar-shaped semiconductor thin film, if this thin film is n-type semiconductor then carriers are predominately electrons not holes with bulk density n. Suppose that a current of constant magnitude I flows along the x-axis from one side to another side in other words from left to right but in the presence of a magnetic field which is z-directed magnetic field. Electrons in case of semiconductor thin film which are subjected to some force which is basically Lorentz force results in initial drifting away from the direction of current towards the negative y-axis, as a consequence of this drifting there is an excess of negative surface electrical charges on this side of the sample in comparison with the other side of the same sample. So there must be difference of potential on both sides of the sample which results in the form of Hall voltage, which is basically a potential drop across the two sides of the sample. On the other hand, the force on holes is obviously toward the same side, reason is that holes have opposite velocity and opposite charges i.e. positive charges. This transverse voltage is termed as Hall voltage V_H and mathematically V_H is equal to

$$V_H = IB/qnd \qquad (1)$$

Where d stands for thickness of the thin film sample, B is magnetic field, I is the current, q is charge and n is for density of charge carriers.

2.4.2 SHEET n_s DENSITY

For using sheet or layer density we have this relation as $n_s = nd$ where n_s is sheet density and n is bulk density if we use sheet density instead of bulk density then equation (1) reduces to

$$n_s = IB/q|V_H| \qquad (2)$$

One can measure the Hall voltage V_H from equation (1) and then from equation (2) with the help of known values of current, magnetic field and elementary charge. One can easily find out the sheet density n_s of charge carriers in case of semiconductors thin films.

2.4.3 IDENTIFICATION BETWEEN N-TYPE AND P-TYPE SEMICONDUCTORS

For n-type semiconductors, Hall coefficient is negative and it should be positive for semiconductors of p-type.

2.4.4 SHEET RESISTANCE

Vander pauw resistivity measurement technique can be used to find out the sheet resistance R_S of the semiconductor.

2.4.5 HALL MOBILITY

As sheet resistance involves with both mobility and sheet density, Hall mobility can be easily calculated from the equation (3) which state as

$\mu = |V_H|/R_S IB = 1/(qn_S R_S)$ (3).

2.4.6 BULK RESISTIVITY AND BULK DENSITY

If one has knowledge about the thickness of the thin film then bulk resistivity and bulk density can be easily estimated from the equations (4) and equations (5) which are stated as

$r = R_S d$(for bulk resistivity) (4)

$n = n_S/d$ (the bulk density) (5)

2.4.7 BULK CONDUCTIVITY

Conductivity is reciprocal of resistivity. If one knows about the bulk resistivity then one can easily determine about the bulk conductivity as well.

2.4.8 MAGNETO RESISTANCE

Magneto resistance is the property of a material which deals with the change of resistivity of material when it is subjected to magnetic field. Different materials show different type of magneto resistance effects which depends upon how much the change in the resistivity occurs when materials are subjected to magnetic field.

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Chapter No.3

MATERIALS AND EXPERIMENTALWORK

3.1 MATERIALS

The materials from which the copolymer is synthesized are listed below

1. Acrylonitrile(AN)
2. Methylmethacrylate (MMA)
3. Potassium persulphate (KPS)
4. Sodium dodecyleSulphate (SDS)

AN was the product of Sigma Aldrich. Methylmethacrylate,Potassium persulphate and Sodium dodecylesulphate was the product of Merck. We discuss these chemicals in a little detail.

3.1.1 ACRYLONITRILE (AN)

Acrylonitrile is a colorless, volatile liquid that is soluble in water and most common organic solvents such as acetone, benzene, carbon tetrachloride, ethyl acetate, and toluene. It melts at 84°C and boils at 77°C. Technical grade acrylonitrile is more than 99% pure. The technical grade products always contain a polymerization inhibitor [1]. Acrylonitrile is a reactive chemical that polymerizes spontaneously and can explode when exposed to flame.

USE OF ACRYLONITRILE

Acrylonitrile is an important chemical. It is used extensively in the manufacture of synthetic fibers, resins, plastics, elastomers and rubber for a variety of consumer goods such as textiles, dinnerware, food containers, toys, luggage, automotive parts, small appliances, and telephones. In 1986, about 40% of the acrylonitrile produced was used to produce acrylic and modacrylic fibers, 28% to produce acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile(SAN) resins, and 15% to produce adiponitrile, an intermediate used in nylon production [2]. The remainder was used in the production of acrylamide (10%), nitrile elastomers, barrier resins, and miscellaneous specialty chemicals (4%) (CMR1986). The manufacture of carbon fibers used for high-performance applications in the aircraft, defense, and aerospace industries is a growing specialty application of acrylonitrile. Other specialty applications include the production of fatty amines, ion exchange resins, and fatty amine amides used in cosmetics, adhesives, corrosion inhibitors, and water-treatment resins (IARC 1999). Acrylonitrile has also been used as a fumigant however, most pesticide registrations of the chemical were canceled in 1978, and its use as a fumigant has been abandoned [3].

3.1.2 METHYLMETHACRYLATE (MMA)

Methylmethacrylate with the chemical formula $CH_2=C(CH_3)COOCH_3$ is a colorless liquid. The methyl ester of methacrylic acid (MAA) is a monomer produced on a large scale for the production of poly(methylmethacrylate) (PMMA).Methylmethacrylate having Auto-ignition temperature 421^oC,Boiling point $100-101^oC$, Explosive limits, vol% in air 1.7-12.5, Melting point -48^oC ,Molecular mass 100.1gram ,Octanol/water partition coefficient (log Pow) 1.38, Relative density (water = 1) 0.94 , Relative density of the vapour/air-mixture at 20^oC (air = 1) is 1.1, Relative vapour density (air = 1) $4.16g(cm)^{-3}$,Solubility in water (at 20^oC) 1.6g/100 ml Vapour pressure (at 20^oC) 3.9kPa [4].

USES OF METHYLMETHACRYLATE

Methylmethacrylate is used in the manufacture of methacrylate resins and plastics (e.g., Plexiglas) [5].The principal uses of methylmethacrylate are cast sheet and other grades (advertising signs and displays, lighting fixtures, glazing and skylights, building panels and sidings, plumbing and bathroom fixtures), molding/extrusion powder, and coatings (latex paints, lacquer, and enamel resins)[6]. Methylmethacrylate is used in the impregnation of concrete to make it water-repellent, and also has uses in the fields of medicine and dentistry to make prosthetic devices and as a ceramic filler or cement [7].

3.1.3 POTASSIUM PERSULPHATE (KPS)

The chemical formula of Potassium persulphate is $K_2S_2O_8$, represented by KSP. It is a white, crystalline, odorless salt. It is used as initiator for the polymerization of monomers and as a strong oxidizing agent in many applications. It has the particular advantage of being almost non-hygroscopic and having particularly good storage stability as a result of its extremely high purity and of being easy and safe to handle.

USE OF POTASSIUM PERSULPHATE

1. Used as desizing agent and bleaching activating agent.
2. Used in oxidation degradation of harmful matters in water pool and closed recalculated water system.

3. Used as modification agent in the production of starch, also used in adhesive and coating production.
4. Used in the oxidation of branched chain, the hydroxyl oxidation of alcohol and aromatic compounds.
5. Used as one of the basic ingredients in hair dye, with discoloring action [8].

3.1.4 SODIUM DODECYL SULFATE (SDS)

Sodium dodecyl sulfate (SDS) or sodium lauryl sulfate(SLS) ($C_{12}H_{25}SO_4Na$) is an anionic surfactant utilized in cleaning and hygiene products. It consists of an anionic organosulfate consisting of a 12 carbon tail attached to a sulfate group, giving the material the amphiphilic properties required for detergent .SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. For example, it is found in higher concentrations with industrial products including engine degreasers, floor cleaners, and car wash soaps. It is used in lower concentrations with toothpastes, shampoos and shaving foams. It is an important component in bubble bath formulations for its thickening effect and its ability to create lather.

Research showed that SDS is not carcinogenic when either applied directly to skin or consumed [9].It has however been shown to irritate the skin of the face with prolonged and constant exposure (more than an hour) in young adults [10].A clinical study found SDS toothpaste caused a higher frequency of aphthous ulcers than both cocoamidopropylbetaine or a detergent-free paste, on 30 patients with frequent occurrences of such ulcers. A clinical study comparing toothpastes with and without SDS found that it had no significant effect on ulcer patterns [11].

USES SODIUM DODECYL SULFATE

SDS is a highly effective surfactant and is used in a variety of task requiring the removal of oily materials and residues. For example, it is a component of industrial products including engine degreasers, floor cleaners, and car wash soaps. It is used in lower concentrations with toothpastes, shampoos and shaving foams. It is an important component in bubble bath formulations for its thickening effect and its ability to create alather.SDS represent a potentially effective topical microbicide, which can also inhibit and possibly prevent infection by various enveloped and non-enveloped viruses such as the Herpes simplex viruses, HIV and the Semliki Forest Virus[12].It has recently found application as a surfactant inqas hydrate or methane hydrate formation reactions, increasing the rate of formation as much as 700 times[13].In medicine, sodium lauryl sulfate is used rectally as a laxative enemas and as an excipient on some dissolvable aspiris and other fiber therapy caplets. Aqueous solutions of SDS are also popular for dispersing (or suspending) nanotubes and also utilized as emulsifier in emulsion polymerization.

3.2 EMULSION POLYMERIZATION

3.2.1 DESCRIPTION

Emulsion polymerization involves the creation of synthetic latexes and resins by the polymerization of a monomer in water emulsion. The resultant polymer dispersion in water may be used in this form, such as for water-based paint, adhesives and the preparation of foam rubber. For other applications the water may be removed by spray drying or other means to produce a free flowing powder or coagulated cake. The following materials are frequently polymerized in the emulsion state:

1. Synthetic rubber latexes - butadiene-styrene, acrylonitrile-butadiene, polybutadiene, polychloroprene and polyisoprene.
2. Coating latex - polyacrylates, polyvinyl acetate, polyvinyl chloride and polyethylene Copolymers.
3. Plastisol resins (a resin mixed with a plasticizer to make a paste) - polyvinyl chloride;
4. Specialty latexes - polyethylene and polytetrafluroethylene. The ingredients used in an emulsion polymerization are listed in the following generalized recipe (Martens, 1964) [14].

Component	**%-Weight Basis**
Monomers	30 - 50
Surface-active agents	1 - 3
Protective colloid	0 - 3
Initiator	1 - 3
Modifier	0 - 1
Buffer	0 - 1
Water	50 – 70

The initiators of the polymerization are usually water-soluble peroxides, hydroperoxides and persulfates. The emulsifiers may be anionic, cationic or nonionic surfactants. The emulsifiers suspend monomer droplets and polymer particles.

Modifiers may be aldehydes, mercaptans or chlorinated hydrocarbons that control the polymerization reaction restricting cross-linking and controlling the molecular weight. Protective colloids, such as polyvinyl alcohol or methyl cellulose, are used to stabilize the final latex. Buffer salts control the pH of the emulsion polymerization batch. These salts, such as phosphates, citrates, acetates and carbonates, are important because pH affects reaction rate, particle size and other reaction conditions.

In some cases the monomer emulsion is seeded with polymer particles. "The purpose of seeded emulsion polymerization is to avoid the uncertainties of the particle initiation stage, obtain better batch-to-batch reproducibility, and give a stable latex of the desired particle size" [15]. The reasons for polymerizing in water include: more rapid polymerization than bulk polymerization at the same temperature with a greater average molecular weight; good heat transfer in water with better control of heat of polymerization; all of the monomer is consumed in the polymerization and the resulting latex can be used directly in coating applications and the aqueous phase lowers the overall viscosity of the emulsion.

3.2.2 POLYMERIZATION GENERAL MECHANISM

The monomer emulsion is made up of water-immiscible monomer droplets stabilized by surfactant molecules, empty micelles (colloidal surfactant vesicles) and monomer-swollen micelles. The monomer droplets can range in size from less than one micrometer to ten micrometers. The size of micelles is about 10 to 15 nanometers. During the reaction, the monomer molecules diffuse from the droplet reservoirs to the micelles where polymerization takes place. The polymer chains grow in the micelles. As polymerization proceeds, the monomer droplets decrease in size and eventually disappear. When the polymer particles become large, the surfactant molecules in the micelles suspend the polymer particles. The final polymer particles grow to a size range of a few tenths of a micrometer up to one micrometer [16]. The physical character of the final polymer depends on the temperature of reaction, the formulation and the manipulation of the reaction conditions, such as when and how much of the ingredients are added to the reactor.

3.2.3 PROCESS

The homogenizer is used in emulsion polymerization to emulsify the monomer into the premix to the reactor. Of all the emulsion monomers, vinyl chloride polymerization is the one that most commonly uses homogenizers to prepare the mix.

In a typical process the ingredients to make the polymer are added in the appropriate sequence to an evacuated, agitated, pressurized tank (pressurized with nitrogen gas). After mixing the ingredients and adjusting the temperature of the mix, the emulsion is homogenized to produce the desired monomer droplet size. The homogenizing pressure may be in the range of 1000 to 5000 psi, depending on the monomer and the required droplet size of the monomer reservoir. This monomer droplet size can affect the physical character of the final latex particles. From the homogenizer the emulsion goes to the reactor, where polymerization occurs at a controlled temperature, until the desired conversion is achieved. After completion of the reaction, the latex is cooled and removed from the reactor. When processing a monomer, such as vinyl chloride, certain safety precautions must be observed. Vinyl chloride monomer is a clear, colorless liquid with a boiling point of -13.3°C [17]. It is flammable in air, has a density greater than air and is listed as a known carcinogen. Therefore, special homogenizer design requirements are necessary for processing vinyl chloride monomer.

3.3 POLYMERIZATION MECHANISM FOR THE FORMATION OF CO-POLYMER FROM ACRYLONITRILE AND METHYLMETHACRYLATE

1. Initiator Decomposition

The initiator decomposes in water for the generation of free radical specie.

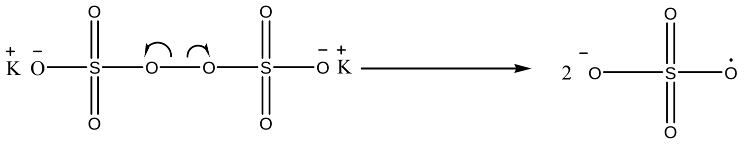
$$I \xrightarrow{K_d} 2R^o \qquad (1)$$

I= Initiator

R^o= Radical

K_d= Rate constant for decomposition

Mechanism



2. Initiation

Methylmethacrylate (MMA); which is first monomer molecule (M_f) attaches with the initiator radical (R^o) to produce real chain initiating specie (R_i) or blank chain radical.

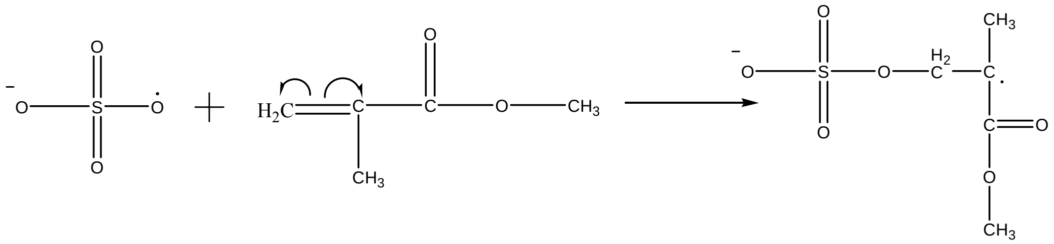
$$R^o + M_f \xrightarrow{K_i} R_i^o \qquad (2)$$

$R^o = S^-O_4^o$

M_f = MMA

K_i = Rate constant for initiating step

Mechanism



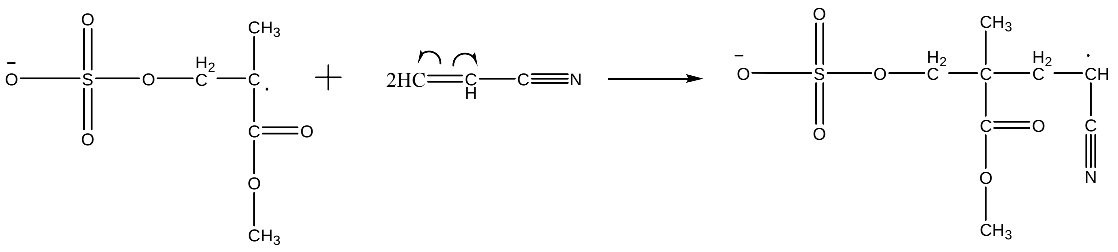
3. Propagation

Single monomer unit (R_i^o) is added to co-polymer (Acrylonitrile)

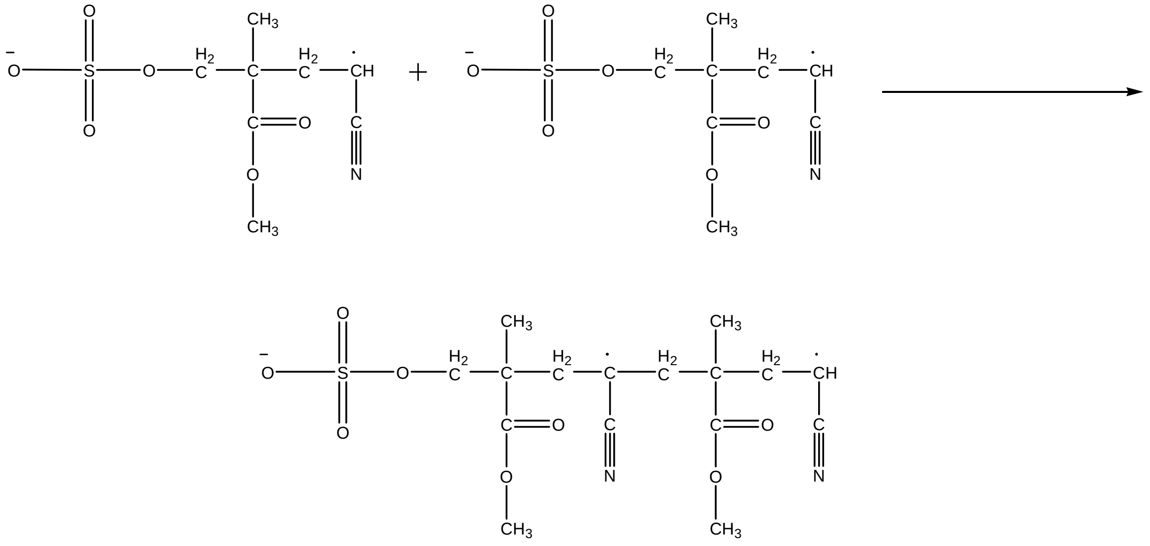
$$R_i^o + M_c \xrightarrow{K_{PB}} P^o{}_B \qquad (3)$$

M_C = Co-monomer (AN)

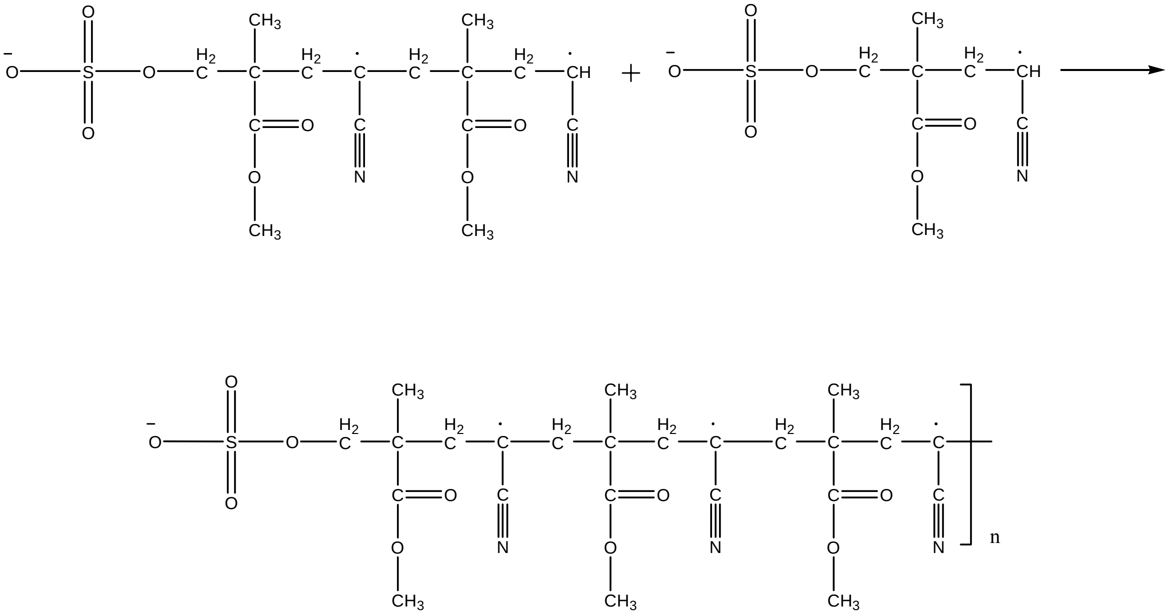
Mechanism



i. Acrylonitrile Methylmethacrylate Dimerization



ii. Acrylonitrile Methylmethacrylate Polymerization



4 Blank Termination

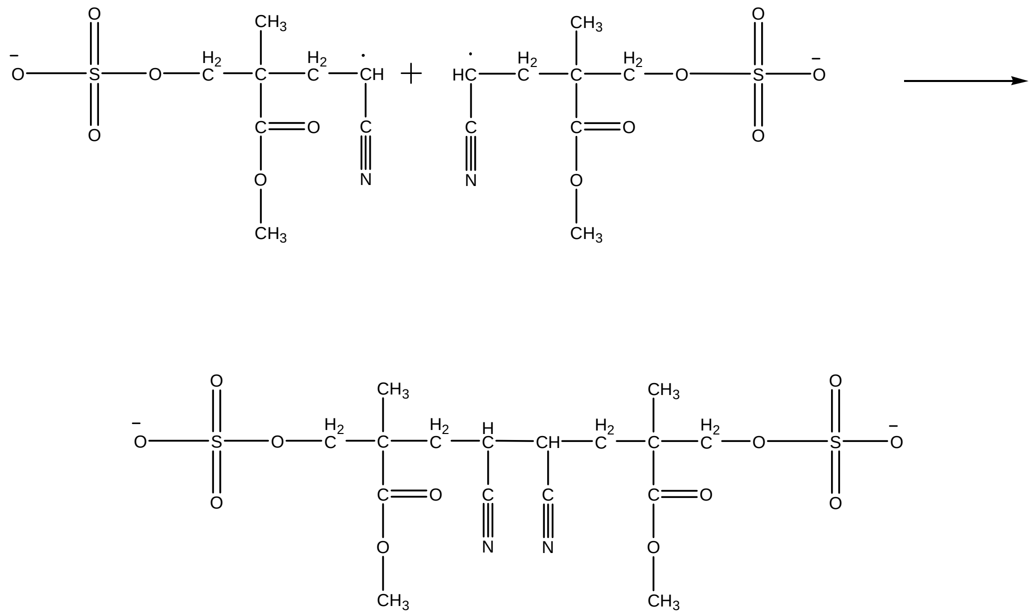
The termination of the polymer chain occurs when the radicals react with each other either by coupling or by dis-proportionation by picking (H^{+}) ions (hydrogen cations from medium).

i. Coupling

$$P^{o}_{Bn} + P^{o}_{Bm} \xrightarrow{K_{t.c}} P^{o}_{bn.m} \qquad (4a)$$

$K_{t.c}$= Rate constant of termination step for coupling

Mechanism

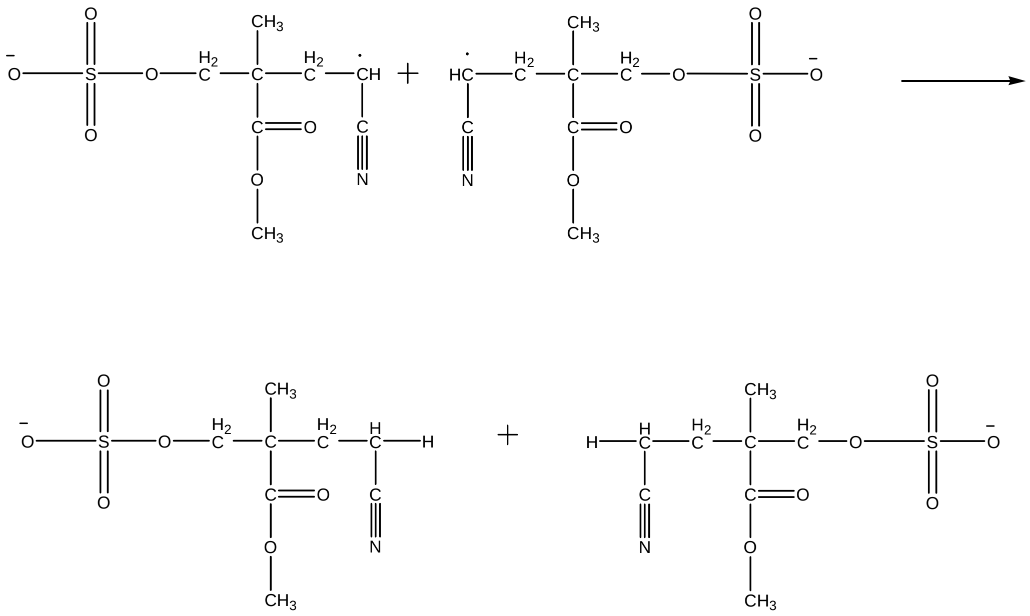


ii. Disproportionation

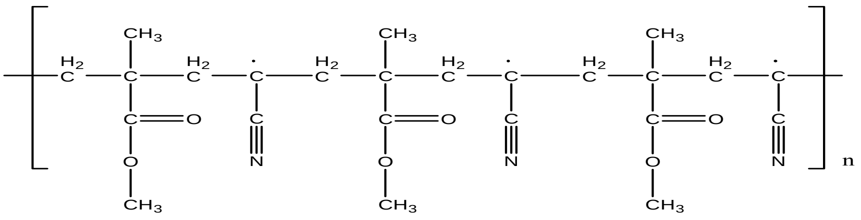
$$P^{o}_{Bn} + P^{o}_{Bm} \xrightarrow{K_{t.D}} P^{o}_{Bn+H} + P^{o}_{Bm} \quad (4b)$$

$K_{t.D}$= Rate constant of termination step for disproportionation

Mechanism



Tentative Structure for Methylmethacrylate Acrylonitrile copolymer



3.4 EXPERIMENTAL APPARATUS AND PROCEDURE

3.4.1 APPARATUS

In order to start the project the apparatus which was arranged in laboratory was composed of three neck flask, refluxer, nitrogen gas cylinder, magnetic stirrer etc. For making the co polymer the reaction was started from reagents composed of Acrylonitrile (AN), Methylmethacrylate (MMA), Sodium dodecyl sulfate (SDS) and Potassium persulfate.The details of reactions are given in table below after procedure.

Figure 3.1. Experimental apparatus arranged in laboratory

3.4.2 PROCEDURE

First the appropriate amount of AN and MMA were poured into a glass beaker then small amount of SDS (emulsifier) and potassium persulphate (initiator) were also added to the glass beaker in which AN and MMA were already present. Appropriate amount of distilled water was also added to the mixture. Then the mixture was poured into three neck flask. Magnetic stirrer was also put into it. In three neck flask, one neck for reflux condenser other two for nitrogen inlet and thermometer respectively as shown in Figure 1. The apparatus were arranged in a fume hood in such a way that the bottom of three neck flask touches the hot plate. Reaction mixture was reflux for 5 hr at 60°C in Nitrogen medium. The experiment was performed several times by changing concentration of reagents, Details are given as:

Table.3.1 Details of reagent concentrations in copolymerization reactions

Experiment No.	MMA (ml)	AN (ml)	MMA:AN	SDS (gm)	KPS (gm)	Water (ml)
1	10.70	37.00	1:3.4	0.05	0.005	45.00
2	10.70	37.00	1:3.4	0.05	0.01	25.00
3	10.70	37.00	1:3.4	0.05	0.01	35.00
4	10.70	37.00	1:3.4	0.05	0.10	35.00
5	10.70	37.00	1:3.4	0.02	0.07	30.00
6	21.40	85.60	1: 4	0.02	0.07	25.00
7	21.70	108.50	1:5	0.04	0.14	60.00
8	20.00	120.600	1:6	0.04	0.14	60.00

With these concentrations of reagents reaction was continuous for five hours with reflux condenser in nitrogen media. After five hours two prominent phases were observed in three neck flask, one was transparent and other was whitish viscous phase. They were separated from one another. The viscous whitish phase was poured into petridish and then placed inside the oven for drying at 70^{o}C. After three hour a white product was left in solid form, the product was washed with running water to remove the impurities in the form of salts etc.After washing the product was again dried and then a very small amount was dissolved in Dimethylformamide(DMF) which conformed that the product is the co-polymer. It was noticed that from reaction 6, 7 and 8 we get maximum copolymer product.

3.4.3 PREPARATION OF POROUS MEMBRANE OR GEL POLYMER ELECTROLYTE

The copolymer which was formed dissolved in 5wt% in Dimethylformamade (DMF). After complete dissolution the paste which was formed from the dissolution of copolymer in DMF was cast on the glass substrate with the help of a blade. When film was formed on glass substrate then it was placed in a clean environment for evaporation of DMF at room temperature for different evaporation times. After evaporation at different evaporation times the film was immersed in water bath for phase inversion. A Substantial number of pores were created in copolymer thin film.

Then the film was dried at $60^{o}C$ for an hour, after drying, the porous membrane was immersed in liquid electrolyte which was the solution of 0.5M LiCl and 0.001M Pyridine in Acetonitrile for an hour for the activation of pores in copolymer membrane. The liquid electrolyte incorporated in the pores of porous membrane which resulted increase in ionic conductivity of the copolymer membrane.

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RESULTS AND DISCUSSION

4.5 CHARACTERIZATION OF COPOLYMER BY FTIR

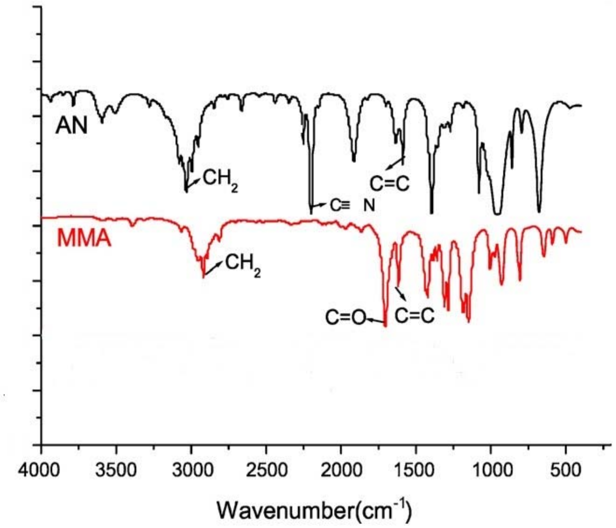


Figure 4.1.FTIR spectra of AN and MMA

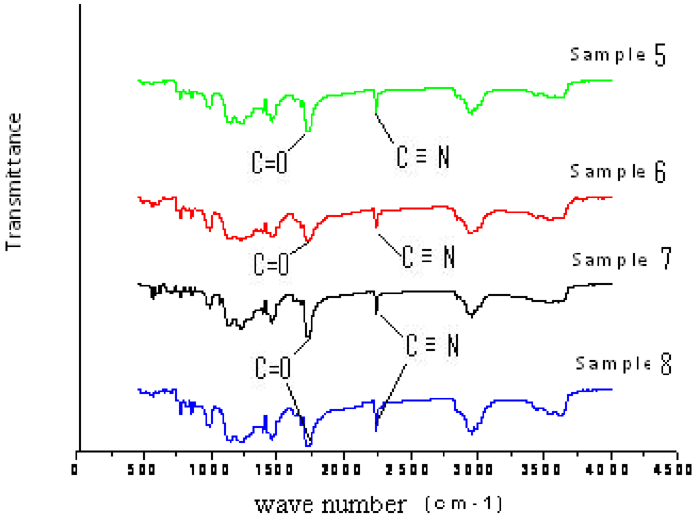


Figure 4.2.FTIR spectra of the copolymers of AN and MMA

Figure 4.1 Represents the FTIR spectra of monomers, Acrylonitrile (AN) and Methylemathacrylate (MMA). The monomer AN is characteristic of the adsorption peaks at 1597 and 2237 cm^{-1}, which correspond to the bonds C=C and C≡N, respectively. The monomer MMA is characteristic of the adsorption peaks at 1616 and 1725cm^{-1}, which correspond to the bonds C=C and C=O, respectively. By comparing the FTIR spectrum of the copolymers in Figure 4.2 with that of monomers in Figure 4.1, it can be found that the copolymer (AN–MMA) keeps the absorptions at 1725cm^{-1} for C=O and 2237 cm−1 for C≡N and loses the absorption at 1597 or 1616cm^{-1} for C=C, indicating that the copolymer maintains the main characteristics of the monomers and the monomers are copolymerized through the breaking of double bonds C=C in both monomers. Due to the cross-linking between two monomers AN and MMA it can be expected that the copolymer has good strength and good conductivity due to the existence of strong polarity bonds CN and CO.

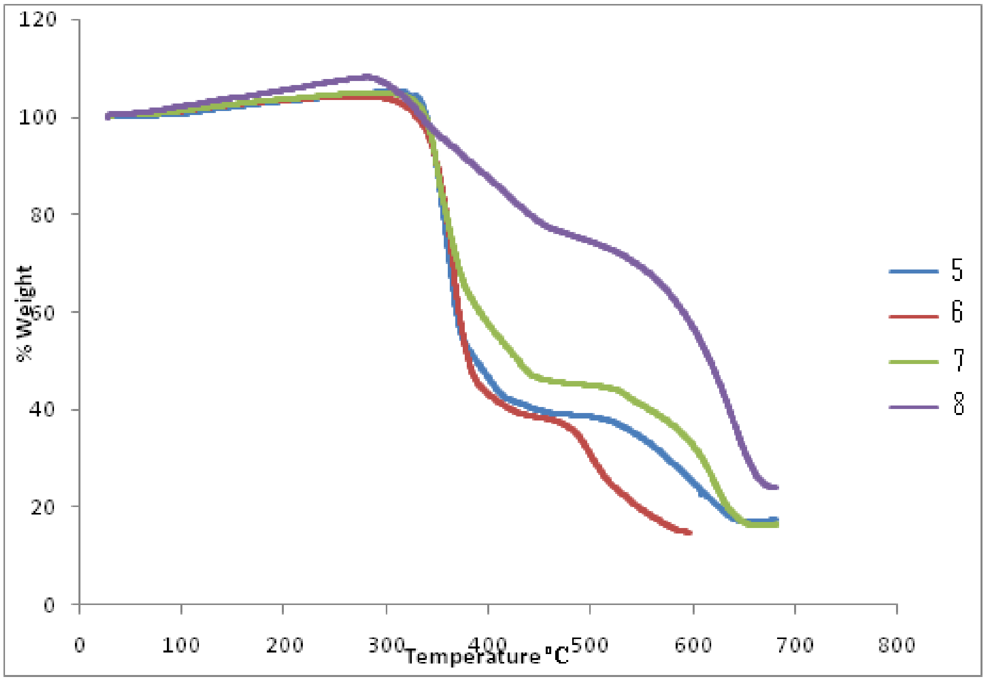
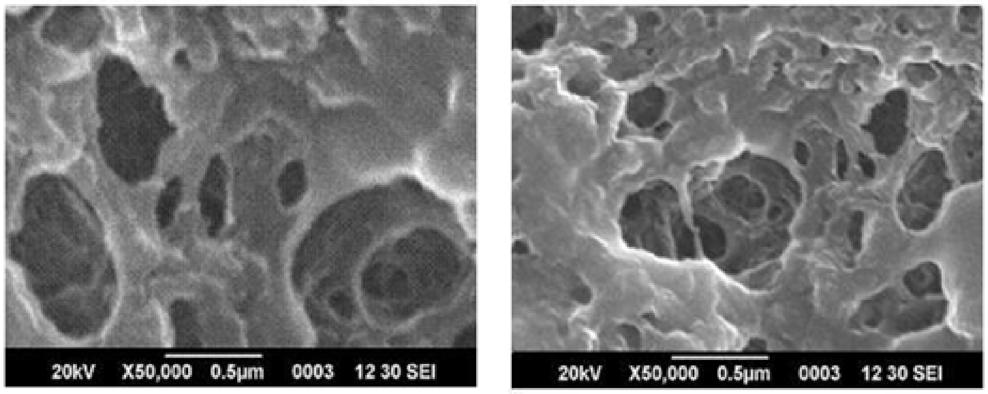


Figure 4.3.TGA curve of the copolymer of AN and MMA

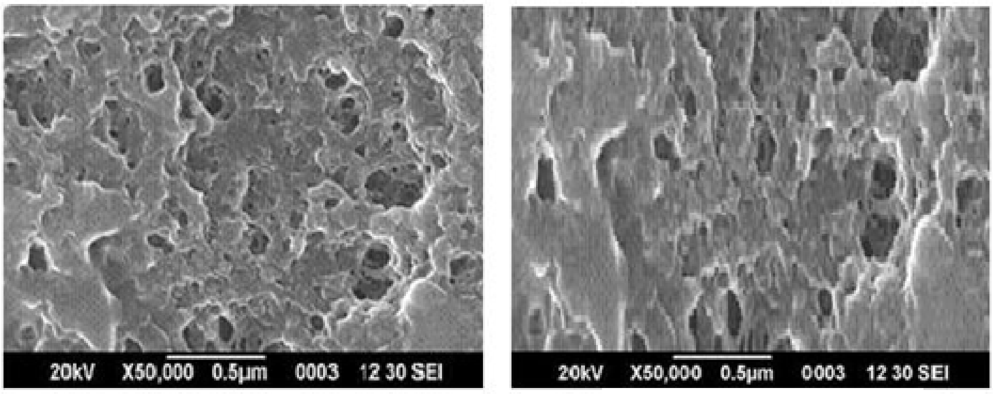
4.6 THERMO GRAVIMETRIC ANALYSIS (TGA) OF THE COPOLYMER

Figure 4.3Represents the TGA curves of the copolymers of Acrylonitrile (AN) and Methylemathacrylate (MMA) synthesized with different ratios of the reagents. There is a prominent decrease in weight at 350◦C for copolymer 5, at 340◦C for copolymer 6, at 320◦C for copolymer 7 and at 300◦C for copolymer 8 which are indicated as 5,6,7 and 8 respectively in Figure 3. These phenomena reflect the decomposition of the copolymer. Therefore the copolymers which we have sensitized are thermally stable at the temperature lower than 300 ◦C, which is better thanPolyMethylemathacrylate (PMMA) and Polyacrylonitrile (PAN) polymers. Apparently, the cross-linking between MMA and AN can improve the thermal stability of the polymer with single monomer. It can be noted fromFigure 4.3that there appears smallweight increase from 0–300◦C which may result due to the adsorption of some gas.

3.7SCANNING ELECTRON MICROSCOPE ANALYSIS OF THIN FILMS OF AN AND MMA COPOLYMER



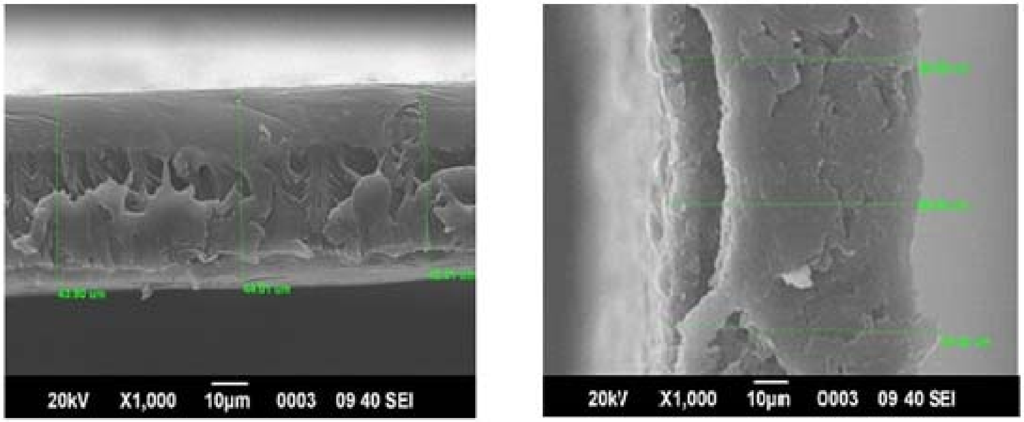
(a) Evaporation time 3hr (b) Evaporation time 5hr



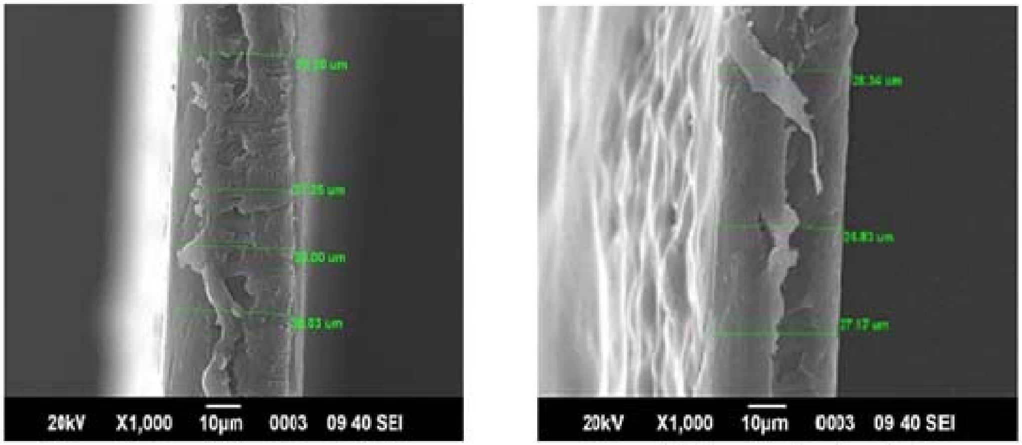
(c) Evaporation time 10hr (d) Evaporation time 24hr

Figure 4.4.SEM images of the surface of the porous membranes of AN and MMA copolymer prepared by the phase-inversion method with different evaporation times

Figure 4.4 shows scanning electron microscopy (SEM) images of surfaces of porous AN-MMA copolymer membranes. The porous membranes were obtained by immersion in a water bath after evaporation of the solvent for 3, 5,10and 24 hour, respectively. During evaporation of the casting solvent, some phase separation was observed before immersion in water, which means that the phase separation was time-dependent. All four membranes exhibited a porous structure. The pore size increases by decreasing the evaporation time. In the phase-inversion process, the membrane is formed by polymer precipitation, which occurs as a result of concentration variations following diffusive interchange between the solvent (DMF) and nonsolvent (water). An increase in the polymer concentration in the casting solution with increasing evaporation time led to the formation of porous membrane in which pore size is small, as shown in Figure 4.4(c,d).Increasing the evaporation time gave a much higher polymer concentration. This implies that the volume fraction of the polymer increased, and so a less porous membrane was obtained. These results suggest that both the pore size and pore volume could be controlled by changes in the evaporation time of the solvent before immersion in a nonsolvent bath, which affects the uptake of the electrolyte solution during the activation step, which is discussed in detail later. An increase in the evaporation time led to the formation of a thinner membrane because the solvent in the casting solution slowly evaporated during the drying period. A decrease in the membrane thickness resulted in an increase in the apparent density of the membrane; this means the formation of less porous membranes. These results are consistent with the SEM images shown in Figure 1: an increase in the evaporation time led to the formation of a denser membrane with a smaller pore volume. However, it should be noted that further evaporation of the solvent after 24 hour had little effect on the thickness and porosity of the membrane. The solvent in the casting solution gradually evaporated from the upper surface of the membrane in contact with air.



(e) Evaporation time 3hr (f) Evaporation time 5hr



(g) Evaporation time 10hr (h) Evaporation time 24hr

Figure 4.5.SEM images of cross sections of the porous membranes prepared from AN- MMA Copolymer by the phase-inversion method with different evaporation times

Figure 4.5 shows the SEM images of cross sections of the copolymer membranes with evaporation times 3,5,10 and 24 hours respectively. The average thicknesses were 43.27µm, 40.37µm, 37.2µm and 27.18 µm for copolymer membranes having evaporation times 3,5,10 and 24 hours respectively. Which show that as the evaporation time increases the thickness of membrane decreases. Thicknesses of copolymer membranes are calculated because it is important for Hall Effect apparatus for the measurement of conductivity.

Table 4.1 Conductivities and physical properties of gel polymer membranes prepared from copolymer of AN and MMA

Evaporation Time (hr)	Thickness (µm)	Avg Hall Coefficient (cm^3/C)	Conductivity (Scm^{-1})
3.00	43.27	1.84×10^{6}	1.87×10^{-4}
5.00	40.37	8.10×10^{4}	2.73×10^{-5}
10.00	37.20	1.46×10^{6}	3.25×10^{-5}
24.00	27.18	6.50×10^{5}	2.28×10^{-6}

4.8 CONDUCTIVITY MEASUREMENTS BY HALL EFFECT APPARATUS

Table 4.1 shows the physical properties and conductivities of the gel polymer electrolytes synthesized from the co polymer of Acrylonitrile (AN) andMethylmathacrylate (MMA).Before conductivity measurement the copolymer membranes were soaked in liquid electrolytes by which liquid electrolyte incorporated in the pores of these porous membranes by which they show good conductivities. It is clear from Table 4.1 that the ionic conductivities of the gel polymer electrolytes for evaporation times of 3, 5, 10 and 24 hours are1.87×10^{-4},2.73×10^{-5},3.25×10^{-5} and 2.28×10^{-6}(Scm^{-1}) respectively at room temperature. The positive values of the average Hall coefficient shows that the gel polymer membranes are p-type materials, means that they are hole conducting not electrons.

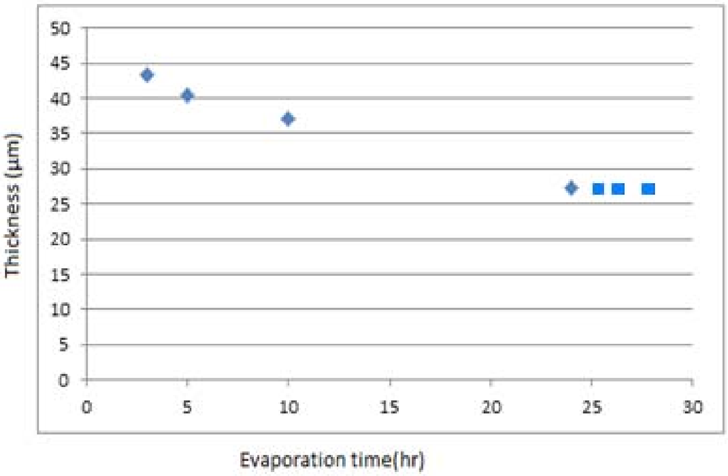


Figure 4.6. Relation of thickness of copolymer membrane with evaporation time

Figure 4.6 represents the behavior of thickness of copolymer membranes with the drying evaporation times. It is very clear from the Figure 4.6 that the thickness of copolymer membrane decreases with the increase in evaporation time. When the paste of copolymer and organic liquid which is dimethylformamide (DMF) is cast on glass substrate and left for drying at room temperature. The organic liquid starts evaporation and gradually the thickness of gel polymer membrane decreases but after 24 hours the thickness does not decreases with increase in evaporation time.

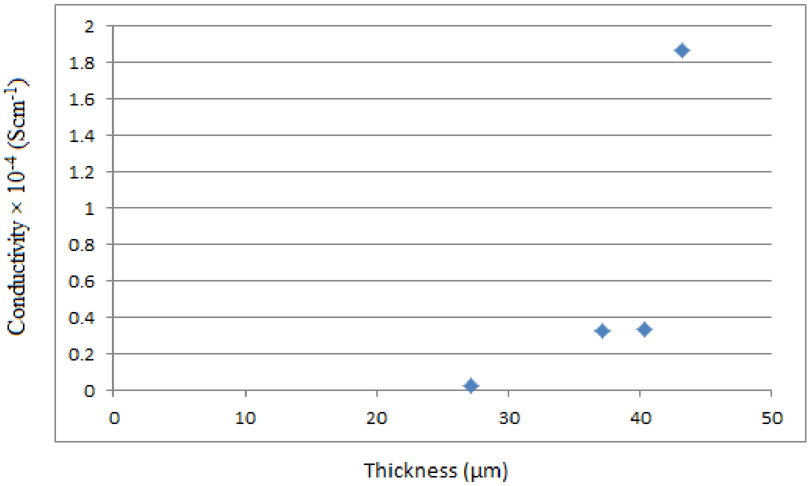


Figure 4.7. Relation of thickness of gel polymer membrane of different evaporation times with ionic conductivities

The ionic conductivity values of the of the gel polymer membranes or gel polymer electrolytes which are obtained from Hall Effect apparatus are plot against their thickness. It is very clear from Figure 4.7 that increase in the thickness of gel polymer electrolytes results in considerable increase in their ionic conductivities.

Chapter No.5

CONCLUSIONS & FUTURE RECOMENDATIONS

5.1 CONCLUSIONS

The copolymer Acrylonitrile-Methylmathacrylate (AN-MMA) was sensitized by emulsion polymerization method and it was investigated that in polymerization of AN and MMA the product copolymer yield increases by increasing the concentration of AN. Porous membranes based on the AN-MMA copolymer were prepared by phase inversion method. And it was reported that physical properties of the porous membranes, such as pore volume, and pore size, could be controlled by changes in the evaporation time before phase inversion. The porous membranes were soaked in organic liquid electrolyte which incorporated in the pores of membrane and make them active. We have also demonstrated that an Acrylonitrile (AN) and Methylmathacrylate (MMA) copolymer (AN-MMA) matrix provides an efficient medium for the transport of ions combining high conductivity and ample free volume for the mobility of solvent. The ionic conductivity of gel polymer membrane varies with thickness of the copolymer membrane and the thickness varies with the drying evaporation time. The maximum room temperature ionic conductivity of the best gel polymer membrane was 1.87×10^{-4}(Scm^{-1}) which has thickness of 43.27µm and evaporation time of 3 hours. From Hall Effect apparatus results it was also confirmed that the gel polymer electrolyte which we have synthesized is a hole conducting material means a p-type material. These gel polymer membranes or gel polymer electrolytes can be a good alternative to the liquid electrolytes as a hole conducting material in Polymer solar cells. The advantage of the polymer membrane is that it can be prefabricated on a large scale and can be hot pressed between electrodes to provide effective electronic contact.

5.2 FUTURE RECOMMENDATIONS

Following future work needs to be done for improvement and further development of organic or polymeric solar cells

1. We have sensitized the copolymer from acrylonitrile, methylemathacrylate, sodium dodecylesulfate and potassium persulfate, other materials should also be used for better result.

2. We utilized emulsion polymerization method for preparation of copolymer; some other polymerization method should also be used.
3. Polymer solar cells should be fabricated with these solid form gel polymer electrolytes and their efficiencies should be calculated.
4. Work should be done on organic photovoltaics in different research organizations that the polymer solar cell should be practically utilized on commercial scale.