Chapter 1

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1.1. A Short History of Polymers:

It is interested to give a very short presentation of the development of polymer materials and idea in polymer science. A detailed presentation of this field is given by Morawetz (1985) [1]. The first polymers used were all obtained from natural products. Natural rubber from Heave trees was being used by the American Indians when Columbus arrived in 1492. Cellulose in different forms, starch and collagen in leather are other examples of natural polymers used. Modification of native polymers started in the mid-nineteenth century and the first wholly synthetic polymer was made at the beginning of the twentieth century. The science of polymers began in the 1920s.

The development of polymer science and technology has occurred primarily during the last 60-70 years and the commercial introduction of new polymers has proceeded through three times stages giving rise to three generations of polymers [2].

The first generation was introduced before 1950 and included polystyrene, polyvinylchloride, low density polyethylene, poly-acrylates, polymethacrylates, glass-fiber reinforced polyesters, aliphatic polyamides, styrene-butadiene rubber and the first synthetic paints (alkyds).

The second generation of polymers was introduced during 1950-65 and included a number of engineering plastics such as high-density polyethylene, isotactic polypropylene, polycarbonates, polyurethanes, epoxy resins, polysulphones and aromatic poly-esters, also used for films and fibers. New rubber materials, acrylic fibers made of polyacrylonitrile and latex paint were also introduced.

The third generation, which has been introduced since 1965, consists mainly of special polymers with a more complex chemical structure. These polymers were characterized by very high thermal and chemical stability and high strength and stiffness. Examples are poly phenylene sulphide, polyamides, aromatic polyesters, aromatic polyamides, and flour-containing polymers. Parallel to this development of new polymers; existing polymers such as polyethylene have undergone significant improvement.
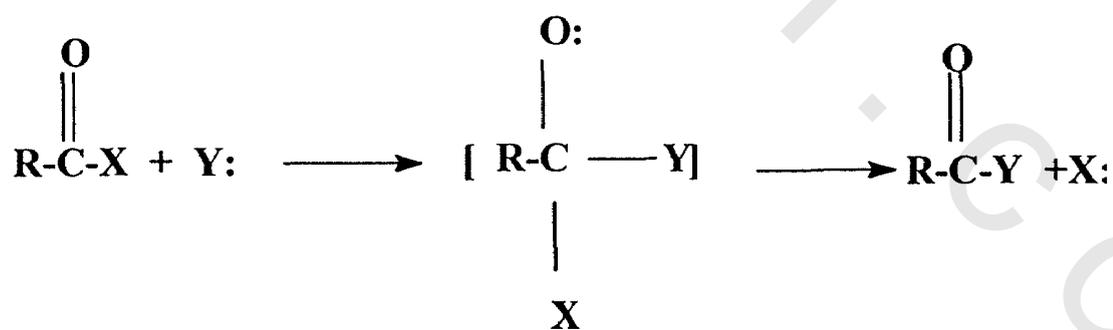
1.2. Classification of Polymers:

Polymers are macromolecules built up by the linking together of large numbers of much smaller molecules, simple chemical units are called monomers. Monemeric residues may combine with each other into a macromolecule to form polymers of linear, branched or cross linked structure.

The process of polymerization was divided by Flory & Mark [3] into two groups known as condensation polymerization and chain polymerization.

1.2.1. Condensation Polymerization or Step Reaction:

In polycondensation process, the condensation takes place between two polyfunctional molecules to produce one large polyfunctional molecule with the possible elimination of small molecules such as H_2O, HCl, and NH_3. The type of products formed in condensation reaction is determined by the functionality of the monomers, that is, by the average number of the functional groups per monomer molecule. Monofunctional monomers give only low-molecular-weight products. Bifunctional monomers give linear polymers. Polyfunctional monomers, with more than two functional groups per molecules, give branched or crosslinked polymers [3].

The most important reaction that has been used for the preparation of condensation polymers is that the addition and elimination at the carbonyl double bond of carboxylic acids and their derivatives. The general reaction is as follows:

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-X \; + \; Y: \quad \longrightarrow \quad [\; R-\overset{\overset{\displaystyle O:}{|}}{\underset{\underset{\displaystyle X}{|}}{C}} \!-\!\!-\!\!Y] \quad \longrightarrow \quad R-\overset{\overset{\displaystyle O}{\|}}{C}-Y \; +X:$$

Where X may be OH, OR', NH_2, NHR` or Cl , Y may be R'-O⁻, R'-OH, R'-$NH_2$ or R'COO⁻ and R & R` may be alkyl or aryl groups,

The size of the polymer molecule increases at a relatively slow rate and the polymerization can take place via the reaction of monomer to dimmer or dimmer to trimmer and so on.

1.2.2. Chain Polymerization or Addition Reaction:

Chain polymerization is characterized by compounds with multiple bonds (e.g. ethylene $CH_2=CH_2$, isobutylene $(CH_3)_2C=CH_2$) and vinyl chloride $CH=CH-Cl$) or unstable rings containing hetero-atoms (e.g. ethylene oxide).

The chain polymerization reaction consists of three main steps:

1- Activation or initiation of the monomer molecule.

2- Chain propagation.

3- Chain termination.

The active center in chain polymerization reaction may be a free radical or anion [4].

Radical chain polymerization is a chain reaction consisting of the main previous three steps:
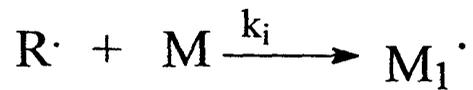
- **Initiation:**

Involves two reactions:

First: The production of free radicals, usually by hemolytic dissociation of an initiator or catalyst species I to yield a pair of radicals R`:

$$I \xrightarrow{k_d} 2 R^{\cdot}$$
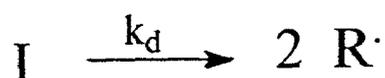
k_d: rate constant for the catalyst dissociation

Second: addition of this radical to the first monomer M chain initiating species $M_1^.$

$$R^. \; + \; M \xrightarrow{\quad k_i \quad} M_1^.$$

ki: rate constant for initiation.

There are several methods of initiation:

1) Thermal initiation.

2) Photochemical initiation.

3) Radiation initiation.

4) Chemical initiation.

5) Oxidation – Reduction polymerization

- ## **Propagation:**

It consists of the growth of M_i by successive addition of large number of monomer molecules. Each addition creates a new radical which has the same identity as the previous one, except that it is larger by one monomer unit. The successive addition may be represented by:

$$M_n^. \; + \; M \; \rightarrow \; M_{n+1}^.$$

- ## **Termination:**

Termination of the propagating polymer occurs with the annihilation of the radical center by bimolecular reaction between radicals. This can be accomplished by two ways:

i) the combination of two radicals with each other (coupling)
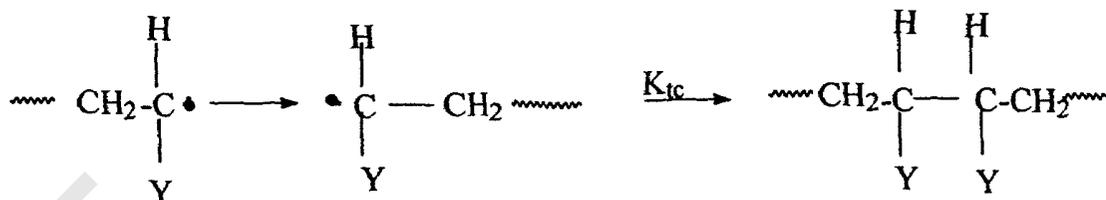
ii) Disproportionate in which a hydrogen atom of one macro radical is transferred to another to form two macromolecules one of them with a double bond at its end :
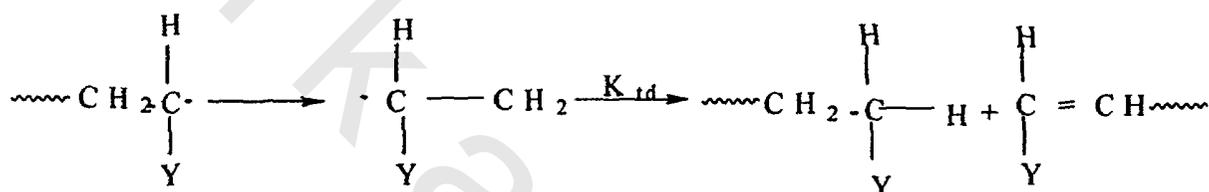
K_{tc} and K_{td} are the rate constants for termination by coupling and disproportionation, respectively.

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1.3. **Homopolymers and Copolymers:**

A homopolymer consists of only one type of constitutional repeating unit (monomer). A copolymer, on the other hand, contains repeating units from two or more monomers. Several classes of copolymers are possible, block copolymer, alternating, graft, statistical copolymers [2].

Copolymerization provides a route for making polymers with special, desired property profiles. A statistical copolymer consisting of units A and B, for instance, has in most cases properties in between those of the homopolymers (ploy A & ploy B). An important deviation from this

simple rule arises if either poly A or poly B is semicrystalline. The statistical copolymer is for most of the compositions fully amorphous. Block and graft copolymers form in most cases a two- phase morphology and different phases obey properties similar to those of the respective homopolymers.

1.4. Literature Survey:

The continuous development of the modern process industries has made it increasingly important to have information about the properties of materials, including many new chemical substances whose physical properties have never been measured experimentally. This is especially true of polymeric substances. The design of manufacturing and processing equipment requires considerable knowledge of the processed materials and related compounds. Also for the application and final use of these materials, this knowledge is essential.

Over the past three or four decades the skills of synthetic chemist have led to polymeric materials with a remarkable diversity of plastics properties, synthetic rubbers, man-made fibers and adhesives [5]. There are well –established electrical applications for synthetic polymers, but they are mostly of a passive character in the sense that the roll of polymer is to inhibit electrical conduction [6]. The concurrent development of solid state electronics has been based on a different area of material science, that of covalently-bonded crystalline semiconducting elements and in organic compounds. These materials are sufficiently simple for the understanding of their behaviors to grow rapidly once the fundamental

ideas were established but, through simple, they provide a remarkable succession of applicable electronic phenomena when appropriately doped [7]. As a consequence, prior to 1970, there had been little motivation exploratory studies of electronic properties of chemically or structurally more complicated compounds. Polymers are almost always good insulators and one can vary their properties by using suitable additives or an ingredient.

Indene is readily polymerized with an acidic [8,9] catalyst to give polymers. For example, Sigwalt [10] first reported that high molecular weight polymers can be obtained from indene in its homopolymerization with Fredil-Crafts catalysts (acidic metal halids) at low temperatures. In addition, Puskas and coworkers [11, 12] and Thomas et al. [13] recently found that indene can be polymerized in a living fashion, [14] although the molecular weight distributions (MWDs) of product polymers were rather broad. Because of its cyclic structure, phenyl rings of polyindene are arranged horizontally along the main chain; hence, the repeating unit of polyindene forms a nearly planar structure. This unique structure renders polyindene having a high glass –transition temperature and special optical properties. Thus, polyindene has elicited much interest in the recent years, although it has been a well-known material for a long time. A possible drawback of polyindene is brittleness that stems from its rigidity. Such a drawback would be eliminated with random copolymers of indene with vinyl monomers that maintain or even improve characteristic features of polyindene to lead to a new class of polymeric optical materials.

In 1990s, living cationic copolymerization of indene and p-methyl styrene (pMeSt) led to their random copolymers which enable as to control the glass-transition temperature Tg of the copolymers by regulating the monomer feed ratio in the copolymerization [15]. However, little research has revealed the reaction condition and comonomer structures that allow us to synthesize high molecular weight random copolymers [10].

Polyacrylonitrile (PAN) is a commercially important and widely used polymer [16]. PAN has a strongly polar nitrile group attached to alternating carbons on a saturated hydrocarbon backbone. In recent reports, it has been found that PAN undergoes polymerization of the nitrile groups followed by conjugation of the hydrocarbon backbone upon pyrolysis [17, 18]. PAN also has interesting electrical properties. The electrical conductivity of the double-coupled conjugated system can be increased by about 10 orders of magnitude upon doping [19].

Polyacrylic acid (PAA) [20] is insoluble in its monomer but highly soluble in water. Further more, PAA exhibits the typical behavior of polyelectrolyte because it has an ionisable group present in its repeat units. It is used as a thicknenig agent for adhesives. Since it is extremely soluble in water, its uses as a plastic is very much limited

Copolyperoxides of different compositions have been synthesized by the free-radical-initiate oxidative copolymerization of indene with vinyl monomers [21 - 24]. The composition of the copolyperoxides obtained from the ^{1}H and ^{13}C NMR spectra have been used to determine the

reactivity ratios of the monomers. The reactivity ratios indicate that indene forms an ideal copolyperoxide with styrene and alpha-methylstyrene and alternating copolyperoxieds with alpha-phenyl styrene. Thermal degradation studies via differential scanning calorimetry and electron-impact mass spectroscopy support the alternating peroxide units in the copolyperoxide chain. The activation energy for thermal degradation suggests that the degradation is dependent on the dissociation of the peroxide (-O-O-) bonds in the backbone of the copolyperoxide chain. Their flexibility has been examined in terms of the glass-transition temperature.

Thuenemann [25], has investigated the dielectric behavior of polyacrylonitrile (PAN) in its pristine and cyclized stage. The homopolymer of polyacrylonitrile displays a strong secondary relaxation at an activation energy of E_a equals 111kj/mol in the pristine stage and weak relation at E_a equal 48kj/mol in the cyclized stage. By contrast, a PAN copolymer with itaconic acid, which is used in carbon fiber production, displays a strong secondary relaxation at E_a equals 134kj/mol in the pristine stage and tow relaxations with activation energies of E_a equals 24kj/mol for the lower frequency relaxation and E_a equals 9kj/mol for the higher frequency relaxation. No relaxations were found for either polymer in the aromatized stage.

Doly et al. [26] reported dielectric measurements on the effect of varying the acrylonitrile content in styrene acrylonitrile copolymers. They also showed that the measurement of the dielectric relaxation strength provides a quantitative measure of the acrylonitrile content.

Detailed analysis of the relaxation behaviour indicates that the measurements are sensitive to changes in the sequence distribution and the microstructure of the copolymers.

Gupta et al. [27], studied the dielectric relaxation in the glass transition region of polyacrylonitrile (PAN), polymethacrylonitrile (PMAN), and their random copolymers containing 6-46wt % PMAN has been studied in the frequency range 10 super 5 HZ and temperature range 40-160 °C. Changes in the dielectric constant increment, relaxation temperature, and the loss peak amplitude with changing MAN content in the copolymers were observed. Dielectric constant increment and loss peak amplitude showed maxima around 6-12wt % MAN content are discussed in terms of the temperature increased continuously over the entire range. The results are discussed in terms of the possible structural differences arising from the effect of the introduction of MAN units on the dipolar interactions between the nitrile groups.

Mokhtar et al. [28], has investigated the donor-acceptor interaction of acrylonitrile (AN) with indene (In) by means of ultraviolet spectroscopy and dielectric polarization measurement. The latter method yielded a value of 0.5 for the association constant of the charge-transfer-complex (CTC) and a 4.02 D for its dipole moment. The copolymerization of the two monomers was characterized by a tendency towards alternation when conducted in the bulk. This might be due to the participation of a weak CTC in the process of copolymerization. However, this tendency disappeared in polar solvents such as DMF.

Wang et al. [29], has prepared poly (styrene-co-acrylic acid) metal (P (ST-CO-AA) metal) particles by chemical metal deposition. Characterization was carried out by transmission electron microscopy and X-ray diffraction. Dielectric behavior and determination of magnetic properties of P (ST-CO-AA) metal microspheres were investigated. Thermogravimetric analysis showed that the Curie temperature (T_C) of P (ST-CO-AA) metal was lower than the T_C of the corresponding block metal and fine metal particles. The susceptibility and hysteresis loop of (ST-CO-AA) metal were studied. The results showed that the composite particles are soft magnetic materials.

Summan et al. [30], has measured the electrical conductivity of polyacrylonitrile homopolymer and polymer complexes of acrylonitrile (PAN) with $CuCl_2$, $CuBr_2$, and CuI_2 at different temperatures. They found that the electrical conductivity increased with temperature. Cyclic voltammetry was used for measuring the shift of the reduction peaks upon heat treatment of the polymer complexes.

Moharram et al. [31], investigated the conduction mechanism in the interpolymer complex resulting from the interaction between polyacrylic acid (PAA) and polyacrylamide (PAAm). The characteristic features of the relation between the logarithm of conductivity, log sigma, and 1/T are different from those corresponding to the individual components of the complex. The value of sigma for the complex was found to be less than its corresponding values for PAA or PAAm. The effects of the weight fraction of each polymer and the ionic strength of the solutions on the conductivity of the complex were also studied. The

data showed that the sigma for the complex depends on the weight fraction of the polymers.

Givehchi et al. [32], initiated the cationic polymerization of indene with cumyl chloride and stannic chloride solution in methylene chloride at -15 ° C and the reaction is controlled up to M_n equals 20000, with a low transfer to monomer constant (k_{tr} M/K_p equals $9*10^{-4}$). Experiments carried out in compensated media allowed kinetic measurements and showed that the sharp decrease of the M_n at high indene concentrations results from zero order transfer due to the change of dielectric constant ($k_{r/kp}$ equals 1.5 multiplied by 10^3 for a dielectric constant of 5.4) in methylene chloride, for indene concentrations higher than 2 mol/L, the heat release of the fast reaction adds up to zero order transfer to lower the molar masses. Bimodal distributions results from propagation on free ions and ion pairs.

Yang et al. [33] have made grafting of the hydrophilic monomer, acrylic acid (AA), onto hydrophobic silicon rubber (SR) film via the gamma-ray preirradiation graft technique. The AA percent graft in SR-g-AA film increases with increasing irradiation dose rate. The iron powder in monomer solution serves as one source of ferrous ion that is generated by the oxidation reaction with water. The swelling of the amount of chloroform taken up by an SR-g-AA membrane decreases with increasing AA grafting, and the amount of water, alcohol, and glycerol taken up by an SR-g-AA film increases with increasing AA percent grafting. The contact angle, ultimate stress, and elongation at break of SR and SR-g-AA copolymers decreases with increasing AA percent grafting.

The oxygen / nitrogen selectivity in these films can be enhanced by the graft modification. The thermal behavior of SR-g-AA copolymers shows the characteristics of SR and PAA. Finally, the dielectric properties show that the SR-g-AA film has a superior dielectric property than the original SR and PAA matrix.

Choi-Woon-Seop et al. [34] to clarify the mechanism of spontaneous copolymerization of styrene with acrylonitrile, the corresponding reaction of its analog, indene, was investigated. The spontaneous free radical copolymerization of indene with acrylonitrile was promoted by Lewis acids. Spontaneous copolymerization rates comparable to those of styrene acrylonitrile were found.

Kavlak-Serap et al. [35] were synthesized poly(maleic anhydride-alt-acrylic acid) was characterized using Fourier transform infrared (FTIR), titration, viscometry, differential scanning calorimetry (DSC), and Thermogravimetric analysis (TGA). The temperature dependence of the conductivity of the copolymers and polychelates of transition metals was investigated between 300 and 453 K. The polychelates and copolymers were analyzed by using FTIR spectroscopy before and after transition point. The observed conductivity followed by a semiconducting behavior with increasing temperature is discussed in relation to the presence of transition metal ions.

Kaji-Hironori et al. (36) have investigated the dynamics of atactic polyacrylonitrile (a PAN) by variable-temperature super 1 super 5N chemical shift anisotropy (CSA), two-dimensional (2D) super 1 super

5N CSA exchange, and 2D super 1 super 5N pure-exchange NMR experiments on an a PAN sample with 100% super 1 super 5N-labeled nitrile side groups and dielectric measurements. In contrast to the dynamics below 110 °C, where only small angle motions are observed with an activation energy Ea = 68 KJ/ mol, it is found that large-amplitude motions with Ea = 180 KJ/mol set in above 110 °C. From the detailed analysis of NMR spectra, it is found that a PAN undergoes restricted uniaxial rotational motion around the chain axis above 110 °C. The 2D spectra prove that there is a distribution of amplitudes of these restricted motions. The standard deviation of the amplitude distribution increases from 30 ° to 100 ° in temperature range 120-140 ° C. At the highest temperature, there is a strong evidence of dynamic averaging within the distribution of angles between C equivalent N bond and the fiber axis. The solid state NMR results are in excellent agreement with those in dielectric relaxation experiments where a relaxation peak of growing amplitude and frequency position is observed.

1.5. The physical States of Polymers:

All polymers may be classified according to their mechanical properties at room temperature into three major groups, glassy state, rubbery state and viscofluid state [37].

1.5.1. The Glassy State:

Glassy state is characterized by random arrangement of fixed molecules without any degree of flexibility. The polymers in this case are brittle and hard like glass. From the physical kinetics, the glassy state may be treated as a state in which the segmental mobility is frozen. If the polymer in the rubbery state is gradually cooled, its viscosity increases and the intensity of the molecular motion caused by the diffusion of the segments are decreased. If the temperature of the polymer in the rubbery state is lowered, the equilibrium state corresponding to a new temperature will be attained only after a certain period. This time period is required for kinetic units of the polymer chain to be rearranged so that they occupy new positions corresponding to an equilibrium state at a new temperature .Thus the transition from the rubbery state to the glassy state may be regarded as a series of relaxational processes [38].

The glassy state is a metastable state in which the polymer may exist for an infinitely long time and it may be treated as a solid state devoides of any crystalline structure. It is sometimes regarded to as a state of typical strongly thickened overcooled liquids.

1.5.2. The Rubbery State (High Elastic State):

The rubbery state is a unique to polymeric materials. Other material classes such as silicate or organic liquids are capable of forming glasses and many classes such as ceramic or metals form polycrystalline

aggregates. This uniqueness is associated with the extended one dimensional chain structure possessed by polymers in contrast to the two dimensional (graphite) or three dimensional (diamond, metals) structures characteristic of other materials[39].

When the glassy polymers heated above a certain temperature, they gradually become soft, elastic and behave like rubbers. The characteristic properties of high elastic state are due to the wide effect of the temperature range, so the thermal motion is sufficient to overcome the mutual attraction of the segments of the macromolecules [40] ,but still insufficient for the macromolecules to be able to move with respect to each other. Under such conditions the flexibility of the polymer chain due to internal rotation of separate parts of the macromolecule with respect to other parts becomes of special significance. The rotation is caused by thermal motion of the molecules and grows stronger with a rise in temperature. It is not quite free even when the substance is in the gaseous state, while in the solid state with a very close distance between the adjacent macromolecules, the hindrance to rotation becomes very high & rotation may then degenerate into twisting oscillations i.e. pendular rotation about some mean position. It's the flexibility of polymer [39] chain that's mainly responsible for the properties specific to high elastic state.

In other words, the requirements for any material to exhibit rubbery properties are [39]:

- Long chain structure with little or no hindrance to rotation between chain segments.

- Low intermolecular interactions.

- The formation of an extended network structure by a few cross linking points between chains.

1.5.3. The Viscofluid State:

It is characterized by the possibility of the intensive thermal motion of the individual units, large fragment of the polymeric chain (segments) and the movement of the macromolecule as a whole .This state is typical of most liquids .The most important specific feature of the polymers existing in this state is the ability to flow under the influence of the applied stress (fluidity). The fluidity is characterized by viscosity and it's relaxational by its nature [38].

1.6. The Glass Transition and Flow Temperatures:

The physical properties of polymers in the glassy state differ very significantly from those in the rubbery state. The conditional borderline between these states is the glass transition temperature. The glass transition temperature is the most important characteristic of amorphous

polymers. Various attempts have been made to define the concept of the glass transition temperature.

The glass transition and flow temperatures are not similar to the transition of a substance from one aggregate state to another. They are not constant even for a given polymer specimen.

The glass transition temperature is the temperature at which the thermal motion of the chain segments becomes sufficient to lend the chain certain flexibility i.e. it overcomes the retarding effect of the interaction with adjacent segments of other chains.

Glassy state	*Rubbery stat*	*Viscofluid state*
Hard & brittle	*Soft flexible state*	*Highly viscous liquid*
(Brittle plastics)	(Tough plastic & rubber)	(Polymer melts)

T_g	T_f
(Glass Transition Temperature)	**(Flow Temperature)**

***The flow temperature i*s** corresponding to the transition from the high elastic state to the viscofluid state; the thermal motion of the particles (always increasing with rise in temperature) reaches a value sufficient to break the comparatively weak bonds between the chains. As a result of a further rise in temperature, the polymer chains gradually acquire the ability of diffusional motion with respect to each other; the polymer softens passing to the viscofluid state [38].

The intrinsic difference between the glass transition & flow temperatures is that the former depends primarily on the strength of the interaction between the segments of the adjacent chains and, for a high degree of polymerization, is often practically independent of the chain length (i.e. of the degree of polymerization), while the flow temperature is determined by the overall interaction of the chains & increases more or less with an increasing degree of polymerization.

1.7. The Aim of the Present Work:

In the past few years, an extensive work was carried out on polymeric materials that are depending on the chemical composition and the structure features. On the other hand, the electrical properties of polymeric materials are strongly affected by heating the polymers to appropriate temperature above its glass temperature. The aim of the present work is the preparation and the investigation of the structural characteristics of the homopolymers polyindene PIn, polyacrylonitrile PAN and polyacrylic acid PAA, and the copolymers of indene with them.

The idea of the present work is to draw a full picture (as far as possible) of the transport mechanisms of these polymers and throw more light about the processes which may occur around the glass transition of the materials. Our study will extend including the effect of temperature, frequency and concentration on the electrical conductivity and dielectric constant of the homopolymers and the copolymers. Our work is extended to further investigations on IR, X-ray, TGA, DTA, and DSC of these polymers. Our studies are raised not only from the desire for a better

understanding of the electrical properties of our materials; but also because of the need for new and low cost materials in many applications, e.g. good insulating materials that work under conditions of high frequencies.