CHAPTER I
INTRODUCTION

1.1 Basic Concepts of Polymers

Polymers are high-molecular-weight compounds that are so important to man and his modern technology. It was not until the 1930's that the science of polymers began to emerge, and the major growth of the technology of these materials came even later. According to the latest report one tenth of chemists, chemical engineers and physicists are associated with polymeric materials and research, throughout the world. There are six major areas of application for polymers: (1) Plastics, (2) rubbers or elastomers, (3) fibers, (4) surface finishes and protective coating, (5) adhesives and (6) electrical conductors. Despite the fact that all six applications are based on polymers, and in many cases, the same polymer is used in two or more, the industries grew up pretty much separately. It was only after Dr.Herman Staudinger [1,2] proposed the "Macromolecular hypothesis" in the 1920's explaining the common molecular makeup of these materials (for which he won the 1953 Nobel Prize in chemistry) that polymer science began to evolve from the independent technologies. Thus, a sound fundamental basis was established for continued technological advances. The history of polymer science is treated in detail elsewhere [3, 4].

1.2 Polymers and Polymerization

Polymers are complex and giant molecules and are different from low molecular weight compounds. A polymer is made up of many small molecules, which have combined to form a single long or large molecule. The individual small molecules from which the polymer is formed are known as monomers and the process by which the monomer molecules are linked to form a big polymer molecule is called "Polymerization". Bifunctionality of the monomer is the most important prerequisite for the continuation of the molecular buildup process.

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When molecules just add on to form the polymer, the process is called 'addition' polymerization. The monomer species in this case retains its structural identity when it gets converted into a polymer. When the molecules just do not add on but also undergo some reaction in forming the polymer, the process is called 'condensation' polymerization. Here, the two molecules (of the same or different monomers) condense to form a polymer. The condensation takes place between two reactive functional groups. However, while forming the polymer water molecules also get eliminated. In 'addition' polymerization, the molecular weight of the polymer is roughly equal to that of all the molecules, which combine to form the polymer. In 'condensation' polymerization, the molecular weight of the polymer is lesser by the weight of the simple molecules eliminated during the condensation process.

In both 'addition' and 'condensation' polymerizations, the polymer molecule formed contains a structural identity, repeating itself several times. These repeating entities are called the repeat units or the monomeric units of the polymer molecule. The number of repeat units present in it decides the size of the polymer molecule. This number denotes the 'degree of polymerization'.

1.3 Classification of Polymers

a. Natural and Synthetic Polymers

Polymers, which are isolated from natural materials, are called natural polymers. Polymers synthesized from low molecular weight compounds are called synthetic polymers.

b. Organic and Inorganic Polymers

A polymer whose backbone chain is essentially made of carbon atoms is formed as organic polymer. A polymer whose backbone chain is not made of carbon atoms is formed as inorganic polymer.

(i) Thermoplastic and Thermosetting Polymers

Polymers that soften on heating and stiffen on cooling are termed 'Thermoplastics'. Polymers that become an infusible and insoluble mass on heating and that cannot be reshaped are called 'Thermosetting' polymers.

(ii) Plastics, Elastomers, Fibres and Liquid resins

When a polymer is shaped into hard and tough utility by the application of heat and pressure, it is known as 'plastic'. When polymers are vulcanized into rubbery products exhibiting good strength and elongation, they are called 'elastomers'. If a polymer is drawn into long filament like materials, whose length is at least 100 times its diameter they are known as 'fibres'. Polymers used as adhesives, polling compounds, sealants, etc., in a liquid form are described as liquid resins.

1.4 Types of Polymerization

Many polymer-producing techniques have been so extensively studied and experimented upon, that we can almost get a polymer of our choice in terms of the required molecular weight, structure, crystallinity etc., The terms 'addition' and 'condensation' polymerization were based on the conventional classification by Carotlers (1929) and have since been modified by H.F.Mark (1950) as chain polymerization and step polymerization. The types of polymerization and polymerization techniques are found elsewhere [5].

Chain Polymerization

      (a). Free-Radical polymerization

      (b). Ionic polymerization

      (c). Coordination polymerization

Step Polymerization

In step polymerization, the polymer build-up proceeds through a reaction between the functional groups of the monomers. The reaction takes place in a

stepwise manner, and the polymer build-up is therefore, slow. Step polymerization reactions are mostly accompanied by the elimination of small molecules.

(a) Polycondensation

(b) Polyaddition

(c) Ring-opening Polymerization

Miscellaneous Polymerization Reactions

(a) Electrochemical Polymerization

(b) Metathetical Polymerization

(c) Group Transfer Polymerization

1.5 Polymerization Techniques

Factors such as the nature of the monomer, the type of polymerization mechanism chosen, the required physical form of the polymer and the viability of the process for industrial production are some of those dictating the physical conditions under which polymerization is to be carried out. These varying physical conditions lead to different polymerization techniques namely,

(a) *Bulk Polymerization*

(b) *Solution Polymerization*

(c) *Suspension Polymerization*

(d) *Emulsion Polymerization*

(e) *Melt Polymerization*

(f) *Solution Polycondensation*

(g) *Interfacial Condensation*

(h).*Solid and Gas Phase Polymerization*

1.6 Ultrasound –The Wonder Mechanical Wave

Sound is our experience of the propagation of pressure waves through some physical elastic medium, such as air, or liquid. The pressure waves are generated from some type of mechanical disturbance. Generally, human hearing cannot go beyond about 18 kHz, sound beyond this limit is inaudible and is defined as ultrasound [6]. Ultrasound as sound above 20 kHz and up to 100 kHz can generate

greater acoustic energy, and affect chemical reactivity [7]. Up to now, the ultrasound range applied in sonochemistry has been extended to 2 MHz. Sonochemistry is defined as the application of ultra sound to chemical reactions and processes [8]. Figure 1.1 shows the frequency ranges of sound and the applied frequencies in the field of sonochemistry.
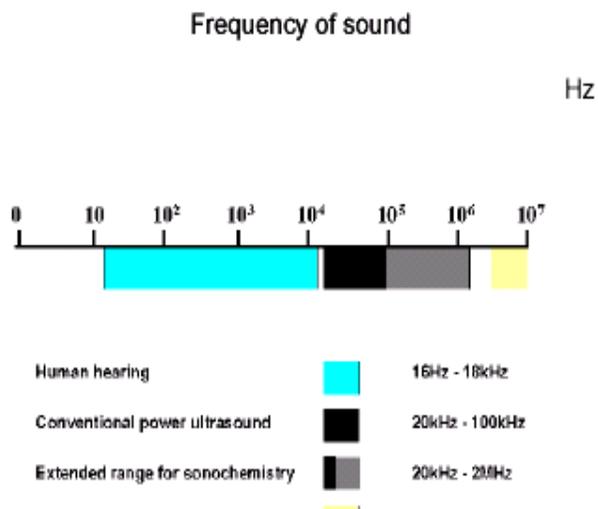
Frequency of sound

Figure 1.1 Frequency range of sound
(Source: T.J. Mason [24])

Acoustic Cavitation

Acoustical energy is mechanical energy, and molecules do not absorb it. Liquids irradiated with ultrasound can produce bubbles, when the pressure within the liquid drops sufficiently, and lower than the vapor pressure of the liquid. This process is called "cavitation". Turbulent flow, laser heating, electrical discharge, boiling, and radiolysis can also cause bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions, these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. Figure 1.2 shows three discrete stages of acoustic cavitation: nucleation, bubble growth, and

collapse in a liquid. In principle, sonochemistry derives from acoustic cavitation [9].
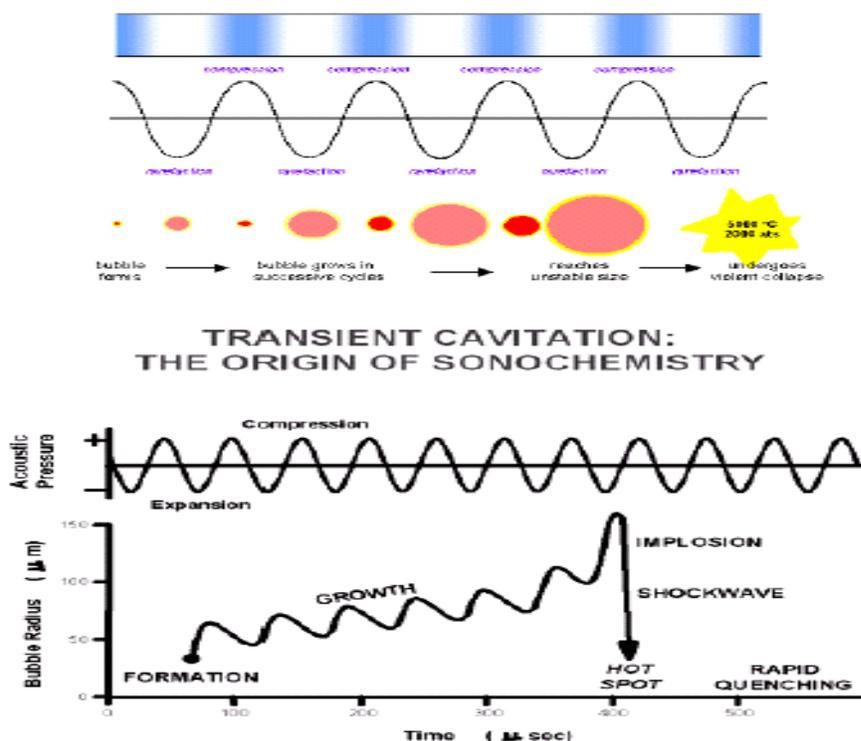

Figure 1.2 Generation and life of an acoustic bubble
(Source: T.J. Mason [25]; K.S. Suslick [6])

Two forms of cavitation are known [6] stable and transient. Stable cavitation means that a bubble oscillates many times with limited change about its equilibrium radius. While transient cavitation, a short-lived bubble undergoes large excursions of size in a few acoustic cycles and may terminate in a violent collapse. Both stable and transient cavitation may occur simultaneously in a solution and a bubble undergoing stable cavitation may change to transient cavitation. The sizes of the cavities before collapse were calculated to be about 170 µm at 20 kHz, 4.6 µm at 500 kHz and about 3.3 µm at 1 MHz. The bubbles are short lived, with maximum lifetimes near 0.4 µs and 10 µs at 500 and 20 kHz respectively [6, 7, 10, 11].

Mechanisms and Sites of Sonochemical Reactions

There are three different theories about cavitation - the hot spot, the electrical discharge, and the plasma theory. Currently, the hot spot theory is the most popular one. The collapse of cavity generates extreme energy for chemical and mechanical effects. It has been experimentally estimated that drastic conditions exist inside the medium for an extremely short time: temperatures of 5000 K and pressures of 500 ~ 1000 atm inside the collapsing cavity [8, 12]. This 'adiabatic' heating in the bubble interior is even thought to reach around 10000 ~ 20000 K [13]. Additionally, the evidence for nuclear emission during acoustic cavitation in deuterated acetone was observed in 2002 [14]. It means that the hot bubble implosion conditions achieve 10^6 to 10^7 K, as required for nuclear fusion reactions. The size, lifetime and fate of a cavitation bubble depend on the following parameters: acoustic frequency and intensity, physicochemical properties of solvent and dissolved gas, and external parameters (temperature, pressure). However, it should be noted that there is often no simple relationship. Assuming adiabatic bubble collapse, Noltingk [15] and Neppiras [16] calculated the maximum temperature and pressure reached inside a collapsing transient bubble by equations *E 1-1* and *E 1-2*

$$T_{max} = \frac{T_0 P_a (\gamma - 1)}{P_v} \qquad\qquad (E\ 1\text{-}1)$$

$$P_{max} = P_v \left[\frac{P_a(\gamma - 1)}{P_v} \right]^{[\gamma/\gamma-1]} \qquad\qquad (E\ 1\text{-}2)$$

where T_0 *is* the liquid temperature, P_a is the acoustic pressure at initiation of collapse, γ is the ratio of specific heats of dissolved gas or vapor, indicating how much heat is released from the gas during the adiabatic compression. P_v is the vapor pressure of solvent. Thus, the vapor pressure of solvent, type of dissolved gas, and aqueous temperature are the most important factors for the bubble collapse. A remarkable event during the cavitational collapse is the emission of

light under certain conditions (sonoluminescence). Sonoluminescence is definitively due to chemiluminescence from species produced thermally during cavitational collapse and is not attributable to electric microdischarge [17]. The thermal theory of sonochemistry holds that the sonoluminescence arise from hot molecules and radicals formed in the cavitational hot spot by molecules cleavage or rearrangement, followed by atomic and radical recombination, and thermal and chemical quenching. Frenzel and Schultes [18] first discovered Sonoluminescence (SL) in 1934. These researchers saw multiple-bubble sonoluminescence (MBSL), i.e. the glow from many bubbles of air in water (Figure 1.3). Since the glow for bubbles is so faint, it must be viewed in a darkened
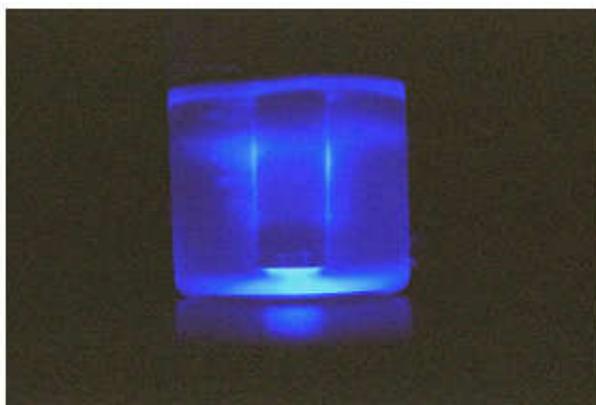

Figure 1.3 Sonoluminescence from a high intensity ultrasonic horn
Source: K.S. Suslick [17]

room. Single-bubble sonoluminescence (SBSL), however, can be seen in a lighted room. Sonoluminescence spectra from solutes and solvents were often applied to measure the temperature of cavitation [19, 20, 21]. Furthermore, the cavitational collapse causes a couple of strong physical effects outside the bubble: shear forces, jets and shock waves [9]. Near an extended solid surface, cavitational collapse is nonspherical and drives high-speed jets of liquid to the surface. This process can produce newly exposed, highly heated surfaces. Shock waves from cavitation in liquid-solid slurries produce high velocity interparticle collisions, the

impact of which is sufficient to melt most metals. Thus, there are basically two groups of effects: radical and mechanical effects, such as [6, 10]:

- Sonolyses of molecules: homolytic fragmentation to radicals, rupture of polymers, generation of excited states, cell disrupture;

- Effects in liquid-liquid systems: improved mass transfer, emulsification, increase of the effect of phase transfer catalysts or even their replacement;

- Effects in gas-liquid systems: degassing of liquids or melts, atomization of liquids in air, thin film preparation;

- Effects in liquid-solid: heterogeneous sonochemistry.

Sites of Sonochemical Reactions

As the bubble expands, gases dissolved in the liquid, volatile solutes and solvent enter the bubble. At the point of adiabatic collapse, some of these substances are trapped inside the hot bubble and start to react [13]. Three possible reaction sites of a collapsing bubble in a homogeneous liquid are illustrated in Figure 1.4: the cavity

Figure 1.4 Acoustic cavitation and reaction sites in a homogeneous liquid
Source: T.J. Mason [24]

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interior, the bubble vicinity and the bulk solution. Suslick et al. [22, 12, 23] used the sonochemistry of n-alkenes and volatile metal carbonyls to determine the sonochemical reactions site. They discovered that the linear dependence of the observed rate coefficients or rates on vapor pressures of n-alkenes or metal carbonyl, and suggested that the reaction occurs in the gas phase. The effective temperatures of these hot spots were measured at ~ 5200 K in the gas-phase reaction zone and ~ 1900 K in the initially liquid zone. In addition, using a simple thermal conduction model, the liquid reaction zone was estimated to be about 200 nm thick and to have a lifetime of less than 2 μs [12].

Most workers apply the so-called "hot spot" theory involving the production of very high temperatures and pressures. Margulis et al. have proposed an "electrical" theory. Some sonochemical effects are similar to those produced in plasma and this explanation is currently under review by a number of groups. Margulis has shown that during bubble formation and collapse, enormous electric field gradients in the region of $10^{11} Vm^{-1}$ can be generated and these are sufficiently high to cause bond breakage and chemical activity [25].

1.7 Interesting Features of Ultrasound in Polymer Synthesis

It is interesting to note that ultrasound can induce radical polymerization (e.g. of vinyl polymerization) even in the absence of chemical initiators [26, 27]. The early 1950's saw the first example of sonochemically induced polymerizations, those of acrylonite [28] and acrylamide, [29] both in aqueous solutions. Further studies in organic media, especially aromatic hydrocarbons, were disappointing as sonification lead to high molecular weight coloured products resembling coal, often referred to as chars. [27]. Formation of normal polymers, such as those derived from polystyrene or poly (methyl methacrylate) requires stable cavitation stages, while under transient cavitiation, higher local temperatures can be reached breaking the C-H bonds and leading to pyrolytic degradation.[30] Experiments with radical scavengers strongly prove that sonochemical polymerizations are due to free radicals formed from thermal

scission of monomers in bubbles or from an intense shock in the liquid immediately surrounding the bubble; this induces shear forces that fragment polymer chains already present. Many useful macromolecules can easily be obtained by sonochemical methods, such as acrylamide, [31] methacrylamide, [32] and copolymers of styrene with anhydride. [33] Ultrasound has also been exploited for graft copolymerization of methyl methacrylate on to regenerate cellulose film [34]. Ultrasonic irradiation not only alters kinetic parameters in polymers synthesis, but also affects polymer properties, resulting for example in a more homogeneous chain growth, hence a narrower distribution of molecular weight. As for heterogeneous and emulsion polymerizations sonication affects the most likely by physical rather than by chemical activation, by increasing mass transfer and continuously sweeping the polymer surface resulting in a greater number of propagation sites [35]. A remarkable possibility is that ultrasound may alter the conformation [36] of the resulting polymer chains, namely the tacticity, a key factor in determining the physical properties of these products. In addition, one should keep in mind the so-called anti-Arrhenius effects of temperature in sonochemical reactions: increasing the temperature will raise the vapor pressure of the liquid and lead to easier cavitation but a less violent collapse. [37] Accordingly, enhanced sonochemical effects, including higher reaction rate, would be expected on lowering the temperature, at least up to the limit imposed by the viscosity of the liquid. The synergic effect of ultrasound associated with an electron carrier can be recognized in a facile preparation of radical anions and their propagation reactions, e.g. in the sonochemical formation in the presence of isoprene. [38].

Ultrasonically enhanced polystyrene synthesis was reported [39] and it showed that the use of ultrasound allowed large degree of control over the polymer structure and hence could be used in controlling the molecular weight distributions. A kinetic scheme of polymerization of styrene with acrylonitrile has been reported. [40]. Ultrasonic radiation did not affect the scheme but some kinetic parameters were found to be affected. The rate constant for styrene homo

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polymerization increased with ultrasonic radiation and the initiator efficiency decreased. The results were attributed to the acceleration of the termination reaction. Effect of ultrasound on aqueous and alkaline solutions of acrylic monomers, acrylamide and methacrylic acid was reported. [41]. The degree of polymerization of polyacrylamide or poly(methacrylic acid) and the rate of reaction depended on the time of irradiation at 20 kHz with amplitude of 0.6 atmosphere and an intensity of 8 W /cm^2, when methacrylic acid was exposed to a similar radiation , rupture of C=C bond and decarboxylation occurred.

Ultrasonic block copolymerization of poly (ethylene oxide) with sodium methacrylate was also reported [42]. The rate of ultrasonic degradation of poly (vinyl acetate) and aqueous copolymerization of acrylonitrile with poly (vinyl acetate) at 20°C with a frequency 21.5 kHz and 490 W/cm^2 under ultrasonic irradiation gave mainly block copolymers [43]. The yields are dependent on the irradiation time and the concentration of acrylonitrile. Ultrasonic polymerization of acrylic monomers can be used as a method of producing stabilizer reagent [44]. The ultrasonic polymerization of acrylamide solutions under pressure variation of six atmosphere amplitude occurred even in the presence of oxygen to give a heat-resistant polyacrylamide of molecular weight approximately 50,000.

Effect of ultrasound on free radical polymerization of methyl methacrylate caused a rapid increase in conversion and a small increase in degree of polymerization [45]. Computer simulation of the effect of ultrasound on the polymerization using a single parameter based on the breaking of polymer chains to give polymeric free radicals gave results, which were in agreement with experimental data [45]. Kruss [46] studied initiation of bulk polymerization with ultrasound in methyl methacrylate. The variation of polymerization rate with time, volume and ultrasound intensity was explained by a simple reaction mechanism. The number average molecular weight of the polymer produced was 400,000. The polymerization mechanism obtained for the molecular weight data agreed well with literature values. Presence of radical scavenger diphenyl picryl hydrazide

DPPH inhibited the polymerization. The temperature dependence of the DPPH reaction was explained for temperatures – 17 to 40°C by relating it to reversible or irreversible adiabatic collapse of cavitation bubble. This was also in agreement with sonochemistry experiments where composition rather than temperature was changed to vary the vapor pressure. Initiation rates calculated from polymerization rates and DPPH consumption rates were of the same order of magnitude but showed an unexplainable difference in temperature dependence.

Price et al. [47] reported ultrasonically initiated polymerization of methyl methacrylate. They polymerized pure, dry, vinyl monomers but observed simultaneous polymerization and degradation processes. The molecular weight of the formed polymer was related to a complex function of sonication time. The decomposition of the thermal initiator, an azo compound at room temperature offered the prospect of a controllable low temperature initiation system for radical polymerization. Stoffer et al. also polymerized [48] methyl methacrylate in the presence of an initiator, dodecanethiol and high intensity ultrasound and obtained poly (methyl methacrylate) with a molecular weight of 330,000. They observed that molecular weight increased and the conversion amount of initiator. The conversion was found to increase when acoustic power intensity was increased.

Later studies Price et al. [49] revealed that irradiation of methyl methacrylate with high intensity ultrasound produces radicals, which can initiate polymerization; although a concurrent degradation reaction occurred. They also made a suitable manipulation of the experimental conditions, namely the temperature and ultrasonic intensity, to achieve the preparation of polymers with controlled molecular weight, polydispersity and tacticity. They proposed that this method could be used as an initiation technique although low conversions have been achieved. Here they carried out their experiments in a solvent, methyl butyrate, in nitrogen atmosphere. Further, they noticed the increased rate of initiation under ultrasound conditions. Reactions were also carried out in the

presence of added initiator, AIBN and they found that the rate of polymerization was faster than in the absence of AIBN, with a better percentage conversion.

Polymerization of styrene in the presence of added initiator aluminum acetylacetonate was studied by Fujiwara et al., [50] using ultrasonic irradiation at 32-60°C. Polymerization was found to be initiated in this system but completely inhibited by DPPH. They found that the initial rate polymerization showed a dependence of square root power on initiator and three halfth powers on styrene concentration. The apparent overall activation energy was 6Kcal/mol in comparison with 2Kcal/mol for radical polymerization. Ultrasonic irradiation of N-Vinylcarbozole in benzene in presence of AIBN was found to lead to polymerization under optimum power conditions. Lorimer et al. [51] noticed initiation of Polymerization of the monomer in that process. Ziegler – Natta polymerization of styrene using a titanium tetrachloride/ triethyl aluminum system has been performed in the presence of high intensity ultrasound [49] and it was found that the polymers were produced in better yield and with more control over the molecular weight distribution than in the conventional unsonicated process. Price [52] also prepared poly (organosilances) with controlled molecular weight distribution by Wurtz coupling reactions under varying ultrasonic conditions.

The effect of ultrasound on the ring opening polymerization of octamethyl cyclotetrasiloxane to give poly (dimethyl siloxane) PDMS, was described [53]. An increased rate of polymerization over conventional procedure and higher molecular weights with lower polydispersities were reported. When dilute solution of PDMS was sonicated, the degradation plays little part in determining the molecular weight in contrast to other polymerizations.

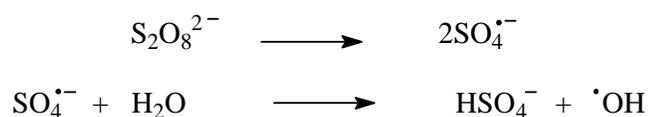## 1.8 Decomposition of Peroxodisulphate (PDS) in the Presence of Ultrasound

Ultrasound (20 KHz) has been found to enhance the decomposition [54] of the non-volatile initiator, PDS. The decomposition data was analyzed by assuming

that reaction took place at an elevated temperature in the interface between the cavitation bubble and the bulk solvent and enhanced decomposition was proportional to both acoustic pressure and square root of the acoustic intensity.

The decomposition kinetics [55] of potassium persulphates in aqueous solution have been investigated using radical trapping method in detail and ultrasound was found to markedly accelerate the decomposition so that the sonochemical process at 25°C could give the same rate as the purely thermal reaction at 55°C. The effect of ultrasound intensity has also been studied. This could be used to control the rate of decomposition of PDS by variation of parameters.

1.9 Peroxo Salts as Initiator for Polymerization

Most of the peroxo salts were found to decompose to produce primary radicals. These radicals were reported to initiate vinyl polymerization. PDS, Potassium peroxodiphosphate, potassium peroxodicarbonate come under this category. Potassium peroxodisulphate has been widely used as a single initiator for monovinyl and divinyl polymerization. Potassium peroxodisulphate has also been used as a one component initiator. An acid salt of PDS, potassium peroxomonosulphate (PMS) has also been employed as a single initiator or as a component in the redox system for the polymerization of vinyl monomers. Potassium peroxodicarbonate can be used as an initiator with advantage at low temperatures. The earlier work on PDS decomposition under different conditions clearly showed the production of such primary radicals which were subsequently used as conditions for initiation of vinyl polymerization. Peroxodisulphate (PDS) a powerful oxidizing agent with an oxidation potential of -2.01V decomposes slowly in aqueous solution at ordinary temperatures. [56] Studies on thermal decomposition of PDS in aqueous medium showed that the reaction obeys first order kinetics. [57-60] The proposed reactions for the decomposition are:

$$S_2O_8^{2-} \longrightarrow 2SO_4^{\bullet -}$$

$$SO_4^{\bullet -} + H_2O \longrightarrow HSO_4^- + {}^{\bullet}OH$$

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$$2\,{}^{\bullet}OH \longrightarrow H_2O_2$$

Isotopic studies [61, 62] showed that the decomposition of PDS in neutral medium occurs by the cleavage of -O-O- bond to produce sulphate ion radical. Studies on the photolytic decomposition [63] of PDS confirm that the sulphate ion radical formed primarily reacts rapidly with water to yield hydroxyl radical. The stability of the sulphate ion radical in aqueous and acid medium tested by Hayen et al. [64] and Dolgotti et al. [63], who found the radical fairly stable in both neutral and acid medium. Dolgotti et al.[63] identified the species, sulphate ion radical, in flash photolysis and Norman et al.[65] reported its ESR signal. Chandra Singh and Venkatarao [60, 66] found out that the homolysis of PDS occurs up to PH 13 to give sulphate ion radical. The sonochemical decomposition of PDS is presented in chapter 3.

Radioactive sulphur S^{35} containing PDS initiated polymerization studies [67 – 70] revealed that the polymer fragments were found to contain radioactive sulphur and this confirmed the initiation by sulphate ion radical. Ghosh et al. [71] found sulphate and hydroxyl end groups in poly (methyl methacrylate), polystyrene and polyvinyl acetal when PDS was used as initiator in aqueous medium. Fronaeus and Ostman [72] expressed a contradictory view from their flash photolysis studies on PDS. They indicated that formation of hydroxyl radical might be significant at PH below 8.5. However, the end group analysis of the resulting polymers indicated a hydroxyl group unit in the polymeric chain [73] Bevington et al. [74] and Banthia et al [75] found only low values for the sulphate end groups during PDS initiated polymerization.

Potassium peroxomonosulphate (PMS) was also used for the oxidation of many organic substrates. Kennedy and Stock [76] suggested the formation of $SO_4{}^{\bullet-}$ and ${}^{\bullet}OH$ in the decomposition, which can subsequently initiate vinyl polymerization.

$$HSO_4^{\bullet-} \longrightarrow SO_4^{\bullet-} + {}^{\bullet}OH$$
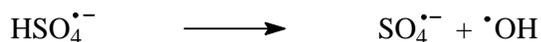
Potassium peroxomonosulphate (PMS) otherwise known as oxone has an high oxidation potential of -1.44 V. Samal et al. [77, 78] started using PMS along with metal ion like Ag^+ and Co^{2+} as initiators for the polymerization of acrylonitrile and methyl methacrylate. Hussain and co-workers studied the aqueous polymerization of acrylamide initiated by PDS and thioglycolic acid [79], and cysteine hydrochloride [80] redox systems. Radical polymerization of acrylamide [81] and methacrylamide [82] with PDS and Copper (II) amino acetate system in aqueous medium was studied. Polymerization of methacrylamide [83] was done under nitrogen atmosphere in the presence of two different activators, malic acid and ethanol amine with PDS as catalyst and a half and zero order dependence on the activator respectively was found.

Primary, secondary, and tertiary aliphatic amines enhanced the rate of polymerization of acrylamide. The effect of different amines on the polymerization of methyl methacrylate was made and compared to that of acrylamide polymerization [84]. The reaction mechanism of the redox initiated system of PDS - N, N, N', N'- tetramethylenediamine was established by spin trapping technique and ESR spectra [85]. The same techniques were used for the initiation with PDS - Pyrrolidine system in acrylamide polymerization and it was found that pyrrolidinyl primary radical is responsible for the polymerization [86].

The effect of single and mixed micelles of surfactants on polymerization of acrylamide [87] in aqueous and micellar solution has been carried out in conduction calorimeter in presence of sodium sulphite – PDS redox system. Polymerization of acrylamide (AA) in Aerosol with PDS as initiator has been studied [88] and the rate of polymerization was found to be of one and half order dependences respectively on the monomer and PDS. Riggs and Rodriquez [89] made an attempt to investigate the PDS ion initiated polymerization of acrylamide in aqueous solution and observed that the rate of polymerization showed

dependences as $[AA]^{1.25}$ and $[PDS]^{0.5}$. The research group led by Venkatarao et al. [90] reexamined the polymerization of acrylamide in presence of PDS and suggested the possible involvement of acrylamide along with PDS in the initiation step and the rate of polymerization showed 1.5 and 0.5 order dependence towards monomer and PDS. Hunkeler and Hamillec [91] reported the limiting conversion in acrylamide polymerization and found that the order with respect to monomer was 1.32. They proposed a hybrid complex - cage theory for acrylamide polymerization.

Kinetics and mechanism of the PDS initiated polymerization of acrylamide at high concentrations were studied [92] and a hybrid cage- complex mechanism was proposed in which hydrogen bonding between acrylamide and PDS leads to donor - acceptor interaction between them.

Kinetic studies on the oxidation of N, N, N', N' - tetramethyl p-phenylenediamine (TEPD) by various metal ions, halogens and peroxo salts like PDS and PMS were reported. Aravindan et al. [93] found radical cation TEPD$^{\cdot\,+}$ formation by decay using stopped flow technique. This pointed out the possibility of exploring this redox system for the polymerization of acrylonitrile with PMS as one component. Gopalan et al. [94] studied the polymerization of acrylamide using PMS and thioglycollic acid (TGA) as redox system where increasing TGA concentration showed a decreasing trend towards rate of polymerization. A suitable mechanism incorporating TGA as a chain transfer agent was reported. Subbaratnam et al. used PDS as initiator for the polymerization of methacrylamide [95], acrylic acid [96], methacrylic acid [97] acrylonitrile [98] and N-vinylpyrrolidone [99]. The sonochemical polymerization of methyl acrylate with the added initiator PDS is presented in chapters 3 and 8.

The challenges of scale-up represent a current concern of non-conventional technologies. A series of commercially available ultrasonic reactors can be readily adapted for scale-up, [100,101] even operating below the ultrasonic threshold.

Because organics are invariably linked to biomaterials and pharmaceuticals, sonochemical reactions conducted on larger scales will doubtless have a wide impact. Besides improving numerous organic reactions, sonication also can initiate crystal nucleation, even selecting a particular polymorph [102]. Both sonosynthesis and sonocrystallization will be very useful in drug discovery.

1.10 Photoacoustic Spectroscopy

A group of such spectroscopic methods based on the measurement of photo-induced heating of the sample is called the photo thermal methods [103,104-108,109-119]. Among the different photothermal methods, the photoacoustic effect is credited with the first observed photothermal phenomena noticed in 1880 during Alexander Graham Bell's voyage for new inventions [120,121]. Though Bell has prophesised, the scope of his novel observation, after the initial flurry of interest generated by his original work, experimentation with the photoacoustic effect is almost in a dormant state. After the advent of microphones, Viengerov is able to observe this effect in gaseous sample [122]. Still the growth of this new branch of spectroscopy is in a hopeless state due to many of the experimental limitations. The emergence of lasers in early sixties paved a new way in the photoacoustic spectroscopy of gaseous samples. But the applications of this technique have been efficiently extended to liquids and solids only after the successful formulation of a general theoretical model by Rosencwaig and Gersho in mid-seventies [123]. Subsequent developments in the theoretical aspects of photothermal phenomena are mere extensions or modifications of Rosencwaig-Gersho model. Though Bennett and Forman in 1976, and Aamodt et.al. in 1977 have modified the basic theoretical model by treating the acoustic wave transport in the gas using Navier-Stokes equations, the basic results of Rosencwaig-Gersho model remains the same [124,125]. Modification to the R-G theory by McDonald and Wetsel in 1978 by taking into account the contributions from thermally induced vibrations in the sample is somewhat intriguing [126]. By this time, a new form of photoacoustic

configuration, namely the open photoacoustic cell has emerged [127]. Nowadays, the open cell photoacoustic technique is in widespread use for the thermal characterizations of solid and even liquid samples [128-138].

The photoacoustic technique is essentially a closed cavity detection of energy liberated by atoms or molecules through nonradiative de-excitation mechanism, subsequent to light absorption by a sample. When a solid sample placed inside an airtight cavity is irradiated with a modulated optical radiation, the energy liberated through nonradiative channels will result in the generation of thermal waves within the sample. The thermal waves diffused through the sample to the gas in the cavity will produce a periodic pressure fluctuation inside the cavity. This pressure variation can be detected using a microphone kept inside the cavity. If the sample to be analyzed is in the gaseous form, then the sample itself can act as the source of signal generation and the acoustic coupler to the microphone. In order to investigate a liquid sample, a piezoelectric transducer is usually used. The piezoelectric transducer kept in contact with the liquid sample will detect the acoustic pulse propagated through the liquid. In 1976, Rosencwaig and Gersho formulated a complete theoretical explanation to this effect in condensed media [123]. Using photoacoustic technique Sankar et al [139], the thermal diffusivity, thermal conductivity and energy band gap on crystals on photonic systems CdS and doped CdS. Thermal diffusivity of polymer foils were studied by Leiti et al., using photoacoustic technique [140]. Singh et al [141] had reported thermal properties of silicon materials using open photoacoustic cell. Zurawska [142] has used Photoacoustics to detect phase transitions in the surface layers of various materials. Ramachandran et al., [143], had studied Photoacoustic study of the thermal and optical properties of Hippuric acid. However, photoacoustic studies on polymers are limited in literature compared to thermal studies on metals and alloys.

1.11 TGA-DTA, DSC Studies on Polymers

High pressure DSC is a powerful method, which gives additional insight into polymer systems. Using DSC, it is possible to investigate the melting and crystallization behavior of polymeric materials as functions of pressure (up to 500 MPa).G.W.H.Hohne reported the results from poly-4-methylpentene-1, syndiotactic polystyrene and different types of polyethylene. In addition, the melting behavior of alkanes and alkane mixtures has been investigated. These results are helpful for better understanding of phase transition behavior under pressure [144]. The differential of heat capacity signal, dC_p/dT, from modulated-temperature differential scanning calorimetry (MTDSC) was used to elucidate the miscibility and glass transition behavior of poly (methyl methacrylate) (PMMA) and poly (epichlorohydrin) (PECH) blends.[145]. The thermal stability of the C_{60} photopolymer, the C_{60} ozo-polymer, and photochlorinated C_{60} was studied by thermogravimetric analysis (TGA) ultraviolet-visible (UV-VIS) and TGA-differential thermal analysis techniques up to 950°C in comparison to graphite and pure C_{60} polymer/clay nanocomposites [146]. Aqueous polymerization of 3-chloroaniline (mCA) was studied using sodium dichromate as oxidant in the presence of hydrochloric acid. The effect of hydrochloric acid, sodium dichromate and monomer concentration on the polymerization rate, specific viscosity of the obtained polymer and ac conductivity was investigated and the Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) results were used to confirm the structure [147]. The influence of water absorption on polyethylene oxide and its complexes with $NH4ClO_4$, $NaClO_4$ and $Mg (ClO_4)_2$ was investigated and the changes in the thermal behavior due to water absorption have been reported using thermogravimetric/differential thermal analyses [148]. Oxidation of polysaccharides leading to the cleavage of the C_2---C_3 bond of the monosaccharide building blocks and formation of dialdehyde groups are difficult products to characterize by infrared (IR) and NMR spectral analysis, due to the formation of hemialdal and hemiacetal structures. A study of the thermal behavior (TGA, DTA and DTG) of a galactomannan (guar gum) and a series of its periodate oxidized

products (1.2, 3.1, 13, 26.7 and 54.9% oxidation, based on periodate consumption) shows that thermal analysis is a sensitive tool for differentiating periodate oxidized products which have very similar IR spectra. [149]. Oxidative behavior of commercial engineering plastics, polyolefins and elastomers has been evaluated by simultaneous thermogravimetric analysis (TGA)–differential thermal analysis (DTA) and pressure differential scanning calorimetry (PDSC).[150]. α-Ethynylnaphthalene has been polymerized into poly (ethynylnaphthalene) (PEN) using [Rh (norbornadiene) Cl]$_2$ in the presence of amines, such as triethylamine and/or S-(−)-methylbenzylamine, as co-catalyst in toluene. In these conditions, the yields were low but the molecular weight was relatively high. Improved yields were obtained by polymerizing α-ethynylnaphthalene in tetrahydrofuran using a strong base such as t-BuOK. The thermal stability of PEN under nitrogen and air flow has been studied in detail by using TGA (thermogravimetry), DTG (derivative thermogravimetry) and DTA (differential thermal analysis) in comparison to poly(phenyl acetylene) (PPA).[151] Synthetic hydromagnesite obtained from an industrial by-product was evaluated as a non-halogenated flame retardant. It was used in combination with aluminium hydroxide (ATH) and compared with commercial flame retardants like magnesium hydroxide (MH) and natural hydromagnesite–huntite (U) in a polyolefin system of low-density polyethylene/poly(ethylene-*co*-vinyl acetate) (LDPE/EVA). The thermal stability and flame behavior of the halogen free flame retarded composites were studied by thermogravimetric and differential thermal analysis (TG-DTA) [152]. The interactions between water and starch during gelatinization as affected by water content, maximum heating temperature and amylopectin crystallinity pattern were investigated by Differential Scanning Calorimetry (DSC) and ^{1}H NMR relaxation [153]

1.12 X-Ray Photoelectron Spectroscopy Studies on Polymers

No special facilities are required for polymer work in general. Contrary to the many workers who are used to study metallic systems, polymeric samples do not present serious outgassing problems and can easily be introduced to the sample

probe or mount by means of double-side adhesive tapes (itself polymeric). Clark has reported experiments in which migration of silicones along with polymer films (not under vacuum) was studied by XPS [154]. The valence bands and the core levels of conducting polymers synthesized through electrochemical process with large organic cation molecules, such as dye molecules with π-electron systems, were investigated by XPS/UPS measurements. [155] Yang et al., reported that X-ray photoelectron spectroscopy (XPS) studies show no Cu-O-C bond formation at Cu-parylene surface while studying the adhesion between copper and n-type parylene (PA-N). The PAN film was deposited on Si (100) substrate by vapor deposition polymerization (VDP), and the Cu film was deposited on PA-N by plasma partially ionized beam (Plasma PIB) as well as other deposition techniques as a comparison. [156] XPS, has been used to examine several polystyrene-clay nanocomposites and reported the accumulation of oxygen, from the almuniosilicate, on the surface of the polymer was observed, along with the loss of carbon.[157. Fire retardancy of polymer may be due to the formation of protective surface coating, i.e. a swollen char layer (intumescence). The intumescent coatings resulting from thermal treatments of the association of ammonium polyphosphate (APP) and pentaerythritol (PER) with or without zeolite 4A (used as synergistic agent) in a polyethylenic terpolymer (LRAM3.5) were studied by X-ray photoelectron spectroscopy.[158] Using angle-resolved X-ray photoelectron spectroscopy (AXPS), the chemical composition and structure of each copolymer surface and interface of water-soluble monomers such as acrylamide, acrylic acid, the sodium salt of 4-styrenesulfonic acid and *N,N*-dimethylaminoethyl methacrylate onto pristine and Ar plasma pretreated film surfaces of high-density polyethylene, poly(ethylene terephthalate) and polystyrene were investigated.[159]. X-ray photoelectron spectroscopic measurements were made on complexes and blends obtained from poly (p-vinyl phenol) (PVPh) and poly (4-vinylpyridine) (P4VPy) or poly (2-vinylpyridine) (P2VPy) [160]. Polyethylene, polyamide-6 and polyimide foils implanted with 100 keV, B^+, P^+ and Sb^+ ions to a fluence range of 10^{15}–10^{17} cm^{-2} have been studied using the X-ray photoelectron

spectroscopy method [161]. Changes in composition and bonding induced by bombardment with argon or nitrogen ions in a commercial poly-methyl-phenyl-cyanopropyl-siloxane fluid were examined by XPS [162]. Plasma polymerized acrylic acid (ppAAc) coatings were deposited on aluminium substrates from acrylic acid plasmas at various plasma powers (P). The chemistry of the ppAAc deposit was characterized using X-ray photoelectron spectroscopy and trifluoroethanol derivatisation of the carboxylic acid functionalities. [163]

1.13 Atomic Force Microscopic Studies (AFM) on Polymers

Binnig, Quate and Gerger [164] invented the AFM in 1986. It was the first of the SPMs, which overcame the limitation of STM (Scanning Tunneling Microscope) in imaging thin samples on electrically conductive materials. The atomic force microscope (AFM) was used to monitor directly the changes in polymer conformation at the solid/water interface while studying adsorption of low-molecular-weight polyacrylic acid (M_r= 2000) on zirconia, as a function of pH.[165]   Ultraviolet-ozone (UVO) treatment of poly(ethyleneterephthalate) (PET) films and polystyrene (PS) dishes of up to 10 minute exposure has been studied.[166] The influence of the lipidic ratio and composition on the physical stability of liposomes during their storage was investigated using atomic force microscopy [167]. The self-assembly of PLA enantiomers has been studied at the nanometer scale using atomic force microscopy. [168] Tapping mode atomic force microscopy was used to investigate the lamellar morphology of poly(L-lactide) and two poly(L-lactide-*co-meso*-lactide) random copolymers containing 3% and 6% *meso-* lactide.[169] Structure and phase transitions of polydiethylsiloxane (PDES) were studied with AFM at temperatures in the 300-268 K range.[170] The formation of molecular networks by retrogradation of gelatinized starch was investigated using atomic force microscopy in tapping mode.[171]. Atomic force microscopy studies of interactions between slurry particles and substrates treated by chemical mechanical polishing (CMP) processes were carried out. [172] The atomic force microscopy is utilized to obtain force spectroscopy results of the

interaction strengths between siRNA and chitosan measured in physiological phosphate buffered saline buffer at different pH.[173]

1.14 Electrically Conducting Polymers

Since the early 1950's, polymers have been used extensively as passive components in electronic devices. Because of their lightweight, flexibility, corrosion resistance, high chemical inertness, electrical insulation and ease of processing. In 1975, an organic conjugate polymer, polythiazyl was discovered, which posses metallic conductivity and becomes a superconductor at 0.29 K. [174] However, the idea of using polymers for their electrical conducting properties actually emerged in 1977 with the findings of Shirakawa and co-workers [175], that the iodine-doped trans polyacetylene, exhibits conductivity of 1000 S/cm. Since then, an active interest in synthesizing other organic polymers posseing this property has been initiated. As a result, other polymers having a pi-electron conjugate structure, such as polyaniline, polypyrrole, polythiophene, polyfuran polyphenylene and polycarbazone [176-179] have been synthesized and studied. Some important conducting polymers and their energy gaps are shown in the table below. Since in the beginning of the last decade, these polymers have been extensively investigated for an understanding of their physical and chemical properties.

POLYMERS	OPTICAL ABSORBTION EDGE (eV)
Trans-polyacetylene	1.4
Cis-polyacetylene	2.0
Polypyrrole	2.5
Polythiophene	2.0
Poly(p-phenylene)	3.0
Poly(p-phenylenevinylene)	2.4

The charge transfer process is one of the most intriguing properties of conducting polymers because the electrical conductivities of this class of polymers vary over many orders of magnitude due to chemical or electrochemical doping. It is understood that a wide variety of phenomena are involved in charge transport in this group of materials. A major source of this phenomenon originates from the quasi-1-dimensional (q-1D) nature of the materials. The poly-conjugated chain can be considered as a q-1D metal, having one charge per carbon atom. It is well-established fact that such a half-filled system gives rise to Peierls instability by opening up an insulating gap at the Fermi level. This leads to the band structure responsible for the important electronic properties in polymers and thereby resulting in the existence of the non-linear excitation called a soliton. This excitation and other excitations, such as polarons and bipolarons found in non-degenerate ground state systems, are produced due to the chain relaxation or deformation that results from adding/removing an electron from the polymeric chain. Under the influence of the applied electric fields, these non-liner defects become mobile, resulting in an increased electrical conductivity. Each of these particles possesses its own characteristic transport properties. A clear understanding of the intrinsic excitations in doped and undoped polymers is still lacking [180,181]. Several researchers focusing on this fundamental problem have carried out a considerable amount of work. The charge transfer properties as a function of temperature, pressure, magnetic fields, etc., for various polymeric samples have also been reported in the literature. The collective contributions from various parameters, such as electron-phonon interaction, electron-electron interaction, quantum lattice fluctuations, inter-chain interactions, etc., make it difficult to estimate the contributions from individual parameters quantitatively. Moreover, contributions from disorder and doping, etc., make it rather difficult to envisage a microscopic mechanism for charge transport properties in conducting polymers is still a challenging problem due to the extreme complexity of the system. However, recent developments in reducing the extent of disorder have

explained many phenomena regarding charge transport in doped conducting polymers.

1.15 Factors Influencing the Transport Properties of Polymers

It may be remarked that the actual charge transport process in a conducting polymer is dependent on several parameters such as disorder (e.g., presence of vacancies, clusters, inhomogeneities) interchain coupling, the degree of doping, and the distribution and nature of dopant ions, etc.

Disorder

It is known that disorder is an inherent feature of polymeric systems. The different sources of disorder in a polymer include inhomogeneous doping that arises due to the nature of the catalyst used and the processing routes. Besides this, the process of preparation modifies the morphology and may lead to partial crystallinity , sp^3 defects , chain termination , cross links ,Cis-segments within trans-chains and impurities ,etc. Chemical defects such as non-conjugated carbon atoms inserted in the chain or impurities may result in localized and strong potential, i.e. strong disorder. On the other hand, static fluctuations in the conformation of chain along its length are spread over some distance, leading to weak disorder. Both types of disorder may limit the conjugation length and hence the transport properties of polymers. Disorder effects are known to produce tails in the bands of regular systems and this usually reduces the energy gap between valence and conduction bands [182].

Several studies on the effect of the disorder have been based on either the HUckel or Suschrieffer – Heeger model with perturbation added in the form of either a screened coulomb potential representing a charge impurity or a completely localized potential acting on a single site [183]. It has been argued in literature that disorder can either act as a barrier to the quasi-particle movement, or trap it. The rotation of rings or bands owing to geometrical fluctuation is another disorder and has been shown to reduce the conjugation length [184]. Wolf and Fesser [185]

have investigated the effect of disorder in interchain hopping. They showed that dimerisation decreases and the density of states in the gap increases as a function of increasing disorder in interchain coupling. The perfectly dimerised Peierls ground state breaks down towards a 'metal-like' state as a critical random distribution of interchain coupling. The random interchain coupling changes the properties of the band gap to a pseudo gap, with a small but non-zero density of states. Harigaya and co-workers have reviewed the doping induced disorder in conducting polymers. Both theoretical and experimental studies suggest that it is difficult to reduce the Peierls gap to zero without taking account of the effects of disorder [186]. Lately the effect of spatial disorder and anisotropy on the mobility of charge carriers has been reported using a dynamical Monte Carlo simulation. It is found that small disorder decreases the mobility of low external fields whereas a considerable increase in mobility is found when spatial disorder reaches value about 5%. Such studies are essential to optimize the performance of devices using these materials. [187] A model was proposed by Levy and co-workers for understanding the experimental features observed due to disorder near medium consisting of spherical regions of ordered polymers, randomly distributed in a much more disorder polymer host. Within each spherical region, the polymer chains are highly oriented, but the axis of orientation varies randomly from sphere to sphere [188]. It can be concluded that, in general, disorder is detrimental to transport phenomena in solids. The higher the disorder, the lower will be the dimensionality of the system.

Although a considerable amount of work has been devoted to investigating the role of disorder in transport properties , systematic investigation of the physical properties by controlling and varying different types of disorder has not been accomplished yet. Therefore, studies that are more extensive are required in order to understand the effect of different types of disorder on structural, electronic and transport properties of conducting polymers. The main problem in understanding the conduction mechanism pertains to the correlation of disorder with that the charge carrier transport.

Doping

During the doping process, the charge is injected or removed from the polymer chain and dopant ions sit in the polymer matrix in order to maintain charge neutrality. In general, the doping process is inhomogeneous and the distribution of dopant ions in the polymer matrix is not uniform. This is mainly due to the complex morphology of the polymer matrix, which consists of both crystalline and amorphous regions [189,190]. The dopants easily diffuse into the vacancies in the amorphous region until saturation level is reached, after which they slowly migrate into the crystalline regions. According to the Kivelson and Heeger [191], after adding or removing electrons to a chain, the dopant ions have a negligible effect on the electronic properties of the system. This has been attributed to high conductivity within the metallic regions and their weak dependence on the dopant species. Considering this fact, doped polymers can be described within an idealized π – electron model with variable electron density.

However, neglecting the effect of impurity potentials arising out of dopant ions is a drastic assumption because random weak potential can sometimes produce bound states in one dimension. A theoretical study has revealed that disorder effectively quenches the Peierls distortions [192]. The influence of dopant ions on interchain coupling may weaken it by either placing chains further away or vice-versa. Cohen and Glick found that in the neighborhood of a dopant ion the intrachain hopping is enhanced by 10% and the interchain hopping is enhanced by 100% [193]. Thus, the dopant may act as a bridge for the interchain transport. The interchain hopping strength at sites in the presence and absence of dopant ions are estimated to be nearly 0.17 eV and 0.10 eV, respectively. The electron-spin resonance (ESR) measurements in conducting polymers studied by Bernier and co-workers have demonstrated that the dopants play a major role in the charge transport process [194]. Salkola and Kivelson suggest that the counterions affect the energy gap [195]. It is suggested that a minor change in the arrangement of counterions relative to the polymer chain is capable of influencing the energy gap of the polymer lattice. If the position of the soliton is taken as centre, then it is

observed that if counterions are located near to odd and even sites, then the gap is enhanced. Conversely, if the counterions are located near to even or odd sites then the gap is reduced.

Yamashiro and co-workers have estimated the dopant-chain interaction and its role in interchain transfer [196]. They showed that the dopants mediate the largest interchain transfer of about 0.3-0.1 eV with five to seven carbon atoms in another chain that is in contact with a common dopant column. The interchain transfer via dopants has little effect on interchain states but yields a modification of the orbital energy spectrum.

It has also been reported that the electronic gap between a soliton and the conduction band is decreased due to coulomb potential of the dopant ions and vanishes at a sufficiently high dopant concentration. A random distribution of dopants can have a strong effect on disordering. The aggregation of dopants into an ordered structure suggests that finite metallic segments exist which increase in length upon doping. As a result, the density of states increases smoothly as a function of dopant concentration. Increase in dopant concentration beyond a critical level leads to the formation of a super lattice in many doped polymers [197].

Interchain Coupling

In contrast to the extensive efforts devoted to the studies of a one-dimensional model of Π-conjugated polymers, no attention has been paid to account for the effect of the three dimensions of the real materials, being isotropic in nature. The interchain couplings have considerable influence on major sources affecting the solid state of polymers and thereby lead to substantial differences between the exact form of conducting polymers and their oligomers. For example, in an infinite idealized one-dimensional polymer material, bond alteration can exist in the ground state, but it does not persist at finite temperatures. Moreover, the domain walls (kink/solitons) connecting the two degenerate bond alteration regions will always be generated by thermal fluctuations at finite temperatures and even a small density of these kinks will destroy the long-range order in one

dimension. Nevertheless, in real materials, even a weak interchain coupling is sufficient to sustain the long range order up to a certain temperature.

Three-dimensional coupling is characterized by the transfer integral, t, which is the ratio of electron-phonon coupling to the electronic intersite coupling. Generally, only nearest neighbour interactions are taken into account, so only one or two transfer integrals are relevant. Another parameter, $t_{anisotropy}$, can be expressed as the ratio of $t_\perp$ to $t_{//}$, $t_\perp$ and $t_{//}$ being the interchain and on-chain transfer integral, respectively. This helps in determining the magnitude of the band structure anisotropy. It has been found that the three – dimensional effect dominates if $t_\perp /t_{//} > 10^{-2}$ [198]. Three dimensional band calculations performed on trans –polyacetylene and polyphenylvinylene yield similar results if $t_\perp /t_{//}$ is at least $3x\ 10^{-2}$ [199].

In an anisotropic Landau –Ginzberg model, it has been argued that interchain coupling can be detrimental to polarons and bipolarons [200]. The result is confirmed by theoretical calculations with Su-Schrieffer –Hegger (SSH) model. It is found that a polaron is destabilized and charge is spread over the whole crystal if the energy gained by the lattice relaxation of a single chain is of the order of 4t. Since the polaron binding energy is small, a small t is sufficient to destabilize the polaron. Bipolaron are stable with respect to transverse delocalization as long as coulombic effects are negligible. *Ab initio* calculations in crystalline polyacetylene also confirm the possibility of instability of polarons and bipolarons [201]

Leising and co-workers have investigated the role of interchain interaction in the case of oriented trans –Polyacetylene extensively [202, 203].Their study has shown that for a highly conducting polymer there is no gap around the Fermi energy consistent with the metallic properties of polymers. The effect of interchain coupling on excitation has been studied by Shi-Jie using a tight-binding model [204]. A new spinless charged polaronic excitation (q= $\pm$ e, s=0) was obtained due to the transverse interchain coupling, which is different from the general magnetic

polaron (q= $\pm$ e, s=1/2) obtained in the perfect 1-D model. A polaron is more easily stimulated energetically in a longer chain than in a shorter one. Additionally, interchain coupling decreases the energy of creation of a polaron. The effect of interchain coupling on the electronic structure of both doped and undoped *trans*-polyacetylene has been studied by Conwell and co-workers [205]. They suggested that the interchain coupling is energy dependent, decreasing at a constant rate from a maximum value at the bottom of the valence band. They suggested that the interchain interaction by itself is not enough for transport into the metallic state in doped conducting polymer samples. Although, in principle, the interchain coupling is sufficient to shrink the energy gap between the soliton band and the conduction band to zero, in reality the coulomb interaction with dopant ions plays a significant role in giving rise to the metallic density of states. The detailed theoretical modeling is carried out only for *trans*- polyacetylene and it should be extended to other polymeric systems in order to delineate a comprehensive picture about the effect of interchain interaction in both doped and undoped conjugated polymers. [206,207].

Recently, Prigodin and Efetov have developed theoretical model for interchain interaction at the M-I transition in a random network of coupled metallic chains [208]. In this model, the interchain disorder due to intrinsic defects and the randomness in the distribution of interchain contacts induce localization. The M-I transition in such a system is determined by the critical concentration of interchain crosslinks, which in turn depends on the localization lengths and interchain coupling. Moreover, a metallic state can exist in such a random network of coupled metallic chains only if the concentration of interfibrill contacts is large enough to overcome the percolation threshold.

The interchain coupling plays a significant role in charge delocalization, screening and coulomb interaction and thereby determines the nature and stability of intrinsic excitations. The transport properties of conducting polymers are highly dependent on the way the chains are organized and arranged with respect to each

other. In spite of innumerable theoretical and experimental work, a quantitative estimation of the effect of interchain coupling on transport properties of various polymeric systems has not yet emerged. The present work is aimed to study this for the PMA system.

1.16 Models of Charge Transport in Conducting Polymers

The mechanisms for the formation of metallic state and charge conduction in conducting polymers have been the subject of intensive study since the occurrence of an insulator to metal transition was reported upon doping. It is proposed that non-linear defects such as polarons, solitons and bipolarons have a major role in these systems [209,210-212]. In earlier synthesized conducting polymers, inhomogeneities often dominated the transport properties, and metallic island models were proposed to explain such features. Most of the transport measurements in such conducting polymers were in the insulating regime. However, recent advances in synthesizing ordered and highly conducting polymers have signaled the onset of a new generation of polymers [213]. Improved homogeneity and a reduced degree of disorder in new kinds of polymers have provided a new opportunity for investigating metallic features through transport and optical measurements [214]. More recently, experimental results obtained in polyaniline and polyaniline derivatives were interpreted by invoking a q-1D variable range hopping model of Nakhmedov, Prigodin and Damukhin [215, 216]. In spite of the rapid progress in observing high quality samples of conducting polymers, the subtle details of the mechanism of charge transport are not yet understood. Firstly, the role of solitons, polarons and bipolarons in the charge transport is not very clear. The Kivelson model pertains to a phonon assisted hopping between soliton states in the case of highly doped polyacetylene [217, 218]. However, the interpretation of experimental data in the framework of alternative models cannot be ruled out [219, 220]. Secondly, the difference between microscopic and macroscopic transport properties has to be understood clearly. Thirdly, the connection between the measured conductivity and structural

parameters of the sample has to be sorted out. The present section deals with the various models reported so far in addressing these problems.

In Kivelson's model [217, 218], it is suggested that the low –energy charge excitations introduced into polyacetylene by light doping are charged solitons because of the large binding energy. At reasonable temperatures the population of solitons is extremely small and consequently thermally activated conduction due to free, charged soliton movement is difficult. At low temperatures, electron hopping between solitons is a less strongly activated conduction mechanism and is a dominant process at low temperatures (Figure 1.5a). For example, the activation energy for phonon – assisted hopping or transition of an electron from the charged soliton to the neutral soliton is small if the neutral soliton happens to be near another impurity. The hopping conductivity is determined by the rate at which an electron hops between a pair of solitons. Because of the disorder (namely the random distribution of impurities), the conduction pathways are essentially three-dimensional, with interchain hops. Kivelson's model predicts a steep power law dependence for the conductivity $\sigma = T^9$, which is close to that observed experimentally. The conductivity versus temperature data can be explained reasonably well in terms of the variable – range hopping (VRH) model, especially in the case of iodine-doped polyacetylene [221]. The temperature and frequency dependence of conductivity is found to be in agreement with VRH among soliton – like states in the lightly doped regime [222,223].

Similar to Kivelson's model, Chance and co-workers proposed interchain hopping for spinless conductivity in doped polyacetylene, doped poly (p-phenylene) and other doped polymers [219] . The mechanism accounts

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for the observed dopant concentration dependence of the conductivity in trans-polyacetylene and the observation of anomalously
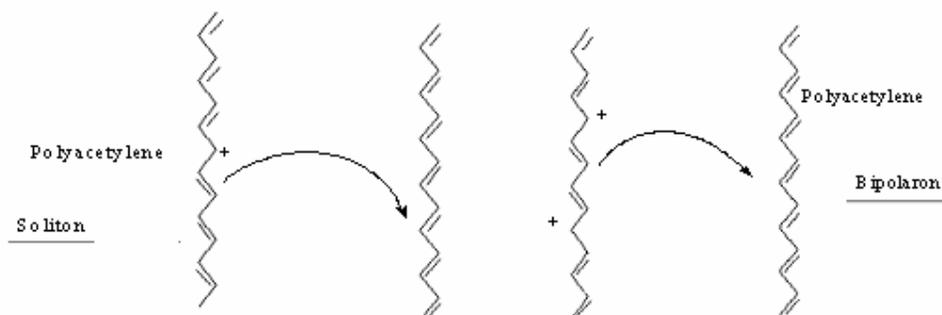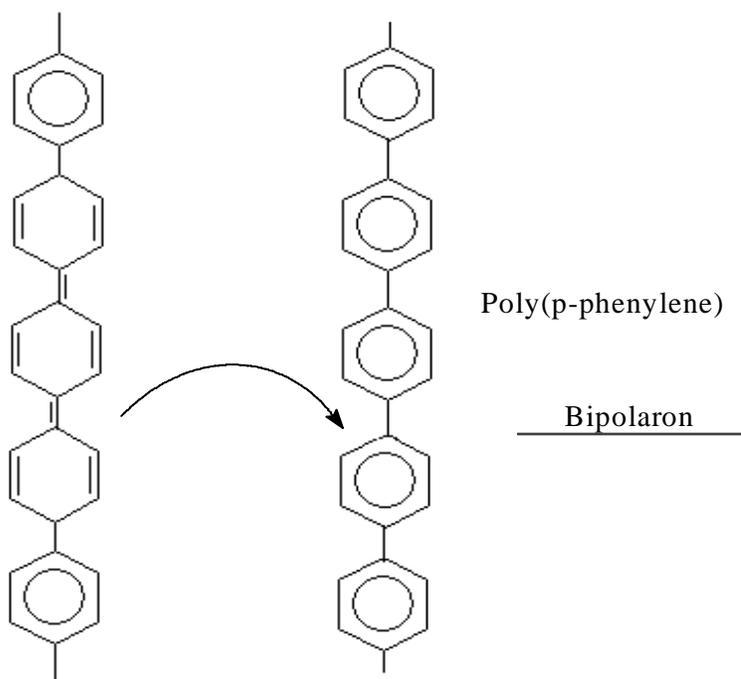

Figure 1.5 (a)

Figure 1.5 (b)

Figure 1.5 Interchain transport of solitons and bipolarons in (a) Polyacetylene and (b) Poly (p- Phenylene)

low magnetic susceptibilities in the highly conducting regimes of several doped polymers (Figure 1.5b) . However, this model does not explain the transition from spinless carriers to carriers with spins upon doping. Pietronero suggested that the main contribution to resistivity in conjugated polymers is due to scattering between the conduction electron and the phonon of the conjugated polymer chains [224]. The observed high conductivity of heavily doped polyacetylene has been explained using the one-dimensional model. The only possible scattering for polymers is from K_f (the Fermi vector) to $-K_f$ or vice versa involving large momentum $(2K_f)$ phonons of high energy (h ν ~ 0.2 eV for Polyacetylene – type systems). With first –order scattering one obtains a strong conductivity increase even at room temperature, because of phonon freezing effects. High-order scattering process with low energy phonons may then become less important. In the case of elastic scattering (k_BT >>hν) where k_B is the Boltzmann constant , the electrical conductivity is estimated as 1.6×10^5 S cm^{-1}, which is nearly an order of magnitude less than the value, estimated for graphite intercalation compounds. However, this estimation is not realistic since, in polymers, only $2k_f$ phonons scatter, i.e. h $ν_0$>> k_B T. At room temperature this analysis gives high intrinsic conductivity, $σ = 1.4 \times 10^7$ S cm^{-1}.

Kivelson and Heeger carried out a detailed study on the intrinsic conductivity of conducting polymers [191]. They described the expression for the conductivity as:

$$\frac{2\pi n v_0 e^2 a^2 t_0{}^2}{\alpha^2 h^2} \exp \frac{h v_0}{k_B T}$$

(E 1-3)

where α (-4.1 eV /Å) is the electron – phonon coupling constant, $ν_o$ is the phonon frequency , t_o is the electron hopping matrix element [224] , h is Planck's constant ,n is the conduction electron density and a is the C-C distance in the chain direction . A large t_o , and a small number of phonons gives the conductivity at room temperature as 10^7 S cm^{-1} . This value increases exponentially at low

temperatures. Since the charged ions are spatially removed from the q-1D conduction path, the usual scattering of phonons is reduced. This is because phonons of wave vector $2k_f$, are required to backscatter electrons. Since these phonons are thermally excited only at higher temperatures, the resistivity is very small at low temperatures, with a rapid rise when the thermal energy k_BT approaches the energy of the $2k_f$ phonons. At 0.12eV, the rapid increase in resistivity can account for the change to metallic temperature dependence, which is a prominent feature of the conductivity in conducting polymers. The interchain couplings are necessary to prevent 1D localization. Even a small interchain coupling $t_\perp \sim 0.1$ eV, may give rise to the suppression of the Peierls distortion. The condition necessary for the system to remain three- dimensional is

$$L/a \gg 2t_o / t_\perp \qquad\qquad (E\ 1\text{-}4)$$

where L characterizes the distance between the chain interruptions or sp^3 defects or crosslinks.

When the concentration of chain interruptions is sufficiently high such that the left hand side of equation1.3 is small, then the wave function will be localized. The possible limits for the conductivity arise from the chain interruptions and /or phonon scattering. All the above factors suggest that in high – quality conducting polymers the electronic mean free path could be much larger than the structural coherence length and real metallic features could be observed.

Prigodin and Firsov [225, 226] have proposed similar charge transport models. According to their model, an abrupt transmission from extended to localized state is expected at the critical interchain exchange integral metallic features could be observed. $t_{\perp c} \sim (3h/2\pi\tau), \tau$ being the scattering time. Therefore , the delocalization in a q-1D metallic chain appears only if $t_\perp$ is larger than the threshold value $t_\perp \sim 0.3 /\tau$. Later, Nakhmedov and co-workers carried out a study of hopping transport in q-1D systems near the M-I transition with weak disorder [215]. They set the cut-off temperature regimes in which band transport crosses

over to hopping transport. In a high temperature regime, the band transport is governed by phonon scattering and disorder while at low temperatures; the hopping has been ascribed to Mott's VRH. In the intermediate temperature region, the temperature dependence of conductivity shows a power law behavior. However, these temperature regions are different in a q-1D system when there is weak interchain coupling. In these cases, the temperature dependence of conductivity gradually varies from 1D behavior at high temperatures to that of an isotropic 3D behavior at low temperatures. In the intermediate range, the conductivity follows $\exp(-T_o/2T)\exp\left[-(T_o/2T)\right]^{1/2}$ dependence. Joo and co-workers extended this model, suggesting that the effect of finite temperature emerges through phonon scattering, which is expected to be highly anisotropic [187-229]. The role of phonon forward scattering is to break the phase coherence of the impurity scattering and thereby destroy the weak localization. Moreover, the conductivity versus temperature curve exhibits a characteristic maximum at temperatures where the phonon backward scattering time becomes comparable with the impurity scattering time.

Epstein and co-workers have widely used q-1D models to interpret transport properties in both metallic and insulating polymer systems [230,231]. Conducting polymers were considered as an inhomogeneous system, which consists of crystalline and amorphous regions. The overlap of π- orbitals gives rise to crystalline regions whereas amorphous regions emerge from weak chain interactions. When the size and volume fraction of the crystalline region increases with respect to amorphous region in between the crystalline region and thereby the movement of charge carriers occurs through the 1D localized regions and often dominates throughout the 3D extended states in crystalline regions. When the volume fraction of 3D extended states increases, the probability of movement of charge carriers is through the path of least resistance and therefore, a percolative metallic transport is expected. Microscopic properties in crystalline and

amorphous regions are different and hence the usual Anderson localization in the homogeneous disorder limits is not appropriate for conducting polymers.

More recently, Samuhin and Co-workers proposed [220] a q-1D model in order to explain the experimental data obtained for poorly conducting polymers. It is found that at low temperatures , the VRH conductivity obeys q-1D Mott's law, $\sigma_{dc} \propto \exp{-(T_1/T)^{1/2}}$,but the characteristic temperature T_1 is greater than T_o for a 1D chain by a factor 1/D-1 , D being the dimensionality of the system. Similar temperature dependence was obtained for dc conductivity. Low frequency conductivity is entirely controlled by the weak charge transfer between clusters, each cluster being very dense and well isolated. In contrast to q-1D models, Qiming and co-workers proposed a granular – rod model for the metallic state of the conducting polymer [232]. In this model, the metallic islands correspond to single strands of polymer. The macroscopic conductivity results from anisotropic three-dimensional VRH in the network of metallic rods. This model explains very well the temperature dependence of the conductivity, $\sigma = \sigma_0 \exp{(-T_o /T^{1/2})}$, the doping dependence of T_o , the anomalous 1/T dependence of the thermoelectric power as well as the linear increase of Pauli susceptibility with dopant concentration. A temperature range, where the variable range hopping is valid, is decreased below the experimentally observed temperature range (over which the above equation holds) if the metallic islands correspond to 3D bundles of the polymer strands.

Sheng's fluctuation induced tunneling (FIT) model was used extensively to interpret transport properties in metallic polymers. This model was originally developed for granular metal [233, 234] and polymers filled with carbon black or alumina flakes. The polymer system is described in terms of highly conducting regions separated by much less conducting or insulating areas. The electrical conduction is dominated by electron transfer between large conducting segments. Since the electrons tend to tunnel between conducting regions at points of their closest approach, the relevant tunnel junctions are usually small and are therefore

subject to large, thermally activated voltage fluctuations across the junction. By modulating the potential barrier, the voltage fluctuations directly influence the tunneling probability and introduce a characteristic temperature variation to the normally temperature independent tunneling conductivity. A non-metallic feature of doped polyacetylene was explained in the framework of this model [235]. A similar model was used to interpret the transport properties of emeraldine polymer as a function of the protonation level, x [236]. At no composition level does the conductivity appear truly metallic. For all compositions, the conductivity behavior is similar to that of a granular metal and this data first transport via charging energy limited tunneling between conductivity islands. The data were found to be consistent with percolation among these islands for $x \geq 0.3$ with the presence of an insulating layer surrounding each island above the percolation threshold. The size of these islands is estimated to be 200-300 Å. Lux and co-workers reported scanning electron microscopy (SEM) and transmission electron microscopy (TEM) pictures of highly conducting polyaniline in support of the conducting island concepts[237]. Experimental measurements of TEM, X-ray diffraction (XRD), temperature dependence of dc conductivity and magnetic susceptibility indicate the applicability of this model. However, electron paramagnetic resonance (EPR) spectroscopy and magnetic susceptibility studies also suggest that pristine and doped polyaniline contain at least two types of spin carriers. It was suggested by Conwell and Mizes that the conduction mechanism is not due to FIT dependence in conducting polymers since the metallic regions in the FIT model have negligible temperature dependence of conductivity. In addition, the phonon scattering, scattering due to imperfections and defects in the metallic regions are not considered in the FIT model. They determined the band motion versus diffusive hopping transport in oriented metallic conducting polymers to understand the effective dimensionality of the system. They showed that for band motion $t_{\perp} \tau_{//}$ is much greater than $h/2\pi$, while for diffusive motion $t_{\perp} \tau_{//}$ is much less than $h/2\pi$, $\tau_{//}$ being the average time for the electron scattering along the chains ($\tau_{//} \sim 10^{-14}$ s from $\sigma_{//} = ne^2 \tau_{//} m^*$, if $\sigma \sim 10^5$ Scm^{-1}, $n=10^{22}$ cm^{-3}, m*= free

electron mass $=9.1 \times 10^{-28}$g ,e$= 1.6 \times 10^{-19}$ C) .If the system consists of high conducting regions mixed with low conducting regions , then $\sigma_\perp$ is the mixture of band motion and hopping . However, the measurements $\sigma_{//} /\sigma_\perp$ as a function of temperature in oriented metallic *trans* – polyacetylene shows that $\sigma_{//} /\sigma_\perp$ is nearly temperature independent and hence it is impossible that $\sigma_\perp$ is due to diffuse hopping in both cases [238,239] . In contrast, experimental results demonstrated by Park and co-workers [240] indicate that $\sigma_{//} /\sigma_\perp$ increases $\sigma_\perp$ and therefore, the issue of transport in highly oriented metallic conducting polymer is still debatable.

Voit and Buttner examined the FIT model critically and it was concluded that physical parameters obtained from this model do not allow consistent description of highly doped polyacetylene [241]. Kaiser and Graham extended the FIT model for heterogeneous systems by introducing geometric factors to the insulating barriers. Such barriers could be due to material imperfections that dominate the total resistance of the sample [242]. If the intrinsic conductivity is very large and barriers from only short segments in the conduction path, the temperature dependence of the measured conductivity reflects that of the barriers, but the magnitude is very much larger than the barrier conductivity due to geometrical factors. Furthermore, if the barriers are reasonably good heat conductors, the temperature differences across them (and therefore, their contribution to thermoelectric power) will be small [243]. In contrast to conductivity, the thermoelectric power could then follow the intrinsic metallic behavior.

In addition to the tunneling transport across the insulating barrier, a parallel phonon assisted hopping transport was included in the Kaiser and Graham model. The bulk conductivity is the combination of Kivelson and Heeger q-1D transport, hopping/ tunneling transport and 3D disordered metallic transport (figure 1.6). Kaiser reviewed this heterogeneous model for understanding the experimental data obtained on Naarman-Polyacetylene. Localisation effects can appear at low temperatures despite the high conductivity. These could be due to charging effects

in interchain transfer at low temperatures or to quantum corrections. The linear thermoelectric power behavior observed indicates a smaller interaction between electrons and phonons than in normal metals, which is consistent with the remarkably high conductivities observed [244]. Paasch was of the opinion that this model contains seven independent data and so may describe the smooth temperature dependence.
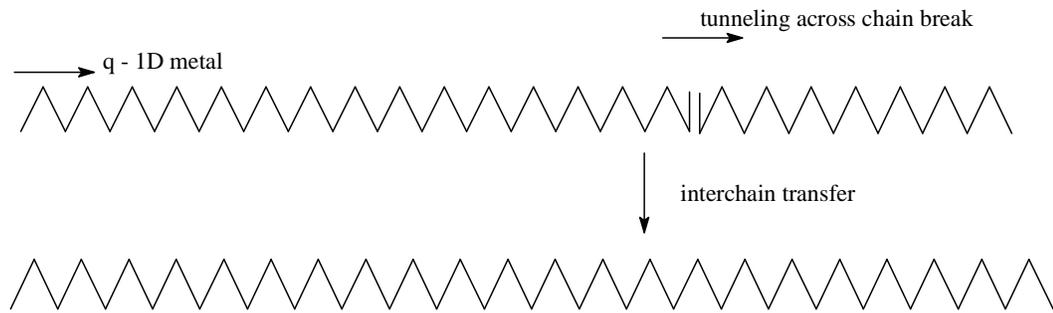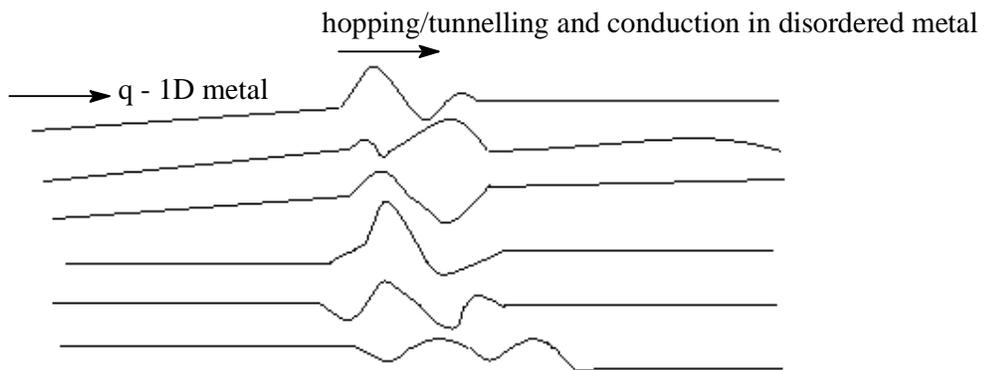

Figure 1.6 (a)

Figure 1.6 (b)

Figure 1.6 Schematic representation of the conduction process in (a) microscopic or (b) macroscopic pictures that are in agreement with transport data in Naarman-polyacetylene.

He argued that multiparameter fits of simple dependencies sometimes make the picture seem unambiguous whether the relative influences of the different contributions are reliable or not [245]. He modified the FIT model, arguing that one of the main barriers for the tunneling process is the chain segments with residual dimerisation. These segments exhibit a dimerisation gap, which acts as a tunneling barrier for the charge carriers. In general, however, the multiple parameter fitting procedure in FIT model has not been found satisfactory to explain the physical properties of conducting polymers.

The exponential dependence of conductivity in the insulating regime of conducting polymers has been usually attributed to VRH. However, a wide range of exponent (d=0.25 - 1) has been observed [212,244,247]. Moreover, $T^{-1/2}$ behavior of conductivity is often observed in granular metallic systems. Schreiber and Grussbach [248] suggested that the fluctuations in meoscopic systems could give a wide range of values of the exponent due to the fractal nature of wave functions near the mobility edge. The transition of polymer system from q-1D to 3D was studied as a function of doping level [249]. Stafsrom [250,251] reported that the enhancement of interchain interaction with increased dopant concentration could induce 3D localisation of the electronic states. He used the many –channel Buttiker – Landaur conductance formula [252] to study the conductance as a function of length of the system. Each channel contains a several polymers segments represented by chain interruptions. The chain interruptions along the channels can be caused by sp^3 defects, crosslinking between chains, etc. The hopping across such a chain interruption should, therefore, be reduced considerably compared to the interchain hopping. He showed that the most relevant parameter for causing localisation in the number of chain interruptions and not the chain length. The conductance of the system is unaffected by the presence of chain interruptions up to a critical value and, therefore, the critical

chain length for which the conductance begins to drop should be used to characterise the transition between diffusive and non-diffusive conductance. Moreover, if the interchain hopping term is equal to the interchain hopping strength (3D case) or if the number of channels is very small (1D case), the usual type of disorder-induced exponentially localized wave functions appear. Therefore, the q-1D nature of conjugated polymeric systems provides an example of a class of materials that differ from previously studied materials in the way the conductance responds to disorder in the form of chain interruptions. Recently. Schon and co-workers suggested the possibility of band-like transport in oligothiophene because of strong observed dispersion of the valence band based on band structure calculations [253].

Philip and co-workers proposed a random dimmer model (RDM) [254-256] that has a set of delocalized conducting states, even in 1D, that initially allow a localized particle to move through the lattice almost ballistically. They showed that any disordered bipolaron lattice could be mapped onto a RDM. The model is found to be applicable to the M-I transition in a wide class of conducting polymers, such as polyaniline and heavily doped polyacetylene. Calculations performed on polyaniline demonstrate explicitly that the conducting state of the RDM is coincident with a recent calculation of the location of the Fermi level in the metallic region[257,258] .A RDM analysis on poly(p-phenylene) also indicates the presence of a set of conducting states in the vicinity of the band edge. In highly disordered conducting polymers, the usual exponential dependence of temperature is explained by phonon assisted hopping or tunneling or both. Zuppiroli and co-workers have proposed a model, which describes adiabatically, the dimensionality, homogeneity, coulomb interactions and multi--phonon character in the framework of hopping conduction [259,260]. It was shown that the electron transport in these materials is due to correlated hopping between polaronic clusters. They showed, both theoretically and experimentally, that the charging energy is the principal

barrier to hopping. Polaronic clusters which originate from fluctuations in the dopant concentration function as metallic grains in the granular metal hopping model. The final temperature dependence is the same as in the case of Sheng, Abels, Efros and Shklovskii [261,262]. Nagashima and co-workers recently described ac transport studies in polymer by using a statistical model of resistor network [263]. The model takes into account the polydispersiveness of the material as well as intrachain and interchain charge transport processes. The real and imaginary part of the resistivity was determined using a transfer – matrix technique. At low frequencies, interchain processes are more important and determine the transport mechanism. On the other hand, at high frequencies charge transport should be restricted along the polymer chains, as interchain processes should be dominant. Both regimes described by the model reproduce the experimental results in a remarkable way.

Among various models proposed by several researchers for conducting polymers in the insulating side, the theoretical work by Ovchinnikov and Pronin [264] and Lewis [265] are slightly different from other models. In the former model, a q-1D percolation model was proposed for explaining the conductivity. According to this model, an impurity captures an electron from one of the adjacent chains and forms a charged impurity centre. Such a carrier can detrap by an activated process and diffuse along the chain. This polaron can recombine with another impurity center near the chain and then escape to an arbitrary chain adjacent to the second impurity centre. Thus, conduction by percolation is possible in such a system if an infinite cluster of chains can be connected by impurity centers. Lewis and co-workers suggested that the charge transport occurs by tunnel transitions between localized states and lattice fluctuations, and electron – lattice coupling tends to broaden and reorganize the energy levels at each site. They estimated the electric field, frequency and temperature dependences of charge transport in conducting and non - conducting polymers. Moreover, in this model

the localized states correspond to the Urbach states in amorphous systems since the optical absorption from a distribution of states extend out from the fundamental absorption band edge.

1.17 Scope of the Investigation

The present investigation is based on proven experimental and theoretical results about polymer synthesis and reliable experimental results on the thermal properties but contradictory and complimentary experimental results about the electrical conductivity of vinyl polymers. In short, the research work can be divided into two parts. First, it was confirmed that polymerization was taking place under the assistance of ultrasound by following the reaction dynamics of polymerization methyl acrylate(MA) in the presence of initiator and ultrasound and poly (methyl acrylate) (PMA) was synthesized. Secondly, the researcher has studied the thermal properties and electrical properties using various characterization and measurement techniques of the synthesized PMA samples.

Since polymerization of methyl acrylate (MA) was carried out using the monomer MA and initiator Peroxodisulphate (PDS) in the presence of ultrasound in a clean and controlled environment, it was essential to study if the initiator decomposed in the presence of low power ultrasound to give free radicals. It was confirmed that PDS decomposed to give free radicals in the presence of low power ultrasound. This is explained in chapter 3.

Having confirmed that PDS underwent decomposition in the presence of low power ultrasound the next step was to follow the kinetics of polymerization of MA with PDS in the presence of low power ultrasound. This was also followed and it was confirmed that MA polymerized to PMA. Though this reaction kinetics was followed experimentally for low power, high frequency ultrasound (5.5 W/cm^2,1 MHz), and reaction mechanisms were proposed, only trial experiments were conducted to confirm that high power, low frequency ultrasound (100 W/cm^2,35kHz), can also be used to polymerize MA and hence obtain PMA with

high level of purity. Hence low power as well as high power ultrasound was used to synthesize the polymers that are investigated in the present work. The sample preparation methods are explained in chapter 2.

The researcher had investigated the thermal properties by photoacoustics spectroscopy and found them in good agreement with the available literature, though the available literature for PMA was not sufficient and hence it had to be compared with some known polymers like poly (methyl methacrylate) PMMA. Moreover, photoacoustics measurements of thermal properties for polymers are not available plenty in literature. It was found out that the thermal properties were dependent upon the processing route of the polymer.

Since thermal properties have a strong influence on the electrical ones of metals, the researcher was motivated to study the electrical properties of pristine PMA synthesized by sonication process and also by giving explanations based on the experimental observations. Moreover research on electrical properties of PMA had been almost stopped in 2001. There are contradictory statements regarding conducting polymers as given below:

a. A key property of a conducting polymer is the presence of conjugated double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately of single and double bonds between carbon atoms, [266]

b. A polymer does not have to be conjugated to become electrically conducting. The correct fundamental basis for a polymer to be conducting is that it must have at least one double bond in the repeat. [267]

c. The electrical conductivity of PMA and its complexes were within the insulating range [268]

Moreover, there are very limited reports in the literature on the range of electrical conductivity of pristine polymers though there are enormous reports found for doped polymer systems. The researcher had tried to find out the electrical conductivity of pristine PMA by simple experiments and using sophisticated

instruments and found that PMA was electrically semi conducting in nature. This had been explained by variable hopping phenomenon physically using various characterization techniques. This is explained in chapters 4.

The following salient features forms the basis of the present investigation,

(i)   Sonochemical works are limited in literature.

(ii)   Ultrasonic irradiation not only alters kinetic parameters in polymer synthesis, but also affects polymer properties.

(iii)   In most of the research works found in literature Ultrasound has been used for polymer degradation than in the synthesis of new polymers from monomers   and added initiators by free radical addition polymerization.

(iv)   There are limited research works on the electrical conductivity of pristine polymers, especially in vinyl polymers synthesized by ultrasound.

(v)   Ultrasound has recently gained momentum in the synthesis of nanoparticles

The above five salient features formed the basis of the present research work.

This thesis deals about,

1. Sonochemical decomposition studies of peroxodisulphate,

2. Polymerization kinetics studies of methyl acrylate under sonication,

3. Thermal measurements on PMA synthesized by low power and high power ultrasound by photo acoustic technique,

4. The relation between Sonication period and thermal diffusivity, thermal effusivity, thermal diffusion coefficient, thermal diffusion time and thermal diffusion length for PMA synthesized by high power ultrasound.,

5. The relation between Sonication period and glass transition temperature by Differential Scanning Calorimetry (DSC), for PMA synthesized by high power ultrasound.,

6. The relation between Sonication period and glass fragility, for PMA synthesized by high power ultrasound.,

7. The relation between Sonication period and thermal degradation by TGA/DTG studies, for PMA synthesized by high power ultrasound.,

8. The relation between Sonication period and electrical conductivity for PMA synthesized by high power ultrasound.,

9. The relation between Sonication period and morphology by AFM studies, for PMA synthesized by low power and high power ultrasound.,

10. Thermal degradation studies on PMMA/montmorillonite clay nanocomposite and finally

11. Two simple instruments that were fabricated by the researcher.

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