Copolymerization of Aniline and Crotonic Acid Using Various Surfactants in Aqueous Media

A Thesis Submitted in

Partial Fulfillment of the requirement for the

Degree of Master's Degree in Chemistry

By

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May-2013

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ACKNOWLEDGEMENT

It has been said that gratitude is the memory of heart; I would like to take the opportunity to express it .It is my bound duty to reveal my soulful gratitude to god the almighty, who had never left me alone during the times of trials and finish this work as a great success.

My whole hearted thanks and my profound respects are to our Chancellor **Dr.(Thiru)T.S.K.Meenakshi Sundaram**,M.A.,M.Phil.,Ph.D.,Avinashilingam Institute for Home Science and Higher Education for Women , University Coimbatore**.**

I devote my sincere and special profound thanks to vice chancellor **Dr.(Tmt)SheelaRamachandran**,M.Sc.,P.G.Dip.,Ph.D.,(Avinashilingam),Avinashilingam Institute for Home Science and Higher Education for Women , University Coimbatore, for Granting me the opportunity to carry out my thesis.

I express my sincere thanks to **Dr. (Tmt) Gowri Ramakrishna,** M.Sc. (Madras), M.Phil., Ph.D., (Avinashilingam), Registrar Avinashilingam Institute for Home Science and Higher Education for Women, University Coimbatore, for providing adequate help required to carry out my work.

I would like to thank **Dr. (Mr).K.Santhana Krishnan**, Director, Research and Consultancy, Avinashilingam Institute for Home Science and Higher education for Women University, Coimbatore, for providing the opportunity to conduct this study.

I express my sincere gratitude to **Dr. (Tmt) Saroja Prabhakaran**, M.A., Dip.Ed. (Madras), Ph.D.(Mother Teresa), The Director, Hall of residence, Avinashilingam Institute for Home Science and Higher education for Women University ,Coimbatore, for all the amenities provided for the conduct of the study.

I owe my indebtness to **Dr. (Mrs.) R. Parvatham**, M.Sc., Dip. Eid, M.Phil.,(Madras), Ph.D., (Avinashilingam), Dean, Faculty of science, Avinashilingam institute of home science and higher education for women, Coimbatore , for the facilities and guidance given to me during the period of my thesis.

I express my deep sense of gratitude to **Dr. (Mrs.). R. Shyamala,** M.Sc., Dip.Ed., (Madras), M.Phil., (Bharathiar), Ph.D., (Avinashilingam, Professor and head of department of chemistry, Avinashilingam institute of home science and higher education for women, Coimbatore , for the valuable moral support throughout the project period.

My Heartfelt thanks to my persevering, enthusiastic and loveable guide **Dr.(Tmt) S.Subhashini** M.Sc., M.H.ED,(Annamali), M.Phil.,(Bharathiar), Ph.D., (Avinashilingam), Professor, department of chemistry, Avinashilingam institute of home science and higher education for women, Coimbatore, for her precious guidance, innovative ideas, constructive thoughts, patience, unflinching encouragement, inspiration at every stage of investigation and motivation right from the selection of the topic to the completion of the work.

Words are insufficient to express to my gratitude of thanks to **all the staff members of department of chemistry** for their vivacious guidance throughout to complete this thesis successfully.

A special thanks to Mrs A. Fathima, Mrs R. Geethanjali, Ph.D., Scholar Avinashilingam institute of home science and higher education for women, Coimbatore, for their unfailing support and encouragement through this work successfully.

I heartily express my gratitude to **my beloved family members** for their constant support, without which I would not have been what I am today.

Finally I convey **my hearty thanks** to all those who helped me directly to carry out this thesis successfully.

M.Subbulakshmi

CONTENTS

List of Tables

List of Figures

LIST OF ABBREVIATIONS

CA - **Crotonic Acid**

PEG - Poly Ethylene Glycol

HCl - Hydrochloric Acid

APS - Ammonium per Sulfate

SDS - Sodium Dodecyl Sulphonate

CAN - Ceric Ammonium Nitrate

1. INTRODUCTION

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of polymerization. The units composing polymers derive, actually or conceptually, from molecules of low relative molecular mass. The repeating units linked by covalent bonds have been the primary focus of polymer science; emerging important areas of the science now focus on non-covalent links.

Polymers can be classified as organic polymers and inorganic polymers. The backbone of organic polymers consists mainly of carbon atoms linked together or separated by hetero atoms such as oxygen or nitrogen. Organic polymers are used heavily in modern daily life.

Some selective inorganic polymers reviewed as advanced materials are polysilanes, polygermanes, polystannanes, polyborazines, and polyphosphazenes. Polysilanes are used for a great deal of applications in ceramics and composites, and photo electronics.

Polysilanes are formed by sigma-conjugation of the silicon atoms in the polymer chain, with varying molecular weight, conformation and substituents of the polymer. Polygermanes and polystannanes possess similar properties like polysilanes. Polyborazines are mainly used as preceramic polymers for preparing drugs, hydro gels, liquid crystalline materials, and low-temperature elastomers, semiconductors, composites, etc.

Polymers are studied in the fields of biophysics, macromolecular science, and polymer science. The polymer science was born in the great industrial laboratories of the world of the need to make and understand new kinds of plastics, rubber, adhesive, fibers and coatings. The first polymers used were natural products especially cotton, starch, proteins and wool. Early in the twentieth century, synthetic polymers were made. Polymer plays an important role in human life in two different ways that is natural and synthetic polymer.

IMPORTANCE OF NATURAL POLYMERS:

The polymers occur naturally in the form of proteins, cellulose (plants), starch (food), and natural rubber. In our body biological constituents like macromolecules, proteins (polyamides), nucleic acid (polynucleotides) and polysaccharides are purely polymeric. Examples of isoprenylated/lipid-modified glycoproteins were small lipid molecules and oligosaccharide modifications occur on the polyamide backbone of the proteins.

The DNA and RNA are one of the natural polymers. They are so important in genes and life processes. RNA and DNA contain polymer backbones which are based on sugar units. This makes them polysaccharides, although in the case of RNA and DNA, there are well ordered groups attached to the sugar units that give these polymers their unique capabilities. Natural polymer materials such as shellac and amber have been in use for centuries. Biopolymers such as proteins and nucleic acids play crucial roles in biological processes. A variety of other natural polymers exist, such as cellulose, which is the main constituent of wood and paper. The natural biopolymers are fundamental for biological structure and function. Other includes polysaccharides (sugar polymers) and polypeptides like silk, keratin, and hair. Natural rubber is a natural polymer, also made from just carbon and hydrogen.

IMPORTANCE OF SYNTHETIC POLYMERS:

They play an essential and ubiquitous role in everyday life, from those of familiar synthetic plastics and other materials of day-to-day work and home life. The field of synthetic polymers or plastic is currently one of the fastest growing materials industries. The interest in engineering polymers is driven by their manufacturability, recyclability, mechanical properties and lower cost as compared to many alloys and ceramics. Also the macromolecular structure of synthetic polymers provides good biocompatibiling and allows them to perform many biomimetic tasks that cannot be performed by other synthetic materials, which include drug delivery, used as grafts for arteries and vein and artificial tendons, ligaments and joints.

Polymers role in human life from in our tablet tube, tooth paste cover, shoes, suppliers, chairs, vehicle, carrying bag, aircraft etc….. By looking all those things we conclude that polymer production is very much useful for human development.

PROPERTIES OF POLYMERS:

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers.

Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

P**hysical properties**, polymers are strongly dependent on the size or length of the polymer chain. For example, as chain length is increased, melting and boiling temperatures increase quickly. Increasing chain length furthermore tends to decrease chain mobility, viscosity increase of over 1000 times, increase strength and toughness, and increase the glass transition temperature (T_G)$^{.}$ This is a result of the increase in chain interactions such as Van der Waals attractions and entanglements that come with increased chain length.

Transport properties, diffusivity relate to how rapidly molecules move through the polymer matrix. These are very important in many applications of polymers for films and membranes.

Mechanical properties, the bulk properties of a polymer are those most often of end-use interest. These are the properties that dictate how the polymer actually behaves on a macroscopic scale.

In dilute solution, the properties of the polymer are characterized by the interaction between the solvent and the polymer.

CONDUCTING POLYMERS:

The evolution of conducting polymers began in 1975 with the discovery of a linear conjugated organic polymer, polyacetylene, by Shirakawa. However, the material showed metallic properties (improvement in conductivity by 9−13 orders of magnitude) only after its oxidation by iodine, which was reported two years after its discovery [**H. Shirakawa et.al, 1977**]. This gave rise to a surge of activity directed towards the exploration, synthesis and characterization of this class of material, also known as **'Synthetic Metals' [A. A. Syed et.al, 1991].** These new materials combine typical properties of organic polymers such as low density, environmental stability, resistance to corrosion and low cost of synthesis with the conductivity of metals. The desirable properties of these materials can be achieved among other possibilities through engineering at the molecular level by modifying the parent monomers.

A conducting polymer is a highly delocalized π-electron system with alternative single and double bonds in the polymer backbone. The π-conjugation of the polymer chain generates high energy occupied and low energy unoccupied molecular orbital leading to a system that can be readily oxidized or reduced **[A. F. Diaz et.al, 1988]**. Their electronic conductivity is called intrinsic as it is caused by the presence of particular molecular structure elements which enable electric charges to move around without any added conducting materials (e.g. metals, graphite). In most of the cases, these polymers are insulators in their neutral state and they become conducting only after introduction of electron acceptors/donors by a process known as 'doping'. One should keep in mind that the term doping used in the field of conducting polymers is somewhat different from the term used in the field of conventional in-organic semiconductors. This discrepancy arises from the amount of dopant which, in some cases, may constitute up to 50 per cent of the final weight of the conducting polymer. Dopants interact with polymers by oxidizing or reducing them and do not participate in the charge transport mechanism directly. An unpaired spin is generated near the valence band or a vacancy in the conduction band is filled when an electron is removed (p-doping) or added (n-doping) to the polymer. Out of several possible ways of doping a polymer, chemical and electrochemical doping techniques are the most widely used ones **[P. S. Rao et.al, 2001].**

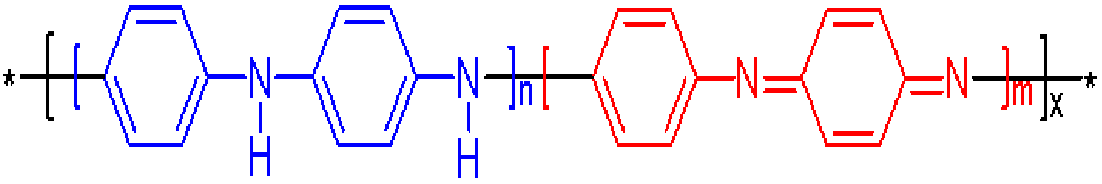
Polyacetylene, the first ever discovered conducting polymer, despite its high conductivity, is environmentally unstable. It has led to the discovery of other conducting polymers such as polypyrrole, polythiophene, polyphenylene, polyphenylenevinylene, polyaniline etc. The electrical behavior of these polymers and their derivatives is similar to that of polyacetylene. Moreover, they show higher stability and better process ability **[T. A. Skotheim et.al, 1998].** Of all these conducting polymers, polyaniline (PAni) is now establishing itself as a novel material due its potential technological applications and low cost of synthesis **[J. Y. Shimano et.al, 2001].**

POLYANILINE:

PAni has been investigated extensively for over 100 years and has attracted special interest as a conducting material for several important reasons; the monomer is inexpensive, the polymerization reaction is straightforward and proceeds with high yield and PAni has excellent stability **[A. J. Heeger et.al, 2001]**. A first fairly detailed description of this product which was earlier known as 'aniline black' was provided by Green and Wood head **[A. G. Green et.al, 1997].** The later discoveries on polyaniline dealt with its electrical conductivity and other properties like electro-chemical redox activity, reversible doping/dedoping, electrochromism etc. **[A. F. Diaz et.al, 1980].** Further attention has been focused on PANI due to two prime reasons: (i) It can be synthesized easily both by electrochemical and chemical oxidation processes and (ii) it shows a particular sensitivity to the proton activity of its environment **[R. Hale in Advanced Functional Molecules and Polymers et.al, 2001]**.

STRUCTURE OF POLYANILINE:

Green and Wood head **[A. G. Green et.al, 1910]** were the first to depict PAni as a chain of aniline molecules coupled head-to-tail at the para position of the aromatic ring. They have proposed a linear octameric structure for PAni. Polyaniline, a typical phenylene based polymer, has a chemically flexible –NH– group in the polymer chain flanked by phenyl rings on either sides. The diversity in physicochemical properties of PANI is traced to the –NH– group. The difference in the composition of amine and imine segments of PANI generates several oxidation states of this material ranging from completely reduced leucoemeraldine to completely oxidized pernigraniline states as shown in Scheme 1.1. The different forms of PANI can be readily converted to one another by simple redox methods. Out of several possible oxidation states, the 50 % oxidized emeraldine salt state shows electrical conductivity **[P. S. Rao et.al, 2001].**



PROPERTIES OF POLYANILINE:

The discovery of electrically conductive polymer compositions based on polyaniline provides conductive materials, which are soluble in selected organic solvents. These materials are melt-process able and exhibit good ambient stability characteristics.

The major target of conductive polymer technology development has been to combine the electrical and optical properties of these new materials with the mechanical and process ability properties of commodity bulk polymers. New conductive materials that offer significant application as substitutes, and new products having properties difficult or impossible to achieve by existing materials, can now be produced.

Some polyaniline based materials are solution and melt process able. They offer clear benefits over traditional plastics made conductive by the addition of fillers (carbon blacks, metal particles and flakes, metal fibers, carbon fibers, and others). They provide precisely controlled electrical conductivity over a wide range, improve phase compatibility and thus bendability with bulk polymers, provide easier means of processing and forming conductive products and provide low cost solutions for the production of transparent and coloured thin films and coatings. In this study aniline was copolymerized with crotonic acid.

APPLICATIONS:

- Polyaniline and the other conducting polymers such as polythiophene, polypyrrole, and PEDOT/PSS have potential for applications due to their light weight, conductivity, mechanical flexibility and low cost.
- It is used for manufacture of electrically conducting yarns, antistatic coatings, electromagnetic shielding, and flexible electrodes.
- The different colors, charges and conformations of the multiple oxidation states also make the material promising for applications such as actuators, super capacitors and electrochromics.
- Attractive fields for current and potential utilization of polyaniline is in antistatic, charge dissipation or electrostatic dispersive (ESD) coatings and blends, electromagnetic interference shielding (EMI), anti-corrosive coatings, hole injection layers, transparent conductors, ITO replacements, actuators.
- It is used for chemical vapor sensors.
- It’s also used for chemical vapor and solution based sensors, electrochromic coatings (for color change windows, mirrors etc.), PEDOT-PSS replacements, toxic metal recovery, catalysis, fuel cells and active electronic components such as for non-volatile memory.
- Polyaniline based compositions can be processed using conventional techniques such as blow and injection moulding, extrusion, calendaring, film casting, and fiber spinning.
- It is used for membranes for gas separation
- Currently, the major applications are printed circuit board manufacturing (final finishes, used in millions of m^2 every year), antistatic and ESD coatings, and corrosion protection.

The key point is that PANI is regarded as a polymer, the behavior of which is subject between PANI and conventional polymers, the polymerization mechanism of which affects their properties in as much as it influences the microstructure, the molecular weight and the molecular weight distribution. Therefore, the mechanism of the oxidative polymerization of to the same principles as the polymerization process itself. PAni has its limitation by poor thermal process ability and solvent solubility. Improved solubility can be achieved by introducing bulky alkyl substituents on the PAni backbone **[MacDiarmid A.G et.al, 1990. Angelopoulos.M et.al, 1988].** By substituting an alkyl group on the polymer backbone, improved solubility can be achieved, but limitations are then imposed on the conductivity of the polymer produced. Combining the conductivity of PAni with the solubility of substituted PAni is important and can be achieved through copolymerization. For example, copolymers of aniline with o- or m-toluidine and *N*-butyl aniline have been reported **[Wang Y.Z et.al, 1994. Shacklette L.W et.al, 1995]**. These copolymers of aniline with substituted anilines show improved solvent solubility, while maintaining high electrical conductivity.

Objectives:

- To prepare Aniline and Crotonic acid copolymers with different compositions by chemical oxidative polymerization varying the feed ratio.
- To study the effect of different oxidant, temperature and surfactants on polymerization.
- To characterize the new materials by techniques such as UV absorption spectra, FTIR and thermal analysis.
- To study the properties like solubility and conductivity.

2. REVIEW OF LITERATURE

A review of past literature helps to proceed with new investigation. The review provides knowledge about the past experience and investigation of chemist about the topic of research .In the present investigation the literature survey is based on the type of copolymerization of two compounds using different surfactants.

- The kinetics of phase transfer catalyzed (PTC) radical polymerization of N-vinyl imidazole (NVI) using potassium peroxy disulfate (PDS) as water soluble initiator and tetraoctylammonium chloride (TOAC) as PTC has been carried out by ultrasound irradiation at constant temperature 60 + 1˚C under nitrogen atmosphere. The concentration of [NVI], [PTC] and [PDS] were found to be 1.01, 1.03 and 0.52 M. Different ratios were used to increase the rate of polymerization process, **Subramanian loganathan et.al. (2012).**

- **Boris A. Trofimov et.al., (2012)** have reported the cationic polymerization of N-vinyl-2,3-diphenylpyrrole affords oligomers with alternating units of pyrrole and ethylene units in up to 61% yields. Free radical polymerization of this monomer leads to oligomers having polyethylene backbone with pendant 2,3-diphenylpyrrole moieties. This oligomers showed semi conducting ($\sigma = 2.6 \times 10^{-7}$– 4.2×10^{-6} S/cm after doping with I_2) and paramagnetic ($N = 1.2 \times 10^{18}$– 4.8×10^{19} spin/g) properties and fluoresce in the region 383–388 nm.

- Acrylicacid-2[(diethoxyphosphoryl) methylamino] ethyl ester (ADEPMAE) has been synthesized and copolymerized with acrylonitrile (AN) through an aqueous slurry route by employing the redox initiator pair, ammonium per sulfate and sodium metabisulfite by **Paul Joseph et.al., (2012)**. The resulting copolymers were characterized by NMR, TGA, bomb calorimetry, PCFC. Polyacryonitrile (PAN) was modified and compared to the unmodified counterpart. Thermal properties of polymers were carried out in the presence of oxygen, air and nitrogen. The heat of combustion and heat release capacity of modified polymer were compared with polyacrylonitrile (PAN), pointing towards inhibition of combustion processes by the modifying moieties.

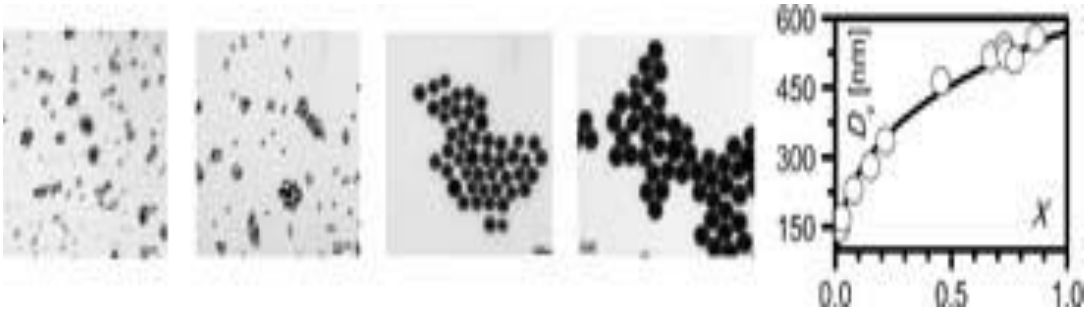
- The free radical copolymerization of aromatic diamine monomer, including o-hemline diamine, p-phenylene diamine 4,4-diamino diphenylene methane (DADPM) and Benzedrine (BZN). The further polymerization carried out by chemical oxidant using various free radical initiators. Aluminium-triflate (Al (OTf)$_3$) was also used as a co-catalyst, **Ismael Amer et.al., (2012).** The copolymers were characterized by FT-IR, ^{1}H and C-NMR, GPC, WAXD, DSC, and TGA. The copolymer solubility, yield, structure, molecular weights were depend on the oxidative catalyst and polymerization condition.

- The chemical oxidative polymerization of aniline and o-anisidine with 5 molar ratios was performed using ammonium persulphate as an oxidant in HCL medium at 0-4^{o}C by **Arun D Borkar et.al, (2012).** The copolymers are independent on the monomer ratio for yield and intrinsic viscosity. The resulted copolymers were characterized by FT- IR and ^{1}H-NMR Spectroscopy. The results showed that the actual content of the o-anisidine unit in the copolymers was much higher than the feed content of the o-anisidine unit. The electrical conductivity of the copolymers is strongly depended upon the amount of aniline incorporation. The electrical conductivity decreased with increasing the o-anisidine content in copolymer.

- The conducting polyaniline (doped PAni) was synthesized by a chemical method in hydrochloric (HCl) and formic acid (HCOOH).The FT-IR and Raman results showed that the doping degree of PAni-HCOOH is greater than that of the PAni-HCl. Additionally, the Raman studies indicated that the oxidation degree of PAni-HCOOH is higher than that of PAni-HCl, and that polaron segments dominate the PAni-HCOOH structure. The thermo gravimetric analysis (TGA) in oxidizing atmosphere also suggests that the doping level of PAni with HCOOH is higher than that of PAni with HCl. The DSC results confirm the difference in the thermal degradation mechanism, in non - oxidative atmosphere, of the polymeric chain of both polyanilines. The electrical conductivity of the PAni-HCOOH was 7.51 S cm^{-1}, while that of the PAni-HCl was 0.143 S cm^{-1}

confirming the results of FT-IR, Raman and TGA, i.e., the oxidation and the doping degree of PAni-HCOOH is higher than that of PAni-HCl, **E.C.Gomes et.al., (2012).**

- **Li Li et.al.,(2012)** have reported the particle growth in the graft free-radical copolymerization of styrene (St) and acrylonitrile (AN) in the presence of poly (propylene glycol)using both experiments and modeling.



The concentrations of chain transfer agent and macromer, and the St/AN ratio play important roles in particle size and its distribution. A particle size model is developed and an analytic expression for the particle size in terms of monomer mass concentration (W_{mt0}), initiator molar concentration ($[I]_0$), and macromer mass concentration (W_{M0}) is derived**.** Particle growth processes under various experimental conditions are well described by the model.

- **Xiaolong Li et.al.,(2011)** potential gene carrier, were prepared by emulsifier-free emulsion polymerization with oleic acid modified magnetite Fe_3O_4, styrene, butyl acrylate and [2-(methacryloxy) ethyl] trimethylammonium chloride) (METAC). The morphology of the particles was characterized by transmission electron microscopy and the composites of particles were characterized by FT-IR spectroscopy and X-ray diffraction. The interactions between the particles with calf-thymus DNA (ct DNA) were confirmed by zeta potential measurement, UV–Visible spectroscopy and fluorescence spectroscopy. The DNA-binding is capacity determined by the agarose gel electrophoresis, showed good binding capacity of the emulsion to DNA.

- The graft copolymerization of three different monomer (chitosan, 2-hydroxy ethyl methyacrylate and itaconic acid) was performed by **Kaliappa Gounder Subramanian et.al.,(2011).** The products are characterized by FT-IR, simulated biological fluids (SBF) and evaluated as a drug carrier with model drug, tramadol hydrochloride (TRM) and thermogravimetry. Grafting decreases depend upon the thermal stability of chitosan and enhanced release rate for the grafts. Increasing the itaconic acid content in the feed were more likely attributed to the enhanced drug-matrix interaction and polymer-SBF interactions.

- **Mahmoud A. AlIssa et .al.,(2011)** have reported the low conversion copolymerization of acrylamide (AM) with acrylic acid (AA) in dry benzene at 70°C, using benzoyl peroxide (BPO) as initiator. The copolymer composition has been determined by elemental analysis. The monomer reactivity ratios have been calculated by the Kelen-Tudos and Finman-Ross graphical procedures. The derived reactivity ratios (r1, r2) are: (0.620, 0.996) for (AM / AA) systems, and found that the reactivity of the monomer AA is more than the monomer AM in the copolymerization of (AA/AM) system. The reactivity ratios values were used for microstructures calculation.

- **Atanu Kotal et.al.,(2010)** have reported N,N-Dimethylanilinium p-toluenesulfonate (PTSA-DMA) as a versatile initiator for the quasi-living free radical polymerization of several alkyl methacrylate monomers such as methyl, ethyl, n-butyl, tert-butyl, and benzyl methacrylates (MMA, EMA, n-BuMA, t-BuMA and BzMA respectively) at 60^{o}C in dry THF. The initiator, PTSA-DMA was prepared by a simple complexation reaction of readily available p-toluenesulfonic acid (PTSA) and N, N-dimethylaniline (DMA).The yield of this polymerization system was moderate to good (60–75 %). The produced poly (alkyl methacrylates) had narrow polydispersities (PDIs). Although, this polymerization follows first order kinetics but the obtained molecular weight remains almost unchanged with conversion. This polymerization proceeds through radical mechanism as confirmed by electron paramagnetic resonance spectroscopy.

- **Zuifang Liu et.al.,(2010**) have synthesized the copolymers of vinyl ferrocene, acrylamide and 2-(diethyl amino) ethyl methacrylate by free-radical polymerization. The incorporation of ferrocene moieties in the copolymer confirmed by Proton NMR and inductively coupled plasma-optical emission spectroscopy. The effect of monomer feed ratio on copolymer molecular weight was studied and it was found that the increase in 2-(diethyl amino) ethyl methacrylate fraction. The incorporation of vinylferrocene led to decrease in copolymer molecular weight. The copolymer displayed reversible redox electrochemical characteristics of the ferrocene moieties and mediation of glucose oxidation with enzyme flavin adenine dinucleotide-glucose dehydrogenase in phosphate buffered saline. A diffusion coefficient of dissolved polymeric mediator was estimated from Randles–Sevcik analysis. The copolymer and the enzyme were mixed with water-based carbon ink and then screen-printed to form working electrodes.

- The copolymerization of N-phenyl methacrylamide and ethyl methacrylate in various feed ratios was synthesized by free radical solution copolymerization using benzoyl peroxide used as initiator in N, N-dimethylformamide at 70°C **G.Jayasimha Reddy.et.al.,(2010).** The copolymer structure was characterized by IR and p-NMR. The compositions of the copolymer were determined from the corresponding ^{1}H NMR spectra. The reactivity ratios of the monomers were determined by application of conventional linear methods like Finemann– Ross and Kelen–Tudos. The molecular weights of the polymers were determined using gel permeation chromatography (GPC). The thermal transitions of the copolymers were determined using differential scanning calorimetry and thermo gravimetric analysis.

- The graft copolymerization of chitosan (CS) with acrylonitrile (AN) by free radical polymerization was carried out using initiator pair of ammonium per sulfate and sodium thiosulfate as redox system .The FT-IR, XRD, and ^{1}H NMR measurements are indicated the graft copolymerization. The mechanism of graft copolymerization and factors affected graft reaction were explored and the optimum reaction conditions were obtained [AN] 0.9 mol/l, [CS] 13.3 g/l,[initiator] 0.006 mol and 2h. The solubility of chitosan -g-PAN was tested in acid solution and NaSCN. The graft copolymer and PAN had a good film forming property and fabrication of acrylic fibers, **Pengju Lv et.al., (2009**).

- The free radical polymerization of system consisting of DPE to prepare magnetic composite microspheres, were reported by **Hepeng Zhang et.al.,(2009)**.The copolymerization of acrylic acid, methyl methacrylate and styrene using DPE as radical control agent in the presence of Fe_3O_4 nanoparticles were carried out. The structure and properties are characterized by FT-IR, ^{1}H NMR, SEC-MALLS, TEM, TGA, VSM and other instruments, and then formation mechanism of composite microspheres was suggested. It was found that the Fe_3O_4/P (AA–MMA–St) microspheres were nano-size with relatively homogeneous particle size distribution, perfect sphere-shaped morphologies, superparamagnetism with saturation were obtained.

- The copolymerization of the monomers (1′ ,2,3,3′ ,4,4′ ,6-hepta-*O*-benzyl-6′ -*O*-crotonyl-sucrose) and (1′ ,2,3,3′ ,4,4′ ,6-hepta-*O*-benzyl-6′ -*O*-methacryloyl-sucrose) with styrene/methyl methacrylate have been examined in the presence of Ziegler–Natta catalyst $TiCl_4/AlEt_3$. The effect of the reaction conditions, the monomer structure and the initial quantity of the commoners on the sugar incorporation and molecular mass of the final copolymers has been carried out. In this way, the coordination mechanism of polymerization had obtained novel linear unbranched polymers and copolymers, potentially useful for biomedical applications were obtained **Maria T.Barros et.al, (2008).**

- The electrically conductive elastomer blends based on styrene-butadiene-styrene (SBS) tri-block copolymer and polyaniline-dodecyl benzene sulfonic acid (PANI.DBSA) were prepared by two methods namely, melt mixing and in situ polymerization of aniline in the presence of SBS. The influence of composition and synthetic methods on the properties of SBS/PANI has been studied by **SOUZA Fernando.G et.al. (2008).** SBS/PANI blends were characterized for density, tensile strength and tensile modulus. Using Porod's law that has estimated the interface thickness and the value turns out to be 0.55 ± 0.04 in all cases. The microstructural parameters such as long mean periodicity (L_M), crystalline length (L_C), amorphous length (L_A), correlation length (L_{COR}) and percentage of crystallinity were estimated in these blends using small angle X-ray scattering (SAXS) data. The results were compared with mechanical and electrical properties.

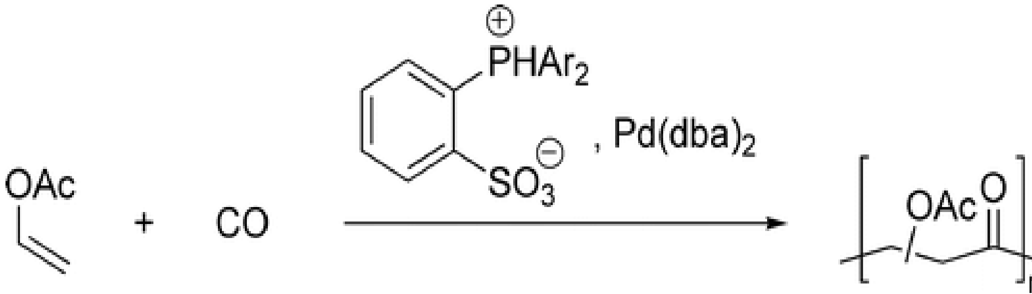
- The polyaniline was chemically grafted onto chitosan by using ammonium peroxydisulphate as initiator, in the presence of 1 M HCl to form Chitaline (chit-*g*-PAni), **S. Hossein Hosseini et .al,(2008).**The electrochemical polymerization was also carried out by coating chitosan on the surface of Pt disk working electrode. The grafted copolymer was identified by FTIR, UV-visible, and ^{1}H and ^{13}C NMR techniques. Spectroscopic studies showed the grafting and demonstrated that the electronic states were similar to those of the emeraldine and protonically doped emeraldine forms of polyaniline. The thermal property of chit-g-PAni was studied by thermogravimetric (TGA) and differential scanning calorimetry (DSC). Morphology of chit-*g*-PAni have been studied by SEM images which confirm grafting polymerization. The effects of concentration, reaction time and temperature on graft copolymerization were studied by determining the grafting percentage, grafting efficiency and percentage.

- **Mohsen Ghorbani et.al.,(2008)** have reported Polyaniline/Polyacrylonitrile (PAni/PAnr) copolymer synthesized in the aqueous/non-aqueous solution by copolymerization of acrylonitrile and aniline using KIO_3 and benzoyl peroxide as an oxidant in the presence of various surfactants such as sodium dodecyl benzene sulfate, poly(vinyl alcohol) and hydroxypropyl cellulose. In this study, the PAn/PANr copolymer was characterized in terms of conductivity, morphology, yield, particle size and structure. The results indicated that the morphology, yield, particle size and conductivity of products were dependent on the type of surfactants used. Also, the structure of obtained product was confirmed by FTIR spectroscopy. The results showed that the intensity of peaks is dependent on the type of surfactant.

- **V.Ferreira et.al., (2007**) have reported the electrochemical polymerization of luminol (Lum) and aniline (Ani) in the presence of acidic medium with different monomer concentration ratios. Aniline incorporation in the polymer structure is observable in the current density/potential profiles of the polymerization and characterization in acidic medium by development of two polyaniline like redox switching process with increasing aniline concentration. Unlike poly (Lum-Ani) polymer redox charge is enhanced with the increase of aniline concentration in the polymerization solution.

- The copolymerization of vinyl acetate and aniline using a mixture of KIO_3 and $(NH_4)_2S_2O_8$ as an oxidant in the presence of the surfactants sodium dodecyl benzene sulfonate, poly(ethylene glycol), and hydroxypropyl cellulose was reported by **P.Hossein Eisazadeh et.al.,(2007).** The PAn/PVAc copolymers were characterized for their conductivity, morphology, and structure. The results indicated the morphology and conductivity of the products that is dependent on the type of surfactant used (anionic or nonionic). Furthermore, it was found that adding vinyl acetate monomer to the stirred aqueous solution containing oxidant, surfactant, and aniline monomer had a great effect on the morphology, it increased the yield of the product. The structures of the products were determined by FTIR spectroscopy.

- The free radical polymerization of Poly (acrylic acid-*co*-crotonic acid) copolymers with acrylic acid (AA) and crotonic acid in toluene using azobis-iso-butyro-nitrile (AIBN) as initiator has been reported by **S.Bassaid et.al. (2007)**.The molecular weights were determined by viscosity method. The thermal analyses of copolymers indicate a hydrophilic behavior and a thermal stability and the irreversible degradation. These copolymers are good fixation agents that can be used in the recovery of heavy metals. This also have high toxicity in aqueous medium. In a second part, the complexes formation of metal ions M (II) with the copolymer of composition 3.0 g (AA)/2.0 g (CA) was also studied. The pH titration of the copolymer alone and in presence of M (II) was realized through the batch method to determine the acid–base properties and complex-forming of ligand copolymers.



- The alternating copolymerization of a polar vinyl monomer and carbon monoxide using vinyl acetate was reported by **Takuya Kochi et.al., (2007).** Alternating copolymers with high molecular weights were prepared employing palladium catalysts with phosphine–sulfonate bidentate ligands. The alternating copolymerization products were characterized by NMR and MALDI-TOF MS analyzer. This is the first nonradical pathway for polymer synthesis with vinyl acetate as one of the most inexpensive and readily available polar vinyl monomer, as a major component.

- The free radical polymerization of acrylamide (AAm) with crotonic acid (CA) in aqueous medium was carried out by the couple of ammonium per sulfate and *N*, *N, N′ N′* -tetramethylethylenediamine. The initiator was also used as cross linking agent, a foaming agent sodium bicarbonate, and a foam stabilizer, a triblock copolymer of polyoxyethylene/polyoxypropylene/polyoxyethylene, were used in the polymerization. The influences of the relative contents of CA, crosslinking agent, and initiator, on the swelling properties of the super absorbent polymer systems were examined by **Doungporn Yiamsawas et.al.,(2007**). The anodic current indicated that acrylamide acting as an electron donor whereas crotonic acid performed as an electron receiver, then providing the cathodic current. Acrylamide–crotonic acid super absorbents containing various cross linker concentrations had a water swelling in the range of 79–289 g g^{-1}. The diffusion coefficients varied between 6.9×10^{-9} and 5.1×10^{-8} cm^{2} s^{-1}. Adsorption of the basic dye by the super absorbent was a monolayer evaluated by the Langmuir isotherm. The super absorbents can thus be used to adsorb cationic dyes in textile industry.

- **Grigority A Mun et.al.,(2007**) investigated the polymerization of chitosan (CS) and 2-hydroxy ethyl acrylate (HEA) using ammonium per sulfate as an initiator in aqueous medium. The grafted polymer was characterized by ^{1}H NMR, FT-IR and SEM images. The effect of APS, HEA concentration, reaction temperature and duration of graft-polymerization were studied by determining the grafting parameters, percentage and efficiency. The HEA-grafted chitosan product is water soluble in a wide pH range and the original unmodified chitosan is water soluble only narrow pH range.

- **Dongxue Han et.al.,(2007**) have prepared the poly aniline –co antharanilic acid nanorods in bundle on alcohol /aqueous medium. The antharanilic acid played all roles like monomer, acid media provider and dopant in complete reaction and ammonium per sulfate played as the oxidant .The morphological studies of PANANA nanorodes in bundles was investigated by SEM, in this study the monomer molar ratio and the formation mechanism were also investigated. The molecular and electrical structure of the self-doped PANANA was done by FT-IR, UV-Visible and XRD. The other properties like conductivity, electrochemical redox activity and room temperature, solubility were measured by direct methods.

- The copolymer of chitosan and poly methyl methacrylate was synthesized by same concentration of two monomers. High grafting was observed by redox initiator used in presence of Ag+ and atmospheric oxygen at 35 ± 0.2˚C. The representation of grafting copolymer was characterized by FT-IR, gravimetric analysis and XRD. The effect of reaction variables as monomer concentration, microwave power and exposure time on the graft–co-polymerization was studied, **Van Dana Singh et.al., (2006).**

- The copolymer of Aniline (ANI) and 2-aminoterephthalic acid (2ATA) was prepared by chemical oxidative polymerization using various feed ratios by **J.Arias-Pardilla et.al., (2006**). The prepared compound has been characterized by XPS, FT-IR, Raman spectroscopies and thermal analysis. The 2ATA units are included in the polymer backbone. Other properties like solubility, conductivity optical absorption, fluorescence and electro activity were also studied. The copolymers are soluble in aqueous alkaline medium and showed clear electroactivity in aqueous acid medium.

- The copolymerization of benzidine and aniline derivatives were prepared by chemical and electrochemical methods. A study of the effect of homonomer composition on the thermal and electrical properties of copolymers was carried out. Copolymers were found to have more electrical conductivity compared to polybenzidine. With increase in temperature, the copolymers showed semiconducting behavior similar to polybenzidine, **Beena Bedekar et.al.,(2006).**

- The copolymerization of polyacrylonitrile-*graft*-polyaniline (PAN-*g*-PAni), has been prepared by chemical and electrochemical methods from a precursor polymer. Poly [acrylonitrile-*co*-(acrylimine phenylenediamine)] (PAN-*co*-PAIPD) was synthesized chemically by reacting PAN with sodium 1,4-phenylenediamine salt. PAN-*g*-PAni was synthesized chemically using ammonium peroxydisulfate as initiator and *p*-toluenesulfonic acid in dimethylsulfoxide solution and adding aniline to oxidized PAN-*co*-PAIPD. Electrochemical polymerization was carried out by spin coating PAN-*co*-PAIPD on the surface of a Platinum electrode, then the growth of the graft copolymer (PAN-*g*-PAni) in the presence of fresh aniline and acidic solution. The structure of the graft copolymer and PAN-co-PAIPD was characterized by UV-visible, FT-IR and ^{1}H and ^{13}C NMR spectroscopies. The thermal property of PAN-g-PAni was studied by thermogravimetric analysis and differential scanning calorimetry. Scanning electron microscopy (SEM) images showed that the morphology of PAN-*g*-PAni copolymer films was homogeneous. Electrical conductivity of the copolymer was studied by four-probe method. SEM and electrical conductivity are used to conform the graft copolymerization in solution, **Hossein Hosseini et.al.,(2006).**

- **Yasemin arslan udum et.al.,(2005**) studied the preparation of a sulfonated conductive polymer by electrochemical oxidation in the presence of anhydrous FSO3H. The sulphur-to-nitrogen ratios indicated the incorporation of polymeric groups. The solubility of copolymer was measured in DMSO and KOH. The conductivity of the copolymer increases with increase in the number of thiophene rings in polymeric groups. The copolymers are characterized by cyclic voltametry, UV-Vis, FT-IR and H-NMR, elemental analysis and SEM studies.

- **Erdener Karadag et.al.,(2004**) investigate that swelling capability of acrylamide (AAm) hydrogels by adding hydrophilic co-monomer such as crotonic acid (CA), The super swelling poly (acrylamide/crotonic)acid, poly (AAm-*co*-CA) hydrogels were prepared by free radical polymerization in aqueous solution of AAm with CA. For each copolymerization, four different composition of CA and a concentration of multifunctional cross linkers as ethylene glycol dimethacrylate (EGDMA) and *N, N″*-methylenebisacrylamide (NMBA) were aced Equilibrium swelling, some swelling kinetics parameters such as the initial swelling rate, swelling rate constant, theoretical equilibrium swelling and diffusional parameters such as swelling exponent, swelling constant and diffusion coefficients of hydrogels have been determined by swelling studies. At the end of dynamic swelling tests, relative content of CA on the swelling properties were examined. It has seen that, if CA contents were increased, equilibrium swellings of the hydrogels were also increased, Poly (AAm-*co*-CA) hydrogels were swollen in the range 1843–2577% in water, while poly (AAm) hydrogels swelled as 1729–1798%. Equilibrium water content of poly (AAm-*co*-CA) hydrogels was calculated in the range 0.9473–0.9626. Swelling exponents of poly (AAm-*co*-CA) hydrogels has calculated as 0.58–0.69. Water intake of hydrogels followed non-*Fickian* type diffusion.

- A method for the determination of reactivity ratios from conversion–composition data has been outlined by **Victor E. Meyer et.al.,(2003)**.The conversion–composition changes during the copolymerization of styrene (M_1) and methyl methacrylate (M_2) have been studied at 60°C. By a method of graphical intersection, the integrated form of Skeist's equation has been used to determine the reactivity ratios which were reasonably good agreement with values reported. The area of intersection was used as a measure of the precision of the data.

- The copolymer of aniline and ortho/meta-amino benzoic acid was synthesized by chemical polymerization using an inverse emulsion pathway. The copolymers are soluble in organic solvents, and the solubility increases with amino acid and benzoic acid content in the feed. The reaction conditions were optimized with emphasis on high yield and relatively good conductivity. The copolymers were characterized by a number of techniques including UV-Vis, FT-IR, FT-Raman, EPR and NMR spectroscopy, Thermal analysis, SEM and conductivity, The SEM micrographs of the copolymers revealed the regions of amorphous and crystalline domain .Thermal studies indicate a marginally higher thermal stability for poly(aniline-co-m-amino benzoic acid) compared to poly(aniline-co-o-amino benzoic acid), **Palle Swapna Rao et.al.,(2002).**

- The graft copolymerization of undecylenic acid, oleic acid, and crotonic acid onto acrylonitrile–butadiene–styrene terpolymer (ABS) was carried out using by benzoyl peroxide (BPO) in 1,2-dichloroethane solution by **H. Huang et.al., (2001).** The IR confirmed the undecylenic acid, oleic acid, and crotonic acid was grafted onto the ABS backbone. The grafting occurred at the butadiene region of the ABS. The grafting degree increased with increasing monomer concentration, initiator concentration and that the time total amount of concentration increased. Increasing reaction time and temperature led to an increase in grafting degree. The grafting of the monomer depence upon the polymer chain length due to steric hindrance and cage effects.

- **Minglong Yuan et.al., (2000)** have reported the poly (ethylene glycol) (PEG)-Poly (amino acid) copolymer. It was synthesized by using amino-terminated PEG as a primary amine. The mechanism of the initiator reaction undergoes a nucleophilic addition to the C-5 carbonyl group of the N-carboxyanhydrides (NCA). The copolymerization improved the solubility of poly (amino acid) in organic solvents. Also, the hydrophilic /hydrophobic and soft/hard of the poly (amino acid) homo polymer can be modulated by copolymerization of PEG with NCA.

- The copolymerization reaction of styrene with butadiene was performed using n-butyllithium (BuLi) as initiator and methyl tert-butyl ether (MTBE) as active center modifier by **Mihaela Corina Iovu et.al. (1999).** The random copolymersation was increased with decreasing polymerization temperature and increasing [MTBE]/[BuLi] molar ratio. The solvent and the initiator ratio strongly influence the copolymerization rate. The reaction rate increased as the [MTBE]/[BuLi] molar ratio increases from 7 to 40. At higher [MTBE]/[BuLi] molar ratios, the copolymerization rate decreased. The microstructure of the butadiene units incorporated into the copolymer chain is little influenced by the polymerization temperature.

- The studies of the free-radical crosslinking copolymerization of styrene (S) and commercial divinylbenzene (DVB) in bulk solution were studied using steady state fluorescence and dilatometric techniques by **Oguz Okay et.al.,(1998).** Pyrene (Py) was used for the fluorescence probe in situ polymerization. The time required for a sudden increase in the fluorescence intensity of Py was recorded for various DVB content and temperature. The monomer conversions and the gel points were recorded by dilatometry. The experimental data were interpreted with a kinetic model. The pendant vinyl groups and Py molecules are affected by the reaction medium. The mobility of the copolymer decreased as the DVB concentration and temperature. The Py intensity in the fluorescence spectra exhibits a sudden increase corresponds to the reaction time at which the rate of polymerization becomes maximum resulting from the gel effect. The results showed that the fluorescence technique can be used to follow the onset of the gel effect in SDVB copolymerization. The mobility of the cross-linked copolymer was decreased with DVB concentration and temperature.

3. MATERIALS AND METHODS

The present investigation has been under taken to synthesize and to characterize copolymer of aniline/crotonic acid. The outline of the investigation was sketched under the following headings.

- Materials used
- Copolymerization of aniline and crotonic acid

CHARACTERIZATION OF COPOLYMERS:

- UV - Visible spectra
- FT-IR
- Thermogravimetric analysis (TGA)
- Solubility
- Conductivity

MATERIALS USED:

S.NO	Chemicals	Manufacturer	Molecular Weight
1	Aniline	Reachem	93.13
2	Crotonic acid	LOBA	86.09
3	Oxalic acid	Finar	126.07
4	Ammonium per sulfate	Fisher	228.20
5	Ceric ammonium nitrate	Suvidhinath	548.23
6	Hydrochloric acid	Finar	36.46
7	Poly ethylene glycol	RFCL-Rankem	1500
8	Sodium Dodecyl Sulphonate	SD Fine	288.372
9	Dimethyl sulphoxide	SDFCL	78.13
10	Acetone	Himedia	58.08

COPOLYMERIZATION OF ANILINE AND CROTONIC ACID:

The polymerization of freshly distilled aniline and crotonic acid has been carried out by free radical chemical oxidative polymerization method by using ammonium per sulfate (APS)/ceric ammonium nitrate (CAN) as oxidants in non-oxidizing acid like oxalic acid. In a chemical reaction, 1 ml of aniline and 0.01 mg of crotonic acid each mixed with 50 ml of 0.1 M oxalic acid, were mixed together by constant stirring for ½ an hour. The solution was precooled to 0-5°C, and an aqueous solution of APS (0.1 M) was added dropwise with constant stirring over a period of 2 hours. During this entire process, the reaction medium was kept in 0-5°C. The reaction medium changed colour, going through brown, blue and green and a solid deposit was formed at the bottom of the reaction flask. The green sediment was filtered, washed repeatedly with deionized water and finally with acetone. The precipitate was air dried.

This procedure was repeated at different temperature viz 5-10°C, 10-20°C, 20-30°C, 30-40°C and 40-50°C. Copolymerization was also carried out using CAN under the above mentioned conditions. The polymerization was performed using 25/75, 35/65, 50/50, 65/35 and 75/25 ratios of aniline and crotonic acid under the optimum temperature range identified for APS and CAN.

Optimum monomer ratio was polymerized in presence polyethylene glycol. Polyethylene glycol was added to the reaction mixture before the addition of the oxidants. The polymerization was repeated with 0.1, 0.2 and 0.3g of polyethylene glycol, the surfactant. Ideal temperature range was maintained during polymerization.

Sodium dodecyl sulphonate **(SDS)** was also used as a surfactant for polymerization. Different aniline-co-crotonic acid were prepared using 0.1, 0.2 and 0.3 g of SDS at the identified temperature range.

CHARACTERIZATION OF COPOLYMERS:

The synthesized copolymers were characterized by UV, FITR spectra and TGA.

UV- Visible spectra:

A UV visible spectrum involves the absorption of UV light by a molecule by the promotion of an electron from a ground electronic state to an exited electronic state. UV provides information on the electronic bonding in the molecule alkenes, carbonyl compounds, alkynes and azo compounds which show the П-П* transition.

The UV Visible spectra of the prepared copolymers (dissolved using dimethyl sulphoxide as solvent) were recorded at room temperature using **Systronics-PC based double beam** spectrometer 2202 in 200-600 nm range.

FT-IR Spectroscopy:

Fourier Transform Infra-Red spectroscopy **(IR)** is a well-established analytical technique for the identification of organic molecules. Over time organic chemist have recorded and catalogued the types and locations of IR absorptions produced by a wide variety of chemical bonds in various chemical environments. The qualitative aspects of IR spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique.

IR spectrum can be used as a fingerprint for identification of unknown compounds. As a general rule, the most important factors determining where a chemical bond will adsorb are the bond order and the types of atoms joined by the bond. Conjugation and nearby atoms shift the frequency to a lesser degree. Therefore the same or similar functional groups in different molecules will typically absorb within the same specific frequency ranges.

The FTIR spectra of all the co-polymers prepared with different monomer ratios using APS or CAN as oxidant and in presence of PEG or SDS as surfactant were measured with a **Bruker Tensor 27** instrument with ATR assembly. The measurements were taken in the region of 400-4000 cm^{-1} at 4 cm^{-1} resolution.

THERMOGRAVIMETRIC ANALYSIS (TGA):

A parameter of particular interest in synthetic polymer manufacturing is the glass transition temperature (T_g). TGA is used to observe the variation of a thermodynamic property with temperature. TGA determined in this manner will vary somewhat depending on the rate of cooling or heating, which reflects the fact that long entangled polymer chains cannot respond instantaneously to changes in temperature.

TGA of the synthesized aniline-crotonic acid copolymer copolymers was performed using **TGA-5 shimadzu** in the temperature range of 30-600^{o}C under N_2 atmosphere. A heating rate of 20^{o}C was used during the TGA tests while a crucible of platinum containing 15 mg of sample was used in the analysis.

SOLUBILITY:

The solubility of the copolymers was tested by dissolving each material in water NH_4Cl, hydrochloric acid, ethanol and DMSO. The mixture was kept for 24 hours at room temperature.

CONDUCTIVITY:

Solutions of various concentrations viz. 0.1, 0.05 and 0.01% of the copolymers were prepared in dimethyl sulphoxide and their electrical conductivity were measured by two probe method.

4. RESULTS AND DISCUSSION

Polyaniline is a one of the most studied conjugated conducting polymer. But the commercial applications are limited owing to its poor process ability because of its poor miscibility with other polymers and low solubility in common solvents. Combining the conductivity of PAni with the solubility can be achieved through copolymerization. In this study aniline-crotonic acid copolymer was prepared in the oxalic acid solution by copolymerization of aniline and crotonic acid using Ammonium per sulfate and ceric ammonium nitrate as an oxidant in the presence of polyethylene glycol/sodium dodecyl sulphonate as surfactants. The results are discussed under the following headings.

I).COPOLYMERIZATION:

I(a). Impact of temperature on copolymerization

I(b). Effect of monomer ratio on copolymerization

I(c). Influence of surfactant on the percentage conversion

I(d). Role of oxidant on polymerization

II) CHARACTERIZATION OF POLYMERS:

II(a). UV absorption spectra

II(b). FT-IR spectra

II(c). Thermal gravimetric analysis

III) PROPERTIES OF COPOLYMERS:

III(a). Solubility

III(b). Conductivity

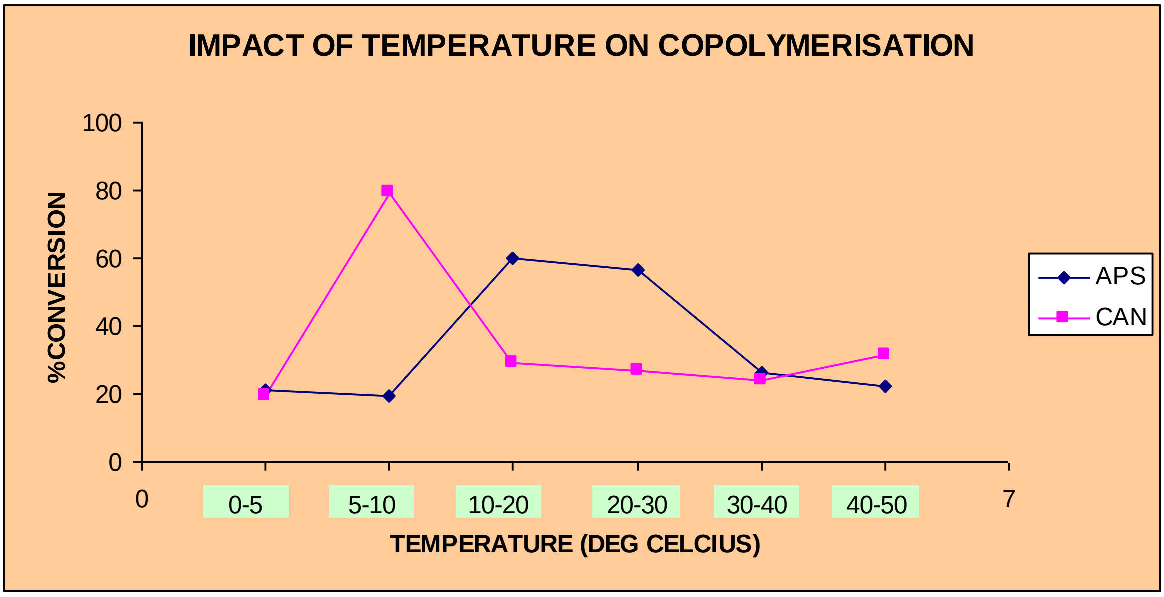
I(a). IMPACT OF TEMPERATURE ON COPOLYMERIZATION:

The copolymers were synthesized by chemical method in media containing oxalic acid. Polymerization of aniline depends on the temperature of the solution. Aniline polymerization was effective at low temperature. In this study to identify an ideal temperature range for the copolymerization of aniline and crotonic acid, the polymerization was conducted in a temperature range of 0-50°C. The best temperature range was located based on the percentage yield. 10-20°C range was chosen as the best when ammonium per sulfate was used as oxidants. When 59.79% conversion was realized. Ammonium per sulfate oxidant performed well at 20-30°C also but the percentage conversion was less than in 10-20°C. At other temperature ranges the percentage conversion was comparatively very low. The actual percentage conversions are given in the table 1 and graphically in figure 1.

Table 1. IMPACT OF TEMPERATURE ON CO-POLYMERIZATION:

S.No	Aniline (g)	Crotonic acid (g)	Temperature (°C)	Oxidant			
				APS		CAN	
				Yield (g)	% Conversion	Yield (g)	% Conversion
1	1.019	0.01	0-5°C	0.216	20.991	0.197	19.144
2	1.019	0.01	5-10°C	0.200	19.436	0.815	79.203
3	1.019	0.01	10-20°C	0.615	59.766	0.300	29.154
4	1.019	0.01	20-30°C	0.584	56.754	0.276	26.822
5	1.019	0.01	30-40°C	0.268	26.044	0.246	23.906
6	1.019	0.01	40-50°C	0.236	22.348	0.324	31.486

Figure 1. IMPACT OF TEMPERATURE ON CO-POLYMERIZATION:



When ceric ammonium nitrate was used as oxidant for the copolymerization 79.2 percentage conversion was noticed at the temperature range of 5-10°C. Ceric ammonium nitrate was found to be more effective only between 5-10°C. Above and below the temperature range the percentage conversion was very low. Table 1 and figure 1 show the variation of percentage conversion at various temperatures when ceric ammonium nitrate was used as an oxidant.

I(b). ROLE OF OXIDANT ON POLYMERIZATION:

The chemical copolymerization of aniline and crotonic acid in oxalic acid has been carried out. A wide range of oxidant is used in chemical synthesis of PAni. As a rule, compounds with high oxidation potential exceeding +1.0 V (per sulfates, dichromate, cerium IV salts, etc.) are employed. In the present study per sulfate and cerium IV salts were used as oxidants for copolymerization from the table 1. It is evident that the copolymerization of aniline and crotonic acid was effective in presence of ceric salt (79.2 %conversion) than in presence of ammonium per sulfate (59.76 % conversion).

I(c). EFFECT OF MONOMER RATIO ON CO- POLY MERIZATION:

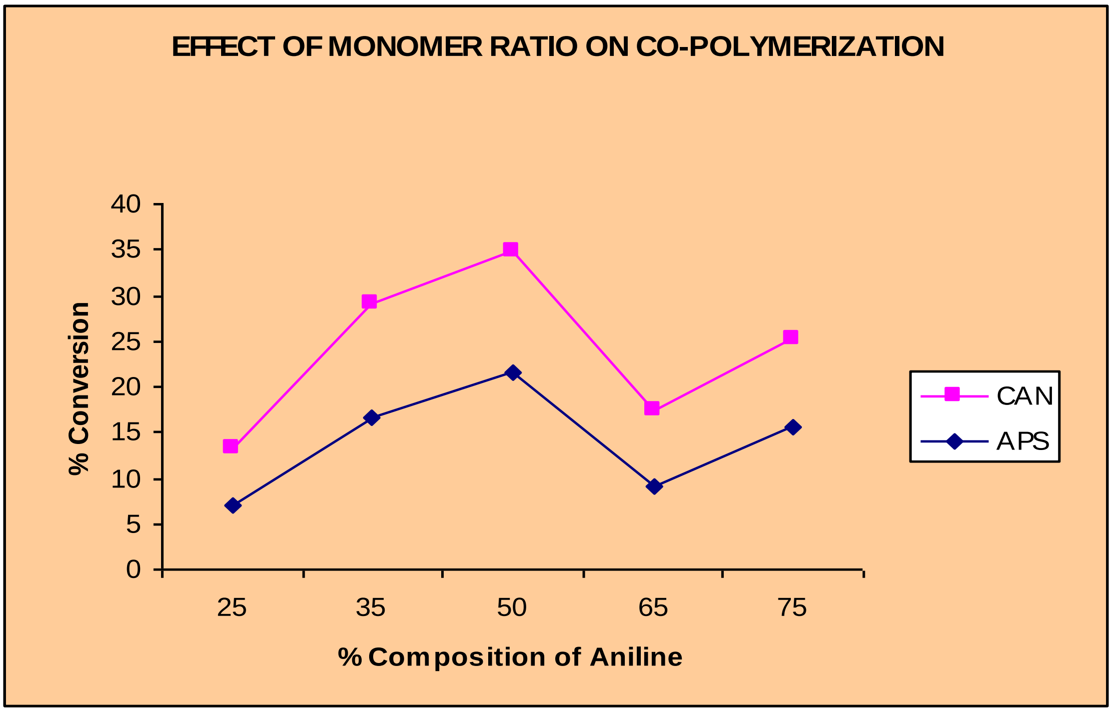
Aniline and crotonic acid copolymers with different composition were prepared by chemical oxidative polymerization varying the feed ratio and with ammonium per sulfate or ceric ammonium nitrate as oxidant. Copolymerization using ammonium per sulfate was carried out at 10-20°C. The feed ratios selected are 25/75, 35/65, 50/50, 65/35 and 75/25 of aniline and crotonic acid. With all feed ratio the percentage conversion was very low. The best among the studied was 50/50 when the conversion was 21.6%. When crotonic acid concentration is increased the percentage conversion decreased. With increase in aniline ratio the conversion is increased. Table 2 and figure 2 depict the variation of percentage conversion with feed ratio of aniline and crotonic acid in the presence of ammonium per sulfate as oxidant.

Table 2. EFFECT OF MONOMER RATIO ON CO-POLYMERIZATION:

Oxidant: Ammonium Per Sulfate   Temperature: 10-20°C

S.No	Aniline (g)	Crotonic Acid (g)	Yield (g)	Percentage conversion
1	25	75	0.280	6.966
2	35	65	0.500	16.561
3	50	50	0.436	21.594
4	65	35	0.279	9.183
5	75	25	0.630	15.528

Figure 2. EFFECT OF MONOMER RATIO ON CO-POLYMERIZATION:



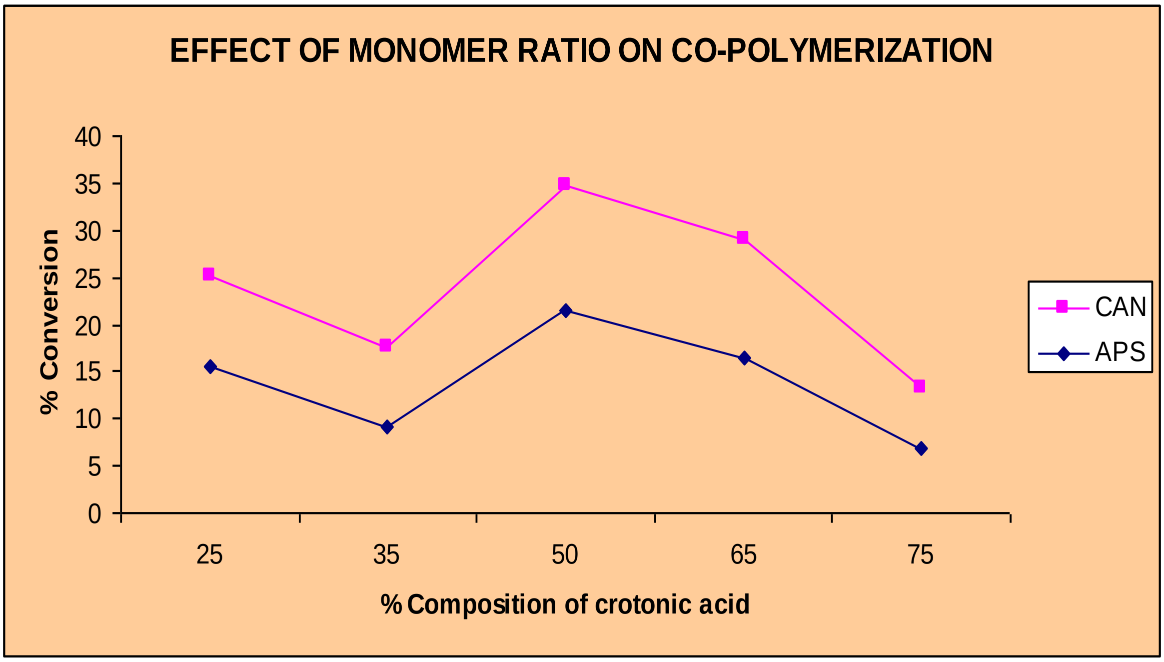
The various ratios of aniline and crotonic acid were polymerized in presence of ceric ammonium nitrate at 5-10°C. The percentage conversion of the copolymer decreased with increase in crotonic acid ratio. With 25/75 feed ratio of aniline and crotonic acid percentage conversion is 6.27 % with 50/50 feed ratio the conversion was 13.22 %. Increased in proposition of aniline increased the percentage conversion. 75/25 feed ratio has given 9.66 percentage conversions while 25/75 has given 6.2 percentage conversions. The effect of monomer ratio on copolymerization was presented in the table 2 and figure 2.

Table 3. EFFECT OF MONOMER RATIO ON CO-POLYMERIZATION:

Oxidant: Ceric ammonium nitrate **Temperature: 5-10°C**

S.No	Aniline (g)	Crotonic Acid (g)	Yield (g)	Percentage conversion
1	25	75	0.252	6.270
2	35	65	0.376	12.454
3	50	50	0.267	13.224
4	65	35	0.253	8.327
5	75	25	0.392	9.662

Figure 3. EFFECT OF MONOMER RATIO ON CO-POLYMERIZATION:



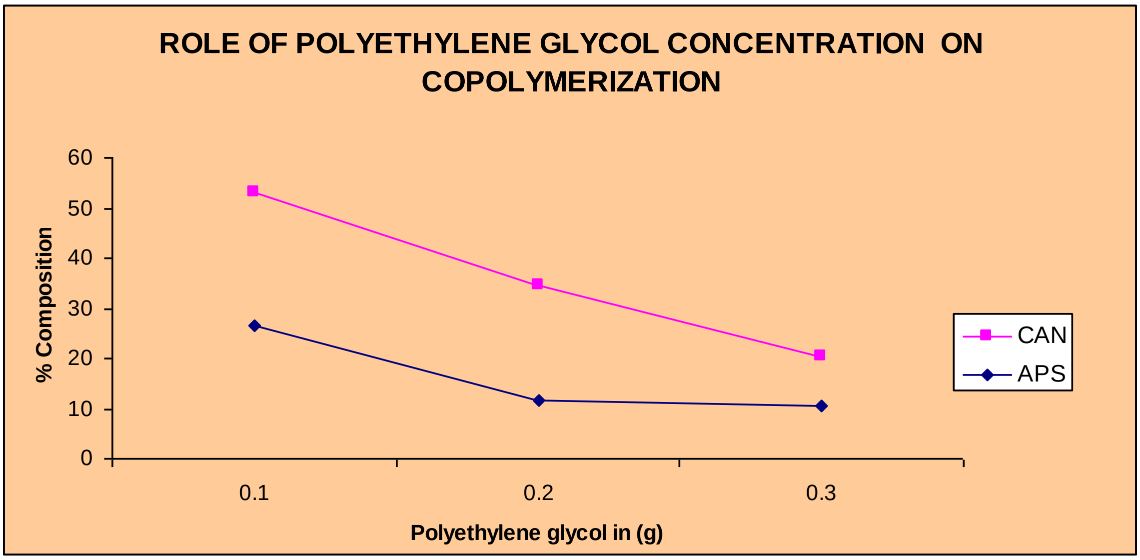
I(d). INFLUENCE OF SURFACTANT ON CO-POLYMERIZATION:

An attempt has been made to improve the poor processability of PAni, by using) sodium dodecyl sulphonate, a balky molecule contaning a polar head and a long non-polar chain which functions both as a surfactant and Dopants. Polyethylene glycol a non-polar long chain molecule, which can act as surfactant was also used Surfactants generally increases the polymerization. In the present study poly ethylene glycol enhanced the copolymerization of aniline and crotonic acid. The percentage conversion was 26.5 % in the presence of both the oxidant (Table 4) and in the absence of poly ethylene glycol. The conversion was below to 10 % (table 3 in the absence of polyethylene glycol.

Table 4. INFLUENCE OF POLY ETHYLENE GLYCOL

S.No	Ratio by weight	Surfactant (g)	Percentage conversion	
			APS	CAN
1	3:1	0.1	26.581	26.581
2	3:1	0.2	11.745	22.668
3	3:1	0.3	10.511	9.685

Figure 4. INFLUENCE OF POLY ETHYLENE GLYCOL:

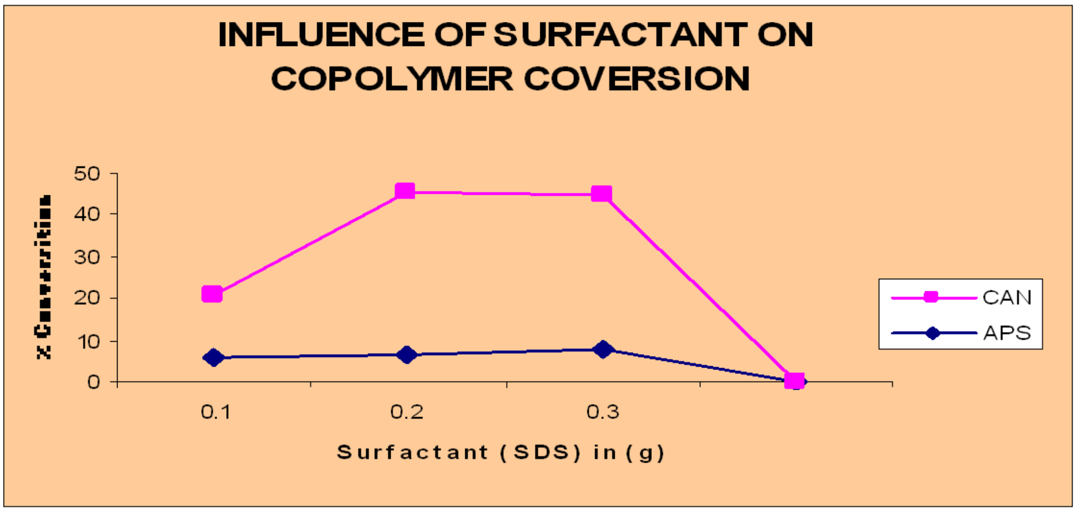


The sodium dodecyl sulphonate acted as best surfactants in presence of ceric ammonium nitrate than in presence of ammonium per sulfate. The percentage conversion was triple time increased in the presence of sodium dodecyl sulphonate, when ceric ammonium nitrate used as an oxidant but the conversion is halved in presence of ammonium per sulfate. The influence of sodium dodecyl sulphonate on copolymerization was show in table **5.** The influence of concentration of the surfactants on copolymerization was show in figure 4 and 5. From the figure it's clear that increased in poly ethylene glycol concentration decreases percentage conversion. Increase sodium dodecyl sulphonate concentration increased percentage conversion.

Table 5. INFLUENCE OF SODIUM DODECYL SULPHONATE:

S.NO	Ratio by weight	Surfactant (g)	Percentage conversion	
			APS	CAN
1	3:1	0.1	5.532	15.227
2	3:1	0.2	6.225	39.229
3	3:1	0.3	7.941	36.952

Figure 5. INFLUENCE OF SURFACTANT ON COPOLYMER CONVERSION



UV SPECTRA:

UV visible spectra of copolymers were recorded at room temperature in 190-700 nm range using UV systronics - PC based double beam spectrometer 2202. The corresponding bands are given in table. The band around 265-330 nm is assigned to Π - Π* (band gap) transition, which is related to the extents of conjugation between the adjacent phenyl rings in the polymer chain.

Table 6. Absorption Wavelength of the Investigated Polymers in UV Region

Polymer	**UV visible absorption band (Π → Π*) transition**					
	λmax	**Abs**	**λmax**	**Abs**	**λmax**	**Abs**
PAni	330.0	3.7575	630.0	1.9682	_	_
PAni/PCA APS	227.2	1.587	211.2	1.270	220.8	1.117
PAni/PCA CAN	227.2	1.587	211.2	1.270	220.8	1.117
PAni Co PCA (APS/PEG)	278.4	0.467	230.4	1.221	224.0	0.997
PAni Co PCA (APS/SDS)	217.6	0.596	275.6	1.041	235.2	1.059
PAni Co PCA (CAN/PEG)	220.8	0.790	278.8	1.242	211.2	0.080
PAni Co PCA (CAN/SDS)	227.2	1.098	232.0	1.171	241.6	0.646

The PAni showed Absorption band around 333nm. Which is attributed to the Π - Π* transition. The inclusion of co monomer (crotonic acid) in the copolymer feed, this band showed hypsochromic shift and absorption band around 270-230nnm. The hypsochromic shit is due to incorporation of crotonic acid in the copolymer back bone. This reduces the conjugation length along the copolymer chain. The absence of characteristic band at the higher wavelength region shows the absence of polaronic bands **[vineet bansal et.al 2009].**

Figure 6. : UV SPECTRUM OF COPOLYMER OF ANILINE AND CROTONIC ACID

Oxidant: Ammonium Per Sulfate, Temperature: 10-20^{o}c

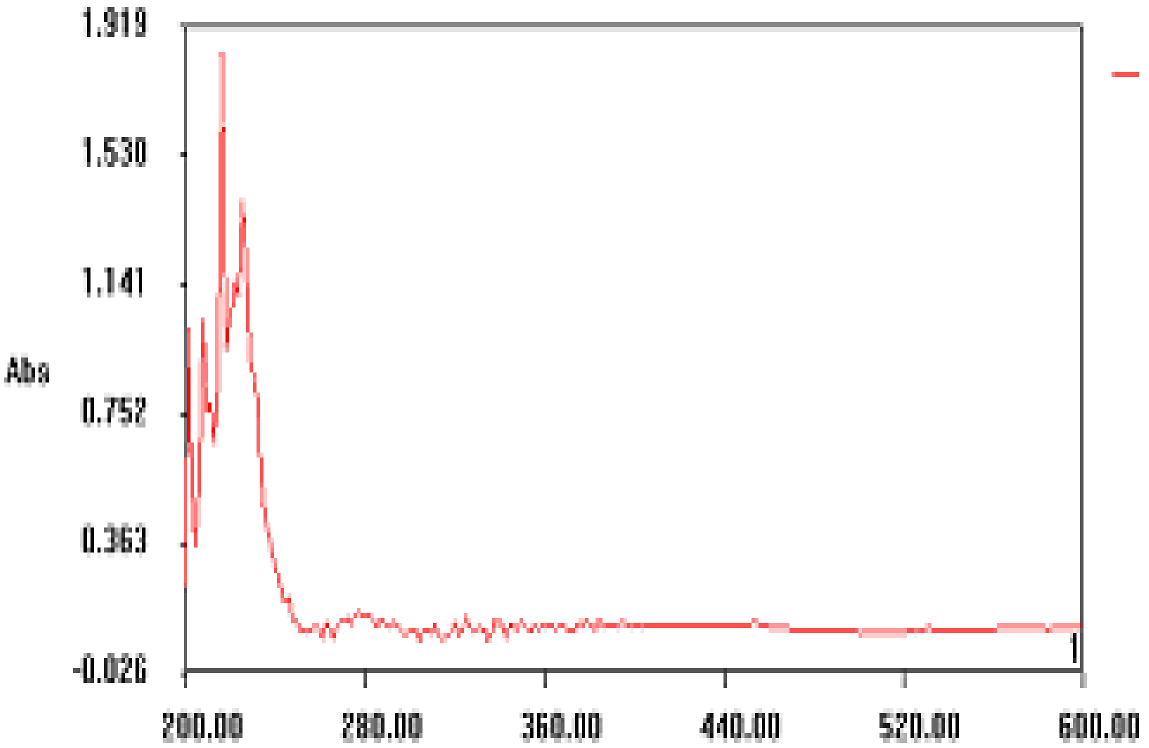


Figure 7. UV SPECTRUM OF ANILINE AND CROTONIC ACID COPOLYMER

Oxidant: Ceric ammonium nitrate, Temperature: 5-10°c

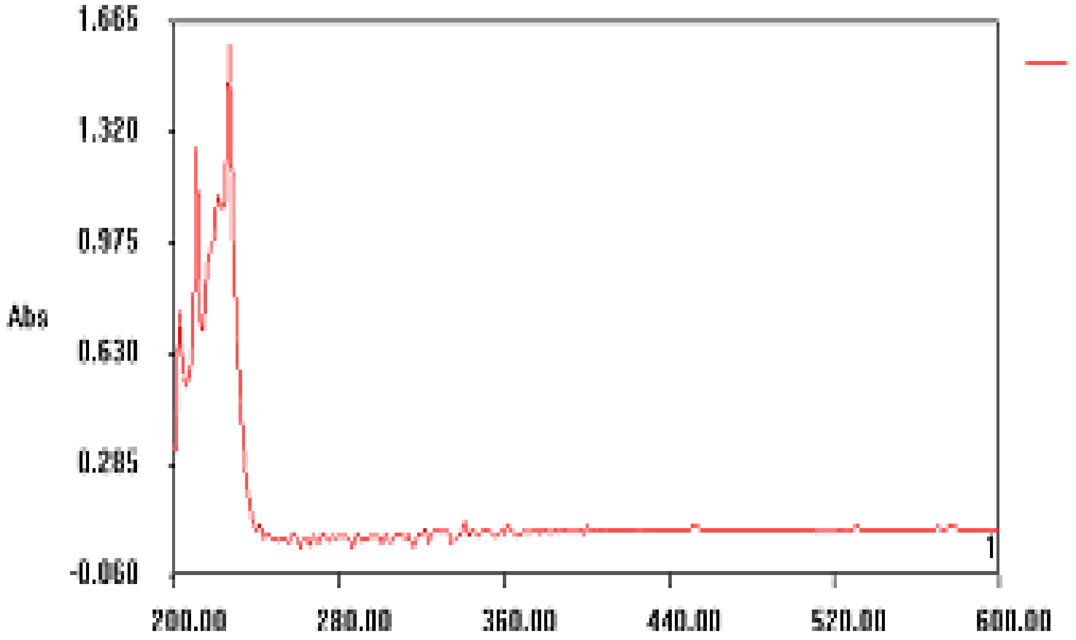


Figure 8. UV SPECTRUM OF ANILINE AND CROTONIC ACID COPOLYMER IN THE PRESENCE OF POLYETHYLENE GLYCOL (APS)

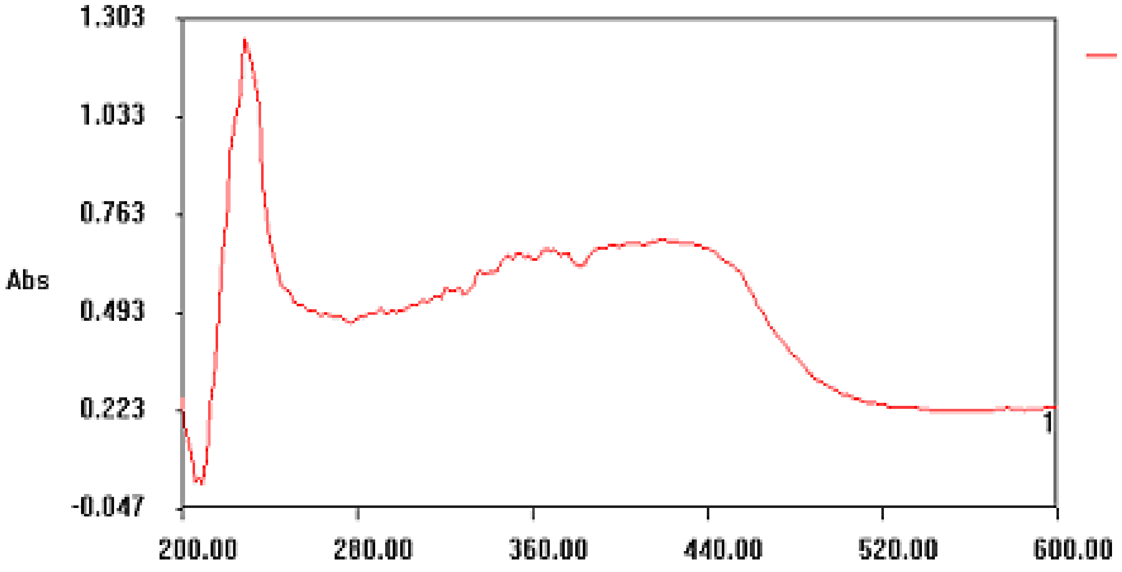


Figure 9. UV SPECTRUM OF ANILINE AND CROTONIC ACID COPOLYMER IN THE PRESENCE OF SODIUM DODECYL SULPHONATE (APS)

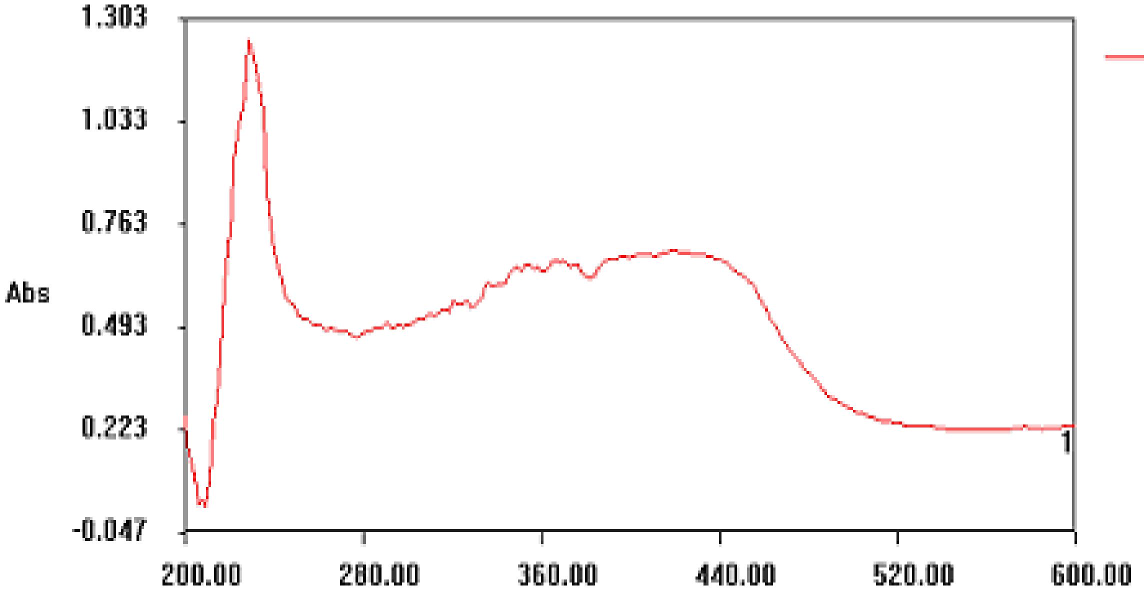


Figure 10. UV SPECTRUM OF ANILINE AND CROTONIC ACID COPOLYMER IN THE PRESENCE OF POLYETHYLENE GLCOL (CAN)

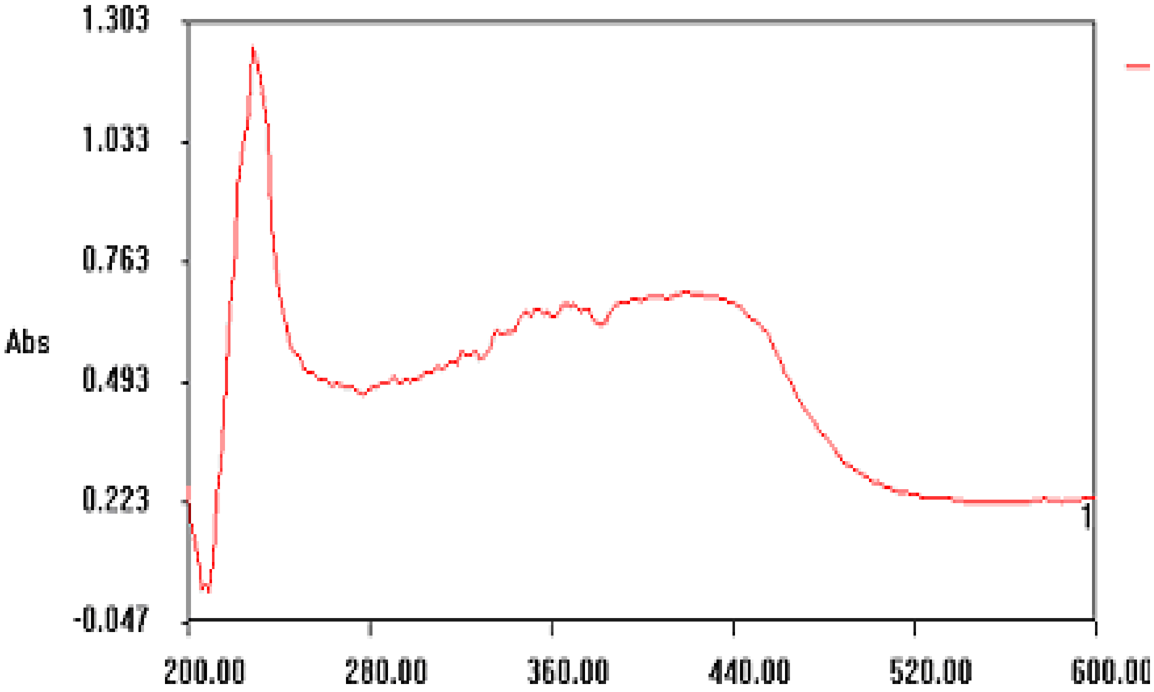
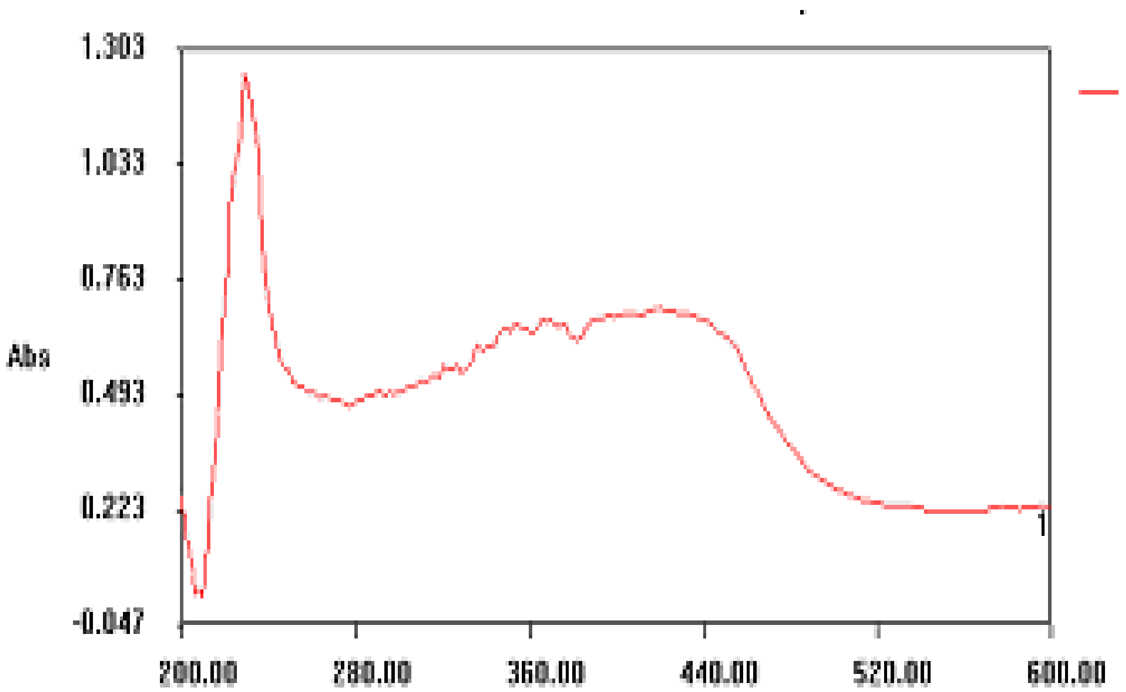


Figure 11. UV SPECTRUM OF ANILINE AND CROTONIC ACID COPOLYMER IN THE PRESENCE OF SODIUM DODECYL SULPHONATE (CAN)



FTIR Spectroscopy:

The band with maximum absorption at 1500- 1604 cm^{-1} in the spectra of the synthesized copolymers is assigned to the stretching vibrations of quinoid rings and the absorption at 1479 cm^{-1} is assigned to be benzenoid of polyaniline. The small intensity band at 1358-1362 cm^{-1} is attributed to the stretching of C-N band next to a quinoid ring (C-N=N-C). The band at 1142-1152cm^{-1} in the FT-IR spectrum of copolymers prepared using ammonium per sulfate as oxidant is attributed to vibration of –NH^{+} structure formed in acid doping process of polyaniline. The region between 900-700cm^{-1} corresponds to aromatic deformation and C—H band vibrations out of ring plane **[Brozova.L, et, al. 2008]**

Moreover, a broad characteristic band observed at 3400 cm^{-1} in copolymers doped with polyethylene glycol corresponds to the –OH group and to the formation of intermolecular and or intra molecular hydrogen band due to the presence of hydrogen atom present at OH and nitrogen atom of aniline unit, In sodium dodecyl sulphonate doped copolymers the inter or intra molecular hydrogen bond is due to the presence of hydrogen atom at SO3H group and nitrogen atom of aniline unit. This strong peak around 3350 cm^{-1} can also be assigned to the stretching vibration of -NH band.

The formation of PANI was revealed by absorption bands at 3200-3400 cm^{-1},1500-1604 cm^{-1}, 1142-1152cm^{-1} and 750-600 cm^{-1}.Which were attributed to the vibrations of –NH, -C=C-, Ph-NH, Ph-NH-Ph and C-N in aniline unit **[Norma Aures Rangel-Vazquez et,al. 2009].**

Figure 12. FT-IR SPECTRUM OF COPOLYMER OF ANILINE AND CROTONIC ACID

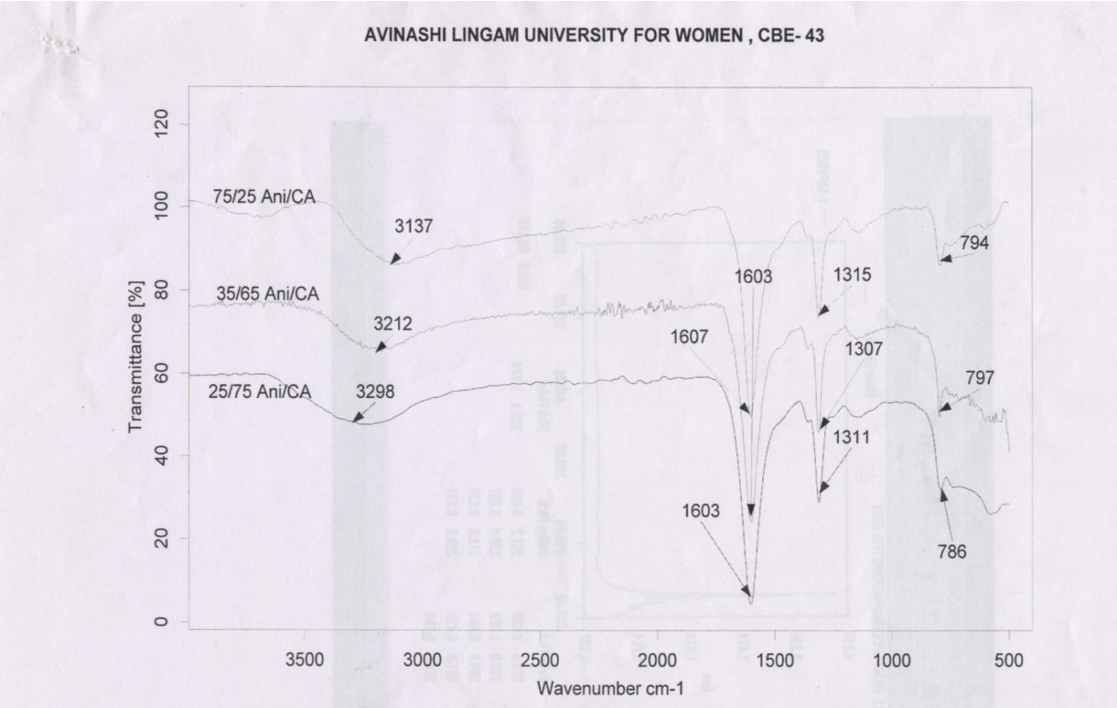
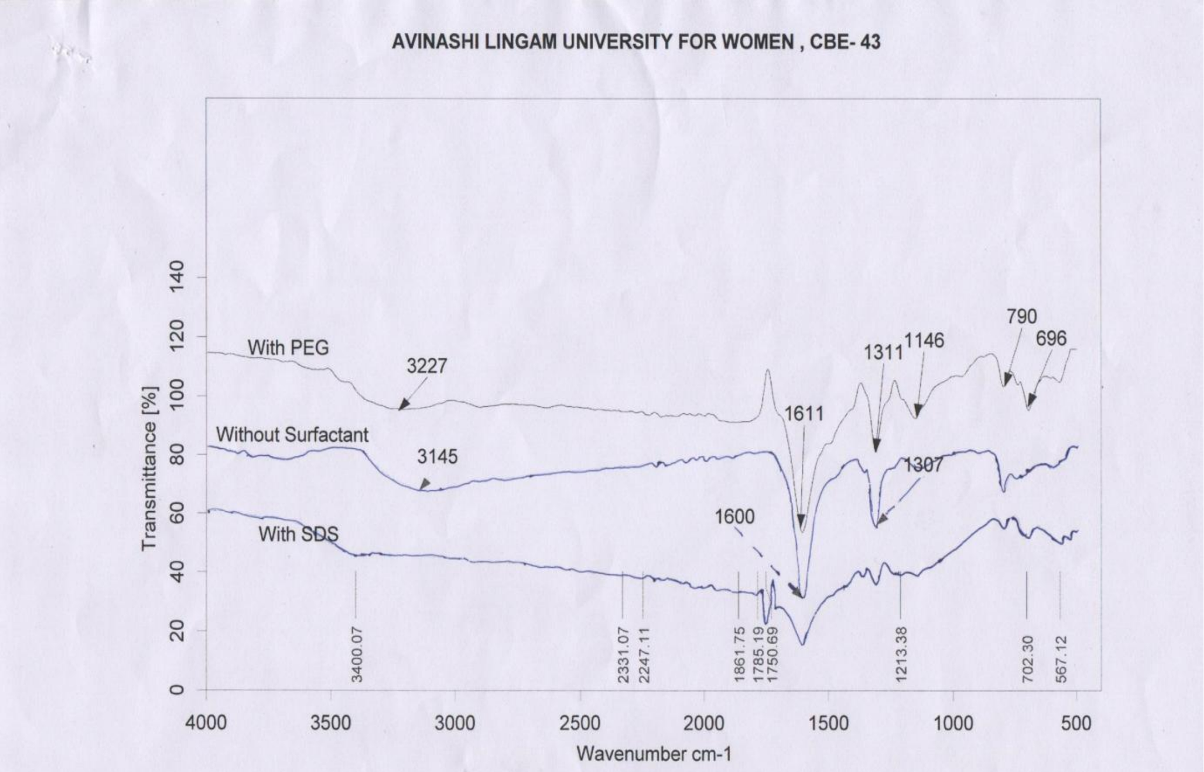


Figure 13. FT-IR SPECTRUM OF COPOLYMER OF ANILINE AND CROTONIC ACID IN THE PRESENCE AND ABSENCE OF SURFACTANTS



THERMO GRAVIMETRIC ANALYSIS:

The copolymers along with polyaniline were thermally characterized by TGA and DTA. Thermal decomposition studies are carried out non oxidative atmosphere (N_2). The thermogram of polyaniline shows a weight loss of 7-8 % up to 100°C, a weight loss of 22 % from 100-450°C and a weight loss of 40% from 450-800°C. our data are found in good agreement with the data reported in literature (gupta neetika 2012) when aniline was copolymerized with crotonic acid in different composition i.e. 1:1, 1:2, 1:3, 2:1 and 3:1 compositions, using ammonium per sulfate or ceric ammonium nitrate a different thermal behavior is shown.

This copolymer shows three weight loss steps. First a minor weight loss occurred upto 110°C which may attribute to the loss of dopant. The third weight loss observed from 200°C onwards is attributed to degradation of polymer backbone, from the comparison of the thermograms of

PAni/PCA synthesized using APS/CAN as oxidants it is observed that the first stage of weight loss was identical whereas, variation was observed in the second and third stage of weight loss. It was observed that PAni/PCA (APS) was thermally stable upto 200^{o}C while PAni/PCA (CAN) was thermally stable upto 373^{o}C.the thermal stability observed in the copolymer could be attributed to the formation of cross linking bonds during the heating process (E.C.Gomes et.al. 2012). Both the copolymers are more stable compare to PAni. This indicates that the thermal stability of the copolymer increased with the incorporation of crotonic acid in PAni Chain.

Thermograms of different feed composition indicate that the increase in crotonic acid composition did not bring change in the decomposition temperature. But increase in aniline composition slightly decreased the thermal stability. The stability range due to cross linking is decreased when the feed ratio was 3:1. This confirms that the cross linking is due crotonic acid. This peak can be associated to the evolution of water in the form of moisture absorbed by the polymer which was observed in the TGA curve at temperatures lower than 100^{o}C. Two less intense endothermic peaks appear around 35^{o}C and around 373^{o}C which can be associated to the loss of the dopant and to the beginning of polymer chain breaking respectively.

Similar endothermic peaks were observed in all thermograms corresponding to the weight loss occurred at TGA.

Figure 14. COMPARITIVE THERMOGRAMS OF COPOLYMER OF ANILINE AND CROTONIC ACID PREPARED USING APS AND CAN:

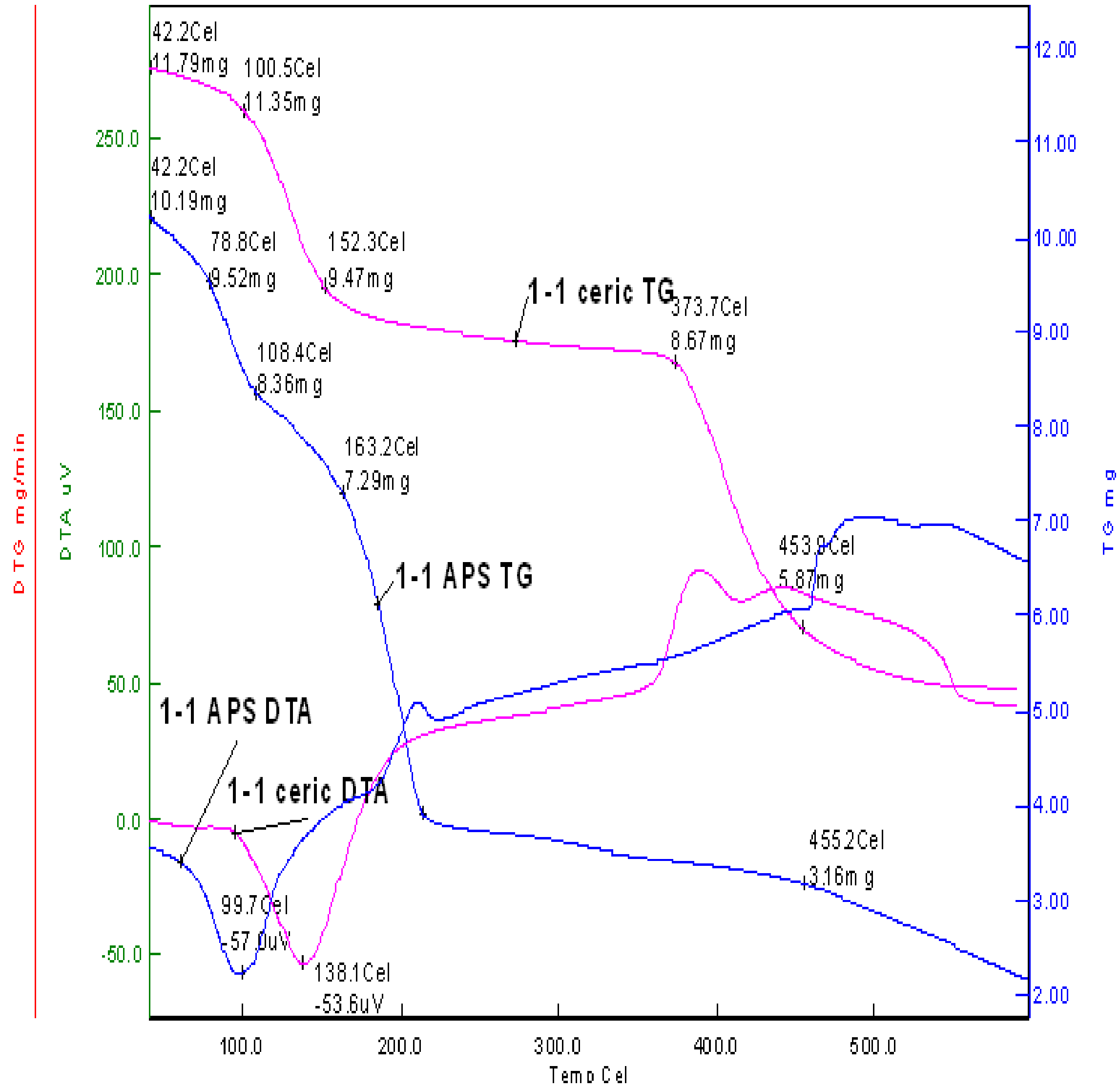


Figure 15. COMPARITIVE THERMOGRAMS OF COPOLYMER OF ANILINE AND CROTONIC ACID IN DIFFERENT RATIOS

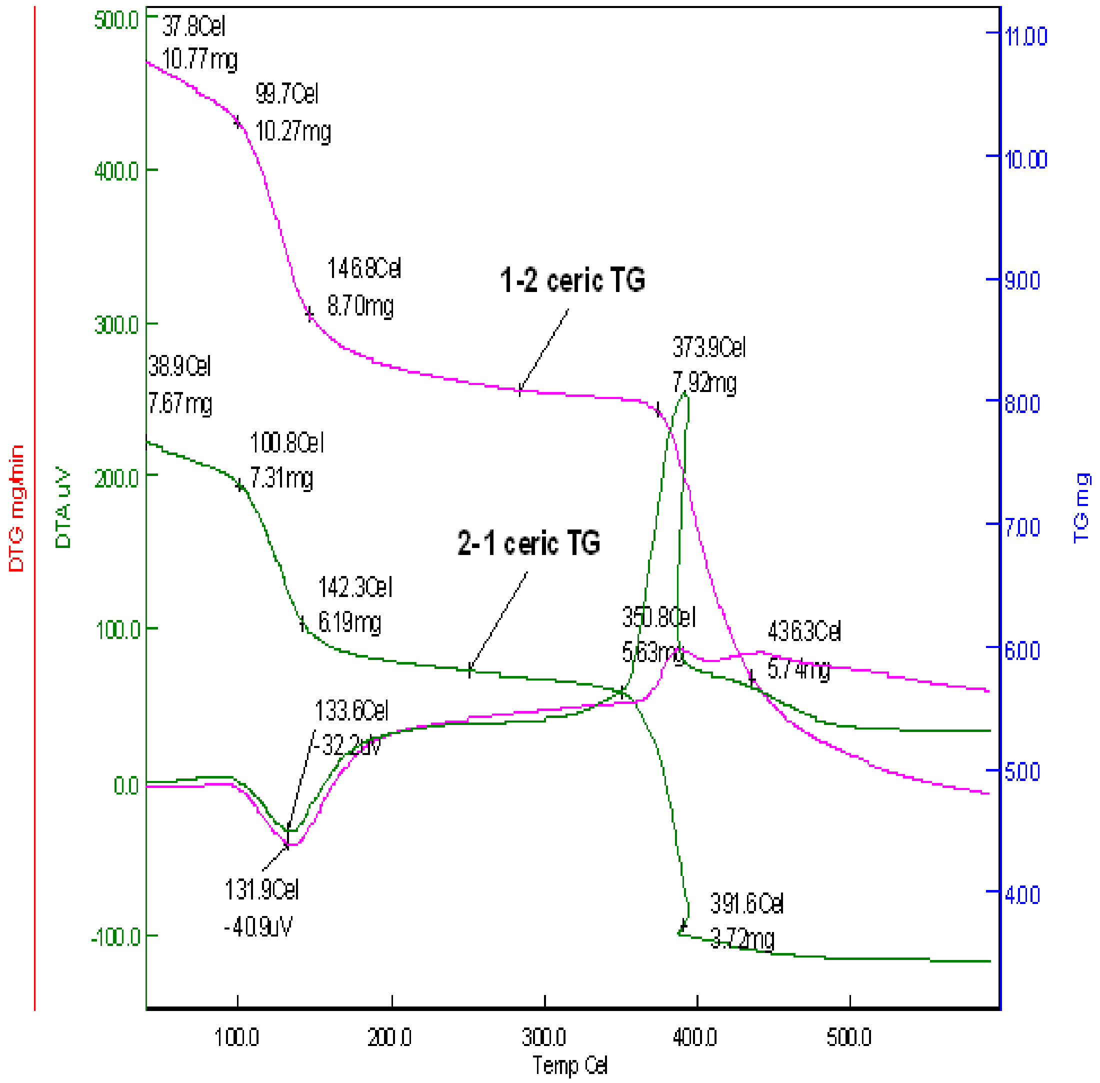


Figure 16. COMPARITIVE THERMOGRAMS OF COPOLYMER OF ANILINE AND CROTONIC ACID IN DIFFERENT RATIOS

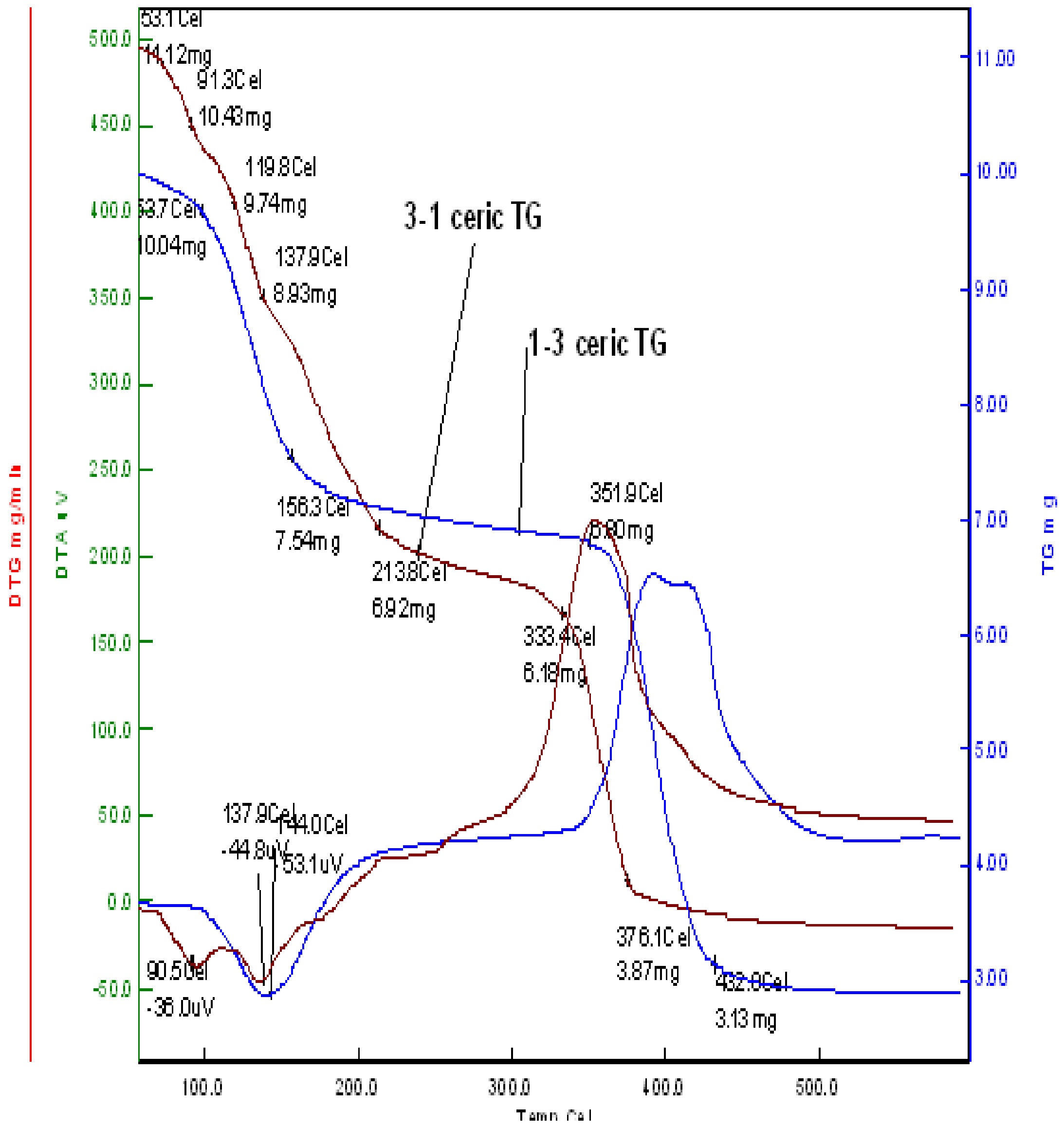
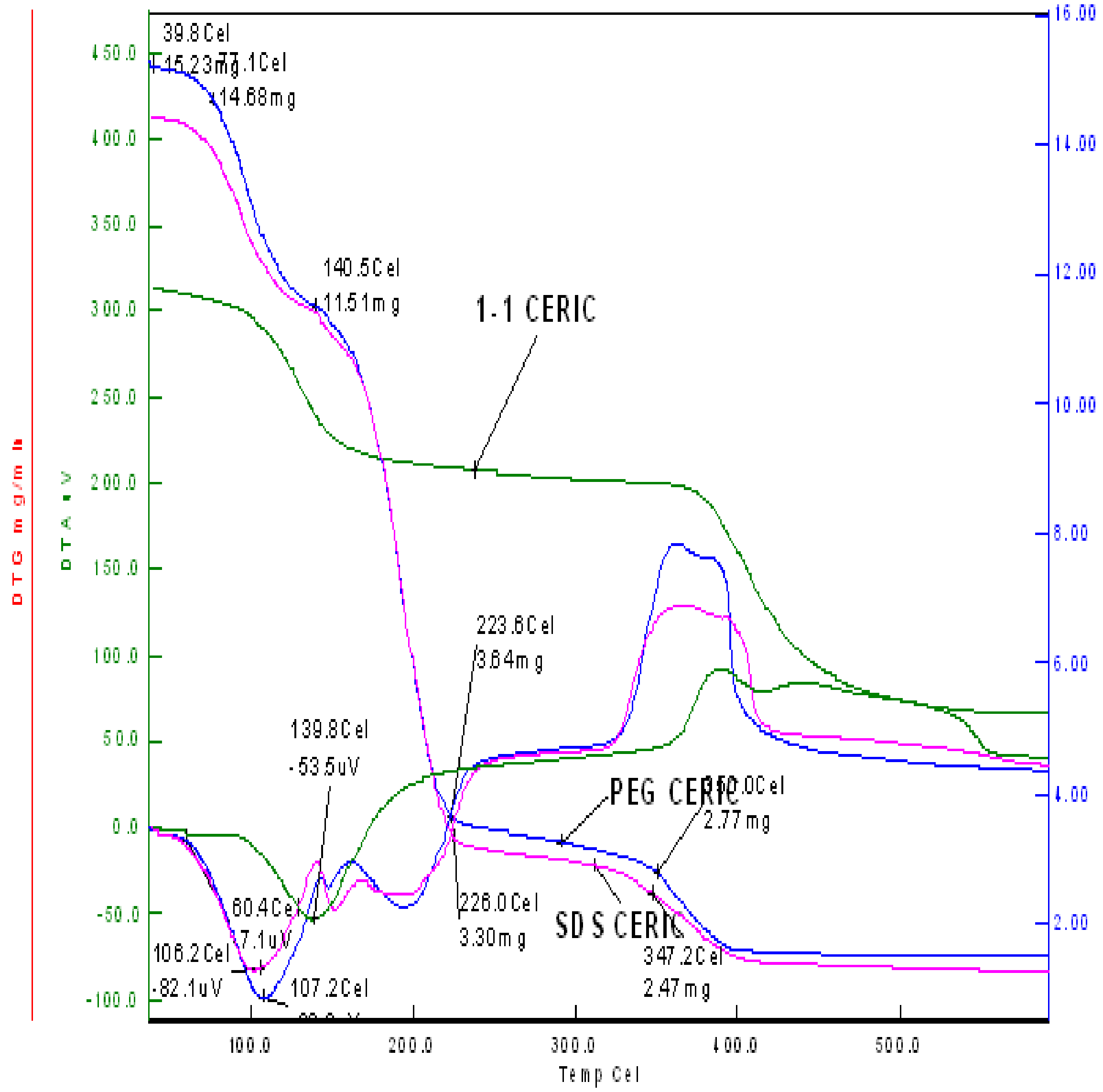


Figure 17. COMPARITIVE THERMOGRAMS OF COPOLYMER OF ANILINE AND CROTONIC ACID IN THE PRESENCE OF PEG AND SDS:



III (a) SOLUBILITY:

The study of the solubility of copolymers in water, ethanol, 1N Hydrochloric acid and dimethyl sulphoxide was performed using the following procedure. 0.01 gm of the polymer was added to 10 ml of the solvent and stirred well. Following observations are noted.

- The change in monomer ratio has no effect on solubility in all the solvents studied.
- All the copolymers prepared with different oxidants and in the absence or presence of surfactants are soluble in dimethyl sulphoxide.
- 1N hydrochloric acid dissolved the copolymers synthesized using ammonium per sulfate as oxidant. All the other copolymers prepared under different conditions are only partially soluble.
- The copolymers prepared using ammonium per sulfate is insoluble in water. When polymerized with polyethylene glycol, they are partially soluble in water. Polymerization with sodium dodecyl sulphonate did not bring any improvement in solubility.
- Ammonium per sulfate initiated copolymerization of aniline and crotonic acid are partially soluble in ethanol. They become soluble when polymerized in presence of polyethylene glycol.
- Inclusion of polyethylene glycol in the copolymers synthesized using ceric ammonium nitrate as oxidant dissolved them in ethanol otherwise they are partially soluble in ethanol.

Table 7. SOLUBILITY OF NEW COPOLYMERS:

S.No	Ratio by weight (g)	Oxidant	Water	Ethanol	Dimethyl sulphoxide	1N HCl
1	25/75	APS	- -	+ -	+ +	+ -
		CAN	+ -	+ -	+ +	+ +
2	35/65	APS	- -	+ -	+ +	+ -
		CAN	+ -	+ -	+ +	+ +
3	50/50	APS	- -	+ -	+ +	+ -
		CAN	+ -	+ -	+ +	+ +
4	65/35	APS	- -	+ -	+ +	+ -
		CAN	+ -	+ -	+ +	+ +
5	75/25	APS	- -	+ -	+ +	+ -
		CAN	+ -	+ -	+ +	+ -

+ + soluble, + - partially soluble, - - insoluble

Table 8.SOLUBILITY OF COPOLYMERS IN PRESENCE OF SURFACTANTS:

S.No	**Ratio by weight (g)**	**Surfactant**	**Oxidant**	**water**	**Ethanol**	**Dimethyl sulphoxide**	**1N HCl**
1	75/25	PEG	APS	- -	+ -	+ +	+ -
			CAN	+ -	+ -	+ +	+ -
2	75/25	SDS	APS	- -	+ -	+ +	+ -
			CAN	+ -	+ -	+ +	+ -

+ + soluble, + - partially soluble, - - insoluble

III (b) ELECTRICAL CONDUCTIVITY:

Conducting polymers have become very popular in the field of material science due to their novel electrical properties. Among conducting polymers, polyaniline has a special representation. Copolymerization of aniline with other monomers enhances the process ability, solubility and conductivity of the polymers. In the present study the electrical conductivity of the copolymers were measured by two probe method.

The electrical conductivity of the copolymer solutions is measured and the results are given in Table (9). PAni shows conductivity of order of 6.550 Scm^{-1} the copolymer shows lower conductivity than PAni, which indicates the ionization potential, band gap and band width are affected by angle between adjacent rings (AD Borkar 2012). The Π electron conjugation was affected by the presence of crotonic acid in between the phenyl rings. The conductivity of the copolymers decreases with increasing content of crotonic acid which may be due to the restricted mobility of the electrons.

Table 9. CONDUCTIVITY OF COPOLYMERS IN DIFFERENT RATIOS OF ANILINE AND CROTONIC ACID USING APS INITIATOR:

S.No.	Weight Ratio of monomers	0.1 % Scm^{-1}	0.05 % Scm^{-1}	0.01 % Scm^{-1}
1	25:75	0.748	0.366	0.081
2	35:65	1.13	0.566	0.126
3	50:50	0.862	0.483	0.096
4	65:35	0.853	0.408	0.092
5	75:25	0.784	0.395	0.088

Table 10. CONDUCTIVITY OF COPOLYMERS IN DIFFERENT RATIOS OF ANILINE AND CROTONIC ACID USING CAN INITIATOR:

S.No.	Weight Ratio of monomers	0.1 % Scm^{-1}	0.05 % Scm^{-1}	0.01 % Scm^{-1}
1	25:75	0.082	0.075	0.072
2	35:65	0.086	0.083	0.074
3	50:50	0.069	0.092	0.068
4	65:35	0.075	0.065	0.059
5	75:25	0.118	0.089	0.072

5. SUMMARY AND CONCLUSION

Conductive polymers are widely studied because of their foremost properties such as high conductivity to weight ratio, corrosion resistance and facile processability. PAni is a conductive polymer which has been extensively studied due to its relatively high conductivity and potential application in electronic device. Nevertheless, a few applications have been reported. Where conducting polymers exhibit poor physical and mechanical properties PAni has its limitations by poor thermal processability and solvent solubility. These can be achieved through copolymerization. In this study efforts have been taken to prepare copolymer of aniline and crotonic acid using Ammonium per sulfate/Ammonium ceric nitrate as oxidant and in the absence and presence of surfactants like polyethylene glycol and sodium dodecyl sulphonate.

- The prepared copolymers are characterized by UV, FTIR spectroscopy and thermal analysis. The solubility of the copolymers in various solvents and their conductivity in solutions were measured. The present study revealed the following.
- Copolymerization of aniline and crotonic acid was effective in presence of ceric salt (79.2 % conversion) than in ammonium per sulfate 59.76 % conversion.
- In presence of ceric salt the polymerization was effective at 10-20^{o}C. In presence of ammonium per sulfate 5-10^{o}C was effective.
- Equimolar ratio of aniline and crotonic acid gave better yield.
- Both the surfactants viz sodium dodecyl sulphonate and polyethylene glycol enhanced the copolymerization.
- All the copolymers synthesized are soluble in dimethyl sulphoxide.
- The solubility in water is improved by polyethylene glycol.
- The copolymers show lower conductivity than PAni. Since the Π electron conjugation was affected
- Thermograms show three weight loss steps at 110^{o}C, 200^{o}C and 373^{o}C. There are due to the loss of water molecules, Dopants and degradation of polymers respectively.

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