CHAPTER I - INTRODUCTION.
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1. Place of Dielectrics in Solid state Physics. Solid state Physics has a very wide field and it is now-a-days subdivided into branches. It is mainly concerned with the physical properties of Solids, particularly the special properties exhibited by their constituents, the atoms and molecules, which exist now in a different phase, the solid phase. The division of solids into metals and metalloids is chiefly motivated by chemical behaviour but may also be deduced from the nature of solid elements. Metals are characterised by their high electrical conductivity, while solid metalloids are usually insulators.

The place occupied by the dielectrics in solid state Physics can hardly be exaggerated. The term dielectric as used here means ' unlike metal ' rather than in the narrow sense, the so called insulator. On the basis of the modern theory of solids, the difference between semi-conductor and insulator is quantitative, rather than qualitative (1). Thus the dielectrics provide, a vast field to physicist to probe into the mystery of matter experimentally as well as theoretically.

The advancement of the theoretical methods in the present Century, has yielded a great amount of literature
which prompted the experimental workers to explore new fields, with the view to verify the existing theories, which in turn brought to light some interesting data regarding the properties of matter. The use to which solid devices have been put in the last two World Wars, gave further impetus to physicists, engineers and chemists to go ahead in this branch of the subject. In the field of electronics new applications of dielectrics continue to rise in computer storage and switching elements, dielectric amplifiers, miniature capacitors for transistor circuits, piezoelectric devices, randomers, microwave components and dielectric aerials and wave guides, to select only a few of the current uses of dielectrics.

Recently there has been considerable increase in interest in the study of the phenomenon of constant internal polarisation of dielectrics and photo semi-conductors (2, 3). As is known, bodies which retain constant volume polarisation over long periods are called electrets (4). Investigation of the electret state enables to provide a new way to the study of the mechanism of polarisation and absorption of charges in amorphous and crystalline dielectrics.

The first electret was prepared by Eguchi (5) in 1920. He melted together equal quantities of Carnauba wax and resin and allowed the liquid mixture to solidify in a D.C. electric field of 10 kV/cm. The solid thus prepared gives rise
to a measurable and sensibly permanent electric field. Following Eguchi's experiment numerous researches have been carried out with the object of finding out substances which can form electrets. The majority of the workers have used more or less well defined mixtures of resins, waxes and chemical compounds. It was however, observed later on that other dielectrics, particularly polar dielectrics, can be used to prepare electrets (6). Gubkin and Skanavi (7) prepared electrets from titanates. Wieder and Kaufmann (8) prepared electrets from plastics and found that plastic electrets were of fairly good characteristics and could be applied in many electronic devices (9).

In the preceding paragraphs it has been seen that dielectrics capable of acquiring a permanent polarisation by the application of an electric field, are known as electrets. In certain crystals an analogous polarisation can be created by photo-conductivity. This phenomenon of polarisation gives rise to photoelectrets (10). It has been studied by a number of workers (11, 12) who have shown that the photo-polarisation is connected with the appearance of a definite charge by the localisation of the electrons. In 1937 Nadjakov (13, 14) discovered the permanent photo-polarisation in poly-crystalline sulphur. He used a sulphur disc which was placed for three minutes in darkness in an electric field of 470 V/cm., and then
illuminated for twelve minutes with 6000 lux., the field being removed after switching off the light source. The electret thus formed when placed in darkness retains its charge for 15 hours. The formation of these electrets is connected with photo-conductivity of the semi-conductors and with reinforcement of the charges displaced to localised levels. The study of the photoelectrets effect have been pursued chiefly in the case of poly-crystalline and mono-crystalline sulphur. Fridkine, Fargyman and Nemirovskii (15, 16) have successfully obtained electrophotographs with the help of the photoelectrets.

Thus the two aspects of dielectrics i.e. electrets and photoelectrets offer a vast field of investigation in solid state physics. This branch of dielectric has attracted a wider attention of workers engaged in unfolding the mystery of these so called 'anomalous' properties of solid dielectrics. A vast amount of solid materials remained untouched except for a few scattered investigations as reported in scientific literature. High polymers, which have got a definite advantage of getting turned in any shape and size and also of rough handling, will prove to be most successful solid devices, so far as their applications in the form of thermoelectret and photoelectret are concerned. If the study
in these materials is to be made, it is desirable to understand their properties under different conditions in the first instance. From the literature it is evidently clear that no satisfactory theory has yet been evolved to explain all the observed and well established facts concerning electrets. Discussion of their properties in the light of the observed effects may help to build a logical sequence to explain this complicated aspect of dielectrics.

2. Plastics as solid dielectrics. The dielectric behaviour of high polymers has been effectively treated by Fuoss and his collaborators (17 - 26) and many measurements have been published. The dielectric behaviour of plastics is similar to that of viscous liquids and organic glasses. The most remarkable feature of high polymers, and the one which differentiates them from other types of dielectrics is their mechanical properties - their tensile strength, elasticity, and hardness. These properties are intimately connected with the structure and configuration of the polymer molecule, and the ultimate aim of investigations in this field, is the direct correlation of structure with the properties of solid.

High polymers cover all types of dielectrics in which they can be classified. The division of polarisation
into three types leads at once to the following division of
dielectric materials into three classes (27).

(i) Non-polar substances showing optical polarisation only.

(ii) Polar substances having optical as well as infra red
polarisation.

(iii) Dipolar substances which, in addition, show also polarisation
due to dipolar orientation.

In the first class of materials, the
non-polar ones, an electric field produces elastic displacement
of electrons only. This class contains all dielectrics
consisting of a single type of atoms, whether they form gases,
liquids or solids. Examples are polystyrene, polyethylene,
polytetrafluoroethylene. The dielectrics of second class,
the polar materials, are capable of infra red polarisation as
well as optical polarisation. Substances of this type may
contain dipolar groups of atoms, but these groups must show only
elastic displacement. Examples are the phenolic plastics,
plasticised cellulose acetate, nylon and monochlorotrifluoroethylene.
If on the other hand, there are several equilibrium positions
for the dipole, then the substance belongs to the third class
of materials.

Electronic and atomic polarisation always
contribute to the dielectric constant of high polymers. Dipole
groups can be produced in polymers by mechanical operation. The laboratory for Insulation Research of M. I. T. (28) and others (29) have measured dielectric constant of polyethylene after various amounts of milling. The milling produces dipole groups probably through oxidation, which cause loss peaks near $10^9$ cycles.

Most high polymeric materials in actual use are mixtures, which frequently consist of more than one phase. The coexistence of two phases may give rise to interfacial polarisation with large effects upon dielectric constant loss.

3. **Definition and subdivision of plastics.** : Ellis (30) has defined the term 'plastic' as being any thing which possess plasticity i.e. anything which can be deformed under mechanical strain, without losing its cohesion and is able to keep the new form given to it. According to Yarsley and Couzens (31) a 'plastic' material is just one which at some stage in its history was capable of flow, and which on the application of necessary heat and pressure, can be caused to flow and take up a desired shape.

The term plastics is reserved primarily for organic combinations, usually resinous or resin like condensation, polymerisation or esterification products.

High polymers can be classified under two
headings - viz. the thermosoftening and thermohardening plastics (32). Thermosoftening materials are those which can be softened and resoftened indefinitely by the application of heat and pressure always providing of course, that the heat so applied is insufficient to cause chemical decomposition. The thermohardening or as they are generally called thermosetting plastics, by contrast, undergo a chemical change when they are subjected to the action of the required heat and pressure, after which their shape cannot be changed by the application of more intense heat or high pressure (33, 34).

(a) Thermosoftening plastics. Fig. A shows a representative thermosoftening plastic in which the large constituents molecules are strung together very much like daisies on a chain.

- M - M - M - M - M - M - M -
- M - M - M - M - M - M -
- M - M - M - M - M - M -

Fig. A

M represents a molecule or so called monomer, a chemical substance capable in suitable circumstances, of joining up with itself to form chains of very great length. When the plastic is heated these chains move apart and under pressure slide past one another to take up, new positions, a process which permits
the easy manipulation characteristics of these plastics. These plastics reach the manipulator in the form of sheets, rods, tubes, strips, and films which can be regarded as thin sheets and moulding powders. All these materials can be regarded very much as if they were ductile metals capable, however, of being deformed or shaped at temperatures seldom exceeding that of boiling water and requiring small forces to affect the desired change in shape. All the machining processes such as drilling, turning etc., can be carried out with thermoplastics. They can be cemented together and are easily polished by the use of softer types of abrasive.

(b) Thermohardening plastics. Fig. 3 shows diagrammatically the end product of a thermohardening polymerisation. Here the end product cannot only join up end to end, but have a spare chemical attraction, which permits chemical links to be formed between the chains.

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- M - M - M - M - M - M - M -
  | | | | | | | | |
- M - M - M - M - M - M - M -
  | | | | | | | | |
- M - M - M - M - M - M - M -
```

Fig. 3.
These chemical links are very strong and maintain the chains at definite distances from one another. Their strength prevents sliding, and as a result they are rigid at all temperatures short of decomposition, so that there is not relative movement of the chains, and consequently no change in overall shape. Moreover in consequence of their close packing, it is virtually impossible for solvent to enter between the chains and cause dispersion, and as a result they are insoluble, though some solvents may cause them in certain circumstances to swell. There are three forms in which these resins are recognised as plastics: moulding powders, casting resins and laminates. Laminates provide an enormous outlet for these types of plastics. They consist of layers of paper or cloth or other suitable fibrous material impregnated with resin and then pressed under heat to give rigid sheets or other structures which can be machined like hard wood.

4. Physical basis of plastics. Plastics are composed of giant molecules based on carbon. Molecular structure is based on a very long chain of carbon atoms each linked to each, the sides of the chain being composed of hydrogen, chlorine or of simple groups of carbon and other atoms. In certain cases the main carbon chain may contain oxygen, nitrogen, sulphur or silicon but most industrial plastics have a purely carbon back bone.
The application of X-ray analysis to cellulose - the raw material used in the production of celluloil and cellulose shows that it is built of bundles of long chain compound of at least a hundred glucose units, joined together end to end, each bundle or 'micelle' as it is called containing, less than hundred chains and each repeating unit, composed of two glucose units being one millionth of a millimeter long (35). The observations about chain length confirm the results of chemical analysis and of the other physical methods, which have been applied to the same problem.

Where the chain structure is extremely symmetrical, or the attraction between units in one chain and those in a similar chain along side it are very strong, the resins are capable of existing in two forms: the amorphous form, in which the arrangement is completely haphazard and a crystalline form, in which there are patches of regular chain arrangement (36). The first form, which can be converted into the second by suitable physical treatment gives no X-ray pattern, but the second will give a diagram from which the dimensions of the units can be accurately calculated (37). Polyethylene which is a typically symmetrical chain is an outstanding example of this type of resin (38).
5. Chemistry of plastics. Plastics are made by combining large molecules into few big ones. The unit in the chain is known as the monomer and is repeated throughout the structure. The chain formation gives rise to a polymer and the process is called polymerization. The polymerization of ethylene gas, depending on the specific behaviour of the double bond, represents the simplest formation of a plastic material. Many variations can be built on this simple theme by substituting other atoms or groups of atoms for certain hydrogens in the ethylene molecule.

The simplest case is the substitution of one chlorine for a single hydrogen in the ethylene molecule, which results in polyvinyl chloride or p.v.c. polymer. Instead of chlorine, one may substitute groups. Such groups are assemblies of carbon atoms, usually with hydrogen, or possibly chlorine or oxygen, so arranged that they have one spare arm with which to link on to a carbon atom and to replace hydrogen.

Vinyl plastics contain a group of CH₃-CH capable of taking up some 'side' group of element and then forming the long chain of carbon atoms indicated. Two extremely important examples are polystyrene and methyl-methacrylate. In polystyrene the group is called 'phenyl' (a type of group often called a radical) with the formula - C₆H₅. In the case
of polymethyl-methacrylate two hydrogen atoms are replaced, one by a methyl group \( \text{CH}_3 \) and the other by carbon methoxy \( \text{C} - \text{OCH}_3 \).

This prowess of substitution and polymerization can be carried out employing a great variety of substituents and can be still further extended by combining a number of different monomer units and forming these long chains. The wide variety of products which are obtained in this way are described by chemists as copolymers.

Some other types of linear polymers are polyesters and polyamides. Polyesters are made by combining various dibasic acids with various glycols. When the acid is terephthalic acid i.e. benzene with two carboxyl groups at opposite ends and the alcohol is ethylene glycol, the product is Decron polyester fibre.

The polyamides include the whole family of nylon. When 6-carbon diamine is combined with 6-carbon dibasic acid the result is 66 nylon. The natural rubber differs from all the previous compounds in that it is unsaturated. This double bond allows reaction with sulphur and accelerates to form cross links and three dimensional structures. If the \( \text{CH}_3 \) group is replaced by Cl, the product is neoprene, the first
commercial synthetic rubber produced.

6. Physical properties of plastics.

(a) X-ray analysis of polymers. (39): The application of X-rays to the study of solid falls broadly into two categories: firstly, the study of the shape, properties, and arrangement of the atoms or molecules within a crystal and secondly, the form arrangement and properties of the crystalline aggregates in a poly-crystalline material. The ultimate object of the first type of investigation is the assignment of the exact position of the atoms in the crystal lattice, and even with simple substances which give high quality single crystal, the analysis is often extremely difficult. In the case of high polymeric molecules which can not be produced as single crystals, the investigation is limited to the poly crystalline mesomorphic, or amorphous forms, and as a consequence the results are less definite and more difficult to interpret than those for single substances (40). In a very few cases only it has been possible to specify completely the detailed molecular configuration and arrangement of the atoms in high polymer. The X-ray measurements, together with chemical and other evidences for those high polymers which exist in the crystalline form have furnished useful data, which have formed a basis for the correlation of the molecular structure of the
molecules with their physical and mechanical properties.

In addition to the fundamental study of molecular structure, there are other important applications of the X-ray method which belong to the second category; for instance the study of the ratio of crystalline and amorphous materials present and the effect of variable, such as deformation thereon, or the size and orientation of the crystals in the polymer (41).

Many naturally occurring polymers such as cellulose, or certain of the proteins, exist in the form of fibres in which small crystalline regions are arranged with one axis parallel, or at fixed angle, to the axis of the fibre. Synthetic fibres polymers such as the polyesters, polyamides and polyethylene may be drawn out or stretched to form similarly oriented fibres (42). The X-ray diagram of these fibrous materials obtained by irradiating at right angles to the fibre axis, is similar to the rotation photograph of a single crystal, since all orientations at right angles to the fibre axis are present, but instead of complete rings, the pattern appear as an array of spots. The spots are broad because the crystalline arrangement is not perfect and they are elongated into arcs because of imperfect orientation. The spots fall on ' layer ' lines which are parallel to the fibre axis. From the layer line separation, the fibre period i.e. the identity period corresponding
to the repetition of the basic pattern of the atoms along the fibre axis can be determined. It is from this type of photograph that much of our information on the inner structure of polymeric substance is obtained.

(b) Crystallinity and crystal structure: X-ray studies of high polymers. have shown that although many of linear high polymers exist in a highly crystalline state, the materials are not completely crystalline, but contain a portion of molecules which are disoriented. Other polymers, such as polystyrene, polymethacrylate or rubber, in their normal states are shown by X-ray methods to be highly of amorphous structures. Evidences have accumulated showing that many of these supposedly amorphous polymers may be transformed under suitable treatment into a state in which they display the properties associated with crystalline materials such as melting or optical double refraction (43). For instance high molecular weight polyisobutene or rubber on stretching, forms a highly oriented state and shows X-ray diffraction patterns and other properties common to truly crystalline materials. This change of phase from the crystalline to the amorphous and vice versa is of extreme importance with regard to physical and mechanical properties of high polymers (44).

Chain polymers, in general, have a two phase
structure of rather complex character. Certain regions of a specimen exhibit a high degree of internal geometrical order, and are usually referred to as crystallites. These regions are unlike true crystals, in that they do not have any well defined geometric shape or boundaries characterized by sharp edges of crystals. Actually, we can picture them as zones in which the polymeric molecules are arranged in an orderly three dimensional arrangement of ill defined shape and size. In the amorphous or disordered regions the molecules are packed in a less orderly manner. The amorphous and crystalline regions are not mechanically separable phases, but the same molecule may at the same time have part of its length in a crystalline and the remainder in an amorphous, region. In fact the same chain may pass through more than one region in which the molecules are highly oriented to regions in which disorder is predominant. It has thus become common to define a crystalline/amorphous ratio in referring to the state of aggregation of high polymers. It must, however, be clearly pointed out that such a differentiation is not sharp, but the crystalline and amorphous regions of all sizes are present and that we have to regard the system as a whole as existing in states of various degrees of order and disorder.

(c) Crystalline/amorphous ratio. Polyethylene, in common with some of
the vinyl polymers, polyesters and polyamides, is partly crystalline at room temperature (45). Increase in temperature causes the growth of amorphous regions at the expense of the crystalline region, until a temperature is reached at which the material is completely amorphous and indistinguishable from a viscous liquid. This change of phase is accompanied by a change in a number of properties. These properties may be used to study melting and crystallization and they enable the calculation of the relative proportions of crystalline and amorphous phases to be made at any temperature. The results obtained with polyethylene (46) by measuring specific heat and specific volume indicate that the crystalline/amorphous ratio seems to be frozen in below 60°C. The crystallinity disappears at 115°C. The material is 75% crystalline at room temperature.

If polyethylene is cooled rapidly from the molten state to room temperature, the solid contains a high proportion of amorphous phase. The product is, however, still partly crystalline. In fact, neither shock cooling nor any other method has yet been found to give an entirely amorphous product (47). Polyethylene obviously crystallizes very easily, and this is understandable in view of the small size of the repeating unit, which makes it most favourable for orientation.
Many polymers on quenching from the melt produce a completely amorphous form, which is stable at room temperature. Others, such as the polyesters, which may be readily produced in the supercooled state in which they are poorly crystalline, anneal and reorientate to crystalline forms at room temperature within a few weeks (48). In contrast, the polyamides on rapid cooling from the melt give a whole range of partially ordered states depending on the degree of quenching. Unlike polyethylene or the polyesters, the stronger intermolecular forces stabilise the disordered states over long periods of time. The change in orientation in these structures can be observed in the appearance of the X-ray diffraction patterns as a sharpening of rings or side spacings. This change of orientation with temperature of quenching manifests itself in a remarkable variation of the properties of the solids. The least ordered polyamides are transparent, pliable and plastic whilst the highly oriented crystalline structures are opaque, hard and waxy.

The physical properties of the material greatly depend on the degree of order. The crystalline regions may be regarded as tying together the constituents molecules. The degree of crystallinity decreases with increase in temperature and the properties change accordingly, and in a fairly well defined temperature range the disorder becomes so
great that the material takes on rubber like characteristics. In a few cases, such as cellulose in which the material exists in highly crystalline state and the intermolecular forces are very strong, chemical decomposition occurs before the rubbery state is reached.

(d) Mechanism of crystallisation. The process of the gradual transition from the amorphous to the partly crystalline state can be understood if we follow the change from the molten state to the supercooled state. The liquid consists of long chain molecules randomly distributed and of irregular and rapidly changing configurations, resulting from the free rotation around single bonds. In spite of this apparent randomness experimental observations show that sections of the chains associate in parallel layers. Electron diffraction measurements on polyethylene (49) show clearly the existence of some degree of orientation even in the liquid. This is confirmed by the observations of Ubbehohde (50) who found that the hydrocarbon, octadecane, melted over a range of 10°C on either side of the temperature normally regarded as the melting point. He regarded the abnormally high specific heat in the region of the melting point as the extra heat necessary to disorder the hydrocarbon clusters, which remained associated in the liquid. These zones of partial alignment of the molecules may be regarded as the
nuclei from which crystallization begins and on cooling, the intermolecular attraction between the chain segments over comes the thermal motion of the chains, and crystallization over small lengths occurs. As cooling proceeds more chains and greater lengths align and the amorphous content decreases. At a sufficiently low temperature, readjustment and mobility of the chain segments becomes increasingly difficult and a state is reached in which the structure is apparently stable but not in true thermodynamic equilibrium. Sudden quenching from the melt will produce a state in which the chains are largely in a completely disoriented state. Attraction between individual pairs or small groups of polar groups will be predominant and if this attraction is great enough, the chains will remain irregularly oriented. The amorphous state will be stable over indefinite periods.

(e) Melting of crystalline polymers. Crystalline high polymers, unlike lower molecular weight substances do not melt at a definite temperature but melting occurs over a range of temperature. This is undoubtedly due to imperfection of the crystallinity. No crystalline polymer is wholly crystalline and, as we have already seen that a part of the material is always present in the amorphous state. The melting behaviour of the simplest structure i.e. of polyethylene, differs from that of the normal
saturated hydrocarbons in two ways.

(1) The change from the ordered state to the disordered amorphous state occurs over a wide range of temperature, as shown by density, specific heat and by optical and X-ray measurements (51).

(ii) The melting point for a chain of 1000 CH₂ units is about 20°C lower than that predicted from the well established relationship for the melting point T_F of the lower chain paraffins with increase in molecular weight. Garner, Van Bibber, and King (52) have shown that T_F is given by,

\[
T_F = \frac{0.6085 n - 1.75}{0.001491 n - 0.00404}
\]

where n is the number of methylene units.

Meyer and Van Der Wijk (53) represents the data by the formula,

\[
\frac{1}{T_F} = 2.395 \times 10^{-8} + \frac{1.71 \times 10^8}{n}
\]

According to these formulae, the melting point of polyethylene, when n = 1000 should be 134°C and 141°C respectively, as compared with the experimental value of 115°C. In order to understand the melting of high polymers, it is necessary to explain these two general facts. It is now believed that the explanation lies in the fact that the chains
do not fit perfectly into the crystal lattice, but pass through or project into amorphous regions. Alfrey and Mark (54) have discussed the behaviour of such chains. As successive segments of a randomly kinked molecule become attached to the crystallites, both the distance $l$ between the ends of the amorphous segment and the number of links $n_1$ in an amorphous region decrease, but $l$ decreases more rapidly than $n_1$. The randomness is related to the entropy and thus the entropy of fusion does not decrease linearly with $n_1$. The heat of fusion $H$ is a linear function of $n_1$ and thermodynamically the melting point $T_m$ is given by,

$$T_m = \frac{H}{s}$$

The entropy change on crystallization is different for different portions of the chain entering the crystallites. This variation in entropy change would then produce a corresponding variation in the melting temperature and hence a melting range. This conception also explains the well known observation that when rubber is crystallised for a long time the tension in the amorphous portion relaxes owing to the slow thermal molecular rearrangement. The amount of amorphous component is reduced and thus the melting point rises with long periods of crystallization. Furthermore, since the entropy change in the formation of large crystallites is different
from that for small ones, the variable range of crystallite size would be expected to give variable melting point ranges.

The foregoing qualitative ideas have been recently expressed quantitatively by Firth and Tuckett (55) using as an idealised model an assembly of long chains in which the amorphous fraction \( \theta \) separates the crystalline regions \( (1 - \theta) \), they show that the free energy \( G \) of the system is a nonlinear function of the proportion of the amorphous material - i.e. the melting point of the crystalline polymer depends on the proportion \( \theta \) of the amorphous material in the structure. By considering the equilibrium state between the crystalline and amorphous phases at any temperature i.e. \( \frac{dG}{d\theta} = 0 \), it is shown that,

\[
\frac{n_1 l_F}{RT_m} = n_1 \frac{Z - 1}{\theta} + \frac{1}{\theta}
\]

where

- \( n_1 \) = number of links between crystal nuclei.
- \( l_F \) = latent heat of fusion per single link.
- \( Z \) = coordination of the lattice.
- \( T_m \) = melting point.

The expression contains two molecular parameters
Z and $n_1$, and one experimental quantity $l_F$. The value of $n_1$ cannot be deduced from chain length measurements and must be partly guessed. The formula is very sensitive to $Z$, and values of the melting points of crystalline rubber and polyethylene in close agreement with experimental values are obtained for $Z$ values of 5.4 and 7 respectively. Using this value of $Z$, the calculated crystalline/amorphous ratio is in surprisingly good agreement with experimental data of Richards (56).

Frith and Tuckett (55) considered only the case of very long unbranched chains. A normal polymer consists of a wide range of molecular sizes and Richards (57) has recently extended the theory to linear paraffins containing a proportion of short chains which are assumed to be concentrated in the amorphous phase. The theoretical expressions are in good agreement with the observed data on the depression of the melting point of polyethylene by added hydrocarbons.

These theories show that a melting range is a consequence of the coexistence of the amorphous and crystalline phases at any temperature. Such a melting range would occur even if the crystallites were of the same size. However, in the normal crystalline polymer a range of crystallite sizes exists and on heating, the smallest crystallites containing the
shortest chains are most likely to disappear first, the largest persisting with a little change until the highest temperatures are reached. The result is that the proportion of amorphous material increases with rise in temperature.

7. Electrical properties of high polymers. Apart from the interest in the electrical properties of polymers arising from their wide use as insulators, the study of these properties provides a valuable method of investigation of the structure of polymers and the relation between chemical structure and mechanical properties (58, 59). Many papers on electrical characteristics of long chain hydrocarbons and high polymers have been published bringing some interesting anomalous properties of these substances to light. Some of the important electrical properties of these dielectrics are to be understood before coming to some plausible conclusions, regarding the anomalies in the behaviour of solid dielectrics. Few of them are mentioned below and discussed in the following paragraphs.

(a) Electrical conductivity, polarisation and space charge.
(b) Electret effect.

(a) Electrical conductivity, polarisation and space charge. Joffe and his Co-workers (60) have put forward the hypothesis that the true conductivity of a
dielectric is exhibited either after a very short application of stress, before any space charge or electrode polarisation has time to develop or after a very long time of application when, adopting the converse theory, the polarisation has either disappeared or reached an equilibrium. Modern advances in the theory of dielectric properties have demonstrated that the majority of the work mentioned was based on a misunderstanding of absorption currents and the phenomenon of dielectric relaxation. It is now recognised that there exists in substantially all dielectrics relaxation and oscillation mechanisms of a dipolar ionic, molecular, or electronic nature which give rise to a time dependent conductivity and a frequency dependent dielectric constant and loss angle without the production of internal electric fields except of local nature. If only the conductivity is observed, it is easy to express the effect as a polarisation. This was demonstrated several years ago by Hartshorn (61) and certain features have recently been elaborated by Whitehead (62).

A great deal of work has been carried out in the U.S.S.R. on the polarisation hypothesis. Nasledow and Scharawsky (63), Tutschewitz (64) and Courtenser and Ignatowitsch (65) decided that the polarisation voltages in Ceresin, paraffin and ebonite respectively were proportional to the applied field. Of more importance are the connections
proposed between the increase of conductivity and the variation of polarisation potential with applied field. Nakanisi (66), Sinjelnikov and Walther (67) quote a polarisation potential for mica which first increased linearly with field strength, as already discussed, then reached a maximum of about 4 kV at $5.6 \times 10^6$ V/cm. and then fell. In the region of maximum, the conduction current rises rapidly and apparently breakdown occurred at less than 10 V/cm.

Considering the thickness of the specimen probably of the order of .001 cm, it is difficult to see how the polarisation potential could be distinguished as a separate phenomenon from the non-linear increase of conduction current which naturally can always be explained in terms of variation of polarisation potential if the true conductivity is chosen to suit the experimental results. Sinjelnikov and Walther have applied higher fields without change of conductivity in mica (67).

It is also clear that polarisation potentials of the magnitude described can only easily arise due to space charges. Even so, an extremely high concentration of charge would be necessary to modify the high fields of intrinsic breakdown. It must be admitted that these fields are capable of drawing electrons from the electrodes. This has been demonstrated in studies of the electric strength with electrodes separated by a vacuum and there seems no reason why the electrons should not readily pass into the dielectric and become trapped
there or induce ionic defects. Guntherschulze (68) and
his coworkers claim to have established the existence of
considerable concentrations of free or feebly bound
electrons in thin oxide films which have been exposed to a
strong field and subsequently discharged. Furthermore, they
state that electrons drawn from the cathode can penetrate
these films and issue with energies of the order of
20–30 eV. This is not in accord with Frohlich's theories
(69), since according to him an electron with an energy
in excess of the ionization potential of the lattice would
be very rare and very transitory, provided the thickness of
the dielectric exceeded the mean free path, about 10⁻⁶ cm.
The evidence therefore, in support of the polarisation
potential hypothesis is generally either consistent with
other known mechanisms or in the form stated by its authors,
introduces theoretical incompatibilities. Von Hippel and
Alger (70) have put forward space charges in explanation
of some of the effects of temperature electrode material
and duration of stress.

A number of mechanisms for the increase
of conductivity with field strength have been explored.
Electronic conductivity due to the escape of electrons through
a potential barrier eV in a field F has been shown by
Zener (71) to give a variation proportional to Fe⁻Const/F
Frenkel (72) inserting the effect of the field on the potential
barrier, obtains a probability of ionization in unit time given by,

$$v_0 \exp \left[-\frac{4\pi}{h} \sqrt{2m(V-2\sqrt{e^3F}) \left(\frac{1}{eF}\right)^2 \left(V^2-4e^3F\right)}\right]$$

where $v_0$ can be identified with the frequency of an ionizing radiation. Calculation shows that outside a small range of field strength the current would be either negligible or impossibly great, so that it is doubtful whether the phenomenon is observable and certainly does not seem to have been observed although a claim has been made to this effect (73). Next there is the thermal activation theory of the escape ions. This has been applied by Frenkel to trapped electrons to give a conductivity proportional of $e^2 \sqrt{e^3F} / kT$ but it is rather difficult to see how Frenkel's hypothesis can yield an appreciable current because, owing to the low inertia and relaxation time of the electrons, other effects such as electronic mobility would be expected to control the phenomena. Austen's (74) application of the activation hypothesis to ions is intrinsically more probable and gives a conductivity proportional to $\sinh \left(\frac{1}{2} e_0 F/kT\right) / \nu e_0 F / kT$.

Guntherschulze (68) suggests alternative forms of variation of ionic current in oxide films which would be
comparable either with activation or with tunnel effect and says that only the former applies to electrons. His idea is that electronic conductivity precedes the ionic conductivity which is due to slipping in a polar crystal of the negative ion lattice over the positive ion lattice. Activation is rather unlikely with heavy ions. As regards amorphous solids it has been seen that Frohlich's theory of interaction between trapped electrons leads to a variation of conductivity with field strength according to

\[ \exp \left\{ \left( \frac{V}{\Delta V} \right) \left( \frac{F^2}{eF_m^2} \right) \right\} \]

where \( V \) is the potential barrier of trapped electrons, \( \Delta V \) refers to the energy barrier of the average excited trapped electrons and \( F_m \) is the intrinsic electric strength.

Poole (75) found an exponential variation of conductivity with field strength, but at that early stage it is unlikely that the results referred to the intrinsic properties of the structure. The experimental evidence on pure crystal is rather negative. Joffe (76) and his coworkers and also Von Hippel (77) and his colleagues have all published conductivity results showing variation with field strengths in support of their various theories. The majority of these results indicate a rapid increase of prebreakdown current but unfortunately this does not occur in
the same field strength range with different experimentors. The observations of Austen, Thomas, Hackett and Whitehead (78) suggest that it is very difficult to remove the influence of stray leakage and impurities in measuring field dependent current in crystals. It is to be noted here that Austen's activation hypothesis is applicable to crystal defects and not in consistent with the qualitative characteristics of the general experimental findings. The results of Von Hippel and Maurer (79) on soda line glass and those of Thomas and Griffith (80) on varnish films seem in quantitative accord with Frohlich theory of amorphous substances. Some support is also afforded by the measurements on soda lime glass by Turner and Lewis (81).

Hartshorn (82) and Whitehead and Nethercot (83) indicated that impurities such as moisture causes the conductivity to increase with field strength. As a first hypothesis the activation theory might be applied to the trapped imperfection ions, the binding energy of which can be estimated from work on diffusion in solids (Thomas and Gent (84)). There remains the difficulty that to a first approximation the experimental dependence on field seems to be an odd function of field strength, whereas according to activation theory an even function should apply. The impurities are often only partially ionised, for example Garton (85) has
shown the water molecule in cellulose to be still capable of rotation. Thus both activation of the ions from the structure and activation with respect to the interaction between ions of opposite sign may be involved yielding an ordinary mixed function in qualitative accord with experiment.

Some interesting observations on the fluctuating character of currents in dielectrics in strong fields have been reported by Hawrath and Bizirth (86) who suggest the analogy of the shot effect in electron emission and calculate that the number of elementary charges released, to the electrodes in a single fluctuation, varies exponentially with field strength. Schulze (87) found discontinuities in the current passing through very thin films of sulphur and solid organ and states that these discontinuities occur at fields in the same numerical relation as the ionization potential of the structure.

An extension of conductivity theory to high fields subject to the usual simplifying assumption is carried out for the cases in which the change of energy of an electron in a collision can be neglected. This yields a relationship between mobility and relaxation time which is valid over a wide range of fields (88).

Measurements of temperature dependence of
conductivity for solid anthracene, naphthalene, pentacene and perylene show that the pure substances obey $\sigma = \sigma_0 e^{E_0/kT}$ relation (where $\sigma_0$ and $E$ being constants for each substance) (89). The conductivity temperature data serve to suggest an ionic mechanism for electrical conduction in polyethylene. In fact the ion contributing most to the conduction in polyethylene may be proton (90). The electrical conductivity of plexiglas in an electric field of 2.6 kV/cm in the temperature range from 21°C to 90°C was found to be represented by the sum of two exponentials, which have activation energies of 1.45 eV and 2.7 eV. At higher temperature curves of current as function of field strength from 2.6 to 29 kV/cm were resolved into the sum of a linear and of an exponential term. The results suggest that ionic conduction dominates at low fields (91).

The electrical conductivity of polystyrene, polymethylmethacrylate, polyvinyl acetate, polyvinyl butyral, polyvinyl formal and polyvinyl ethylal were measured below and above the vitrification temperature. The temperature dependence was found to be similar to those of supercooled monomeric liquids and glasses (92).

The electrical properties of polyvinyl chloride plastics depend on thermal history. Increased time and temperature of heating give decreased D.C. conductance. The
dielectric constant changes with time in a way which suggests a relaxation mechanism. There is one to one correlation between D.C. conductance, dielectric constant and loss factor. It points out a characteristic difference between free dipoles and dipolar polymers. The former can assume a normal distribution of orientation while the latter have a distribution determined by chain orientation (93).

The experiment conducted on the electrical conductivity of high polymers both during and after exposure to ionizing radiation brings out some outstanding facts. In the absence of space charge the conductivity is proportional to the number of electrons released if all the free electrons can move to the anode or are permanently trapped after traversing a constant range. If electrons are released from shallow traps by thermal activation, they make an additional contribution to the observed conductivity until permanently removed from the cycle by a deeper traps or through escape to the electrodes.

Thermal activation leads to an exponential relation between conductivity and temperature $\sigma = \sigma_0 e^{-u/kT}$ where $u$ is the activation energy for thermal untrapping and $k$ is the Boltzmann factor. Conductivity by ions may also involve an activation energy for untrapping and exhibits an exponential temperature dependence. Contribution of ionic conductivity should be larger in polyethylene on account of
higher mobility of hydrogen ions. In the absence of localised space charges or polarisation, the velocity of the charge carriers should be proportional to the applied electric field. The current is essentially proportional to the applied voltage, although the slight hysteresis observed indicates the presence of space charges (94). Hysteresis in dielectrics appears when current-temperature and current-field curves do not coincide on increasing and decreasing side of temperature and field cycles. Hysteresis effect has been obtained by Jackson (95) in the case of paraffin wax, over the range of 0 to 80°C. Scisłowski (96) also reported this effect in paraffin wax in the temperature range from 17 to 46°C. Bhatnagar and Bhawalkar (97) have shown that the hysteresis effect reported in the conductivity temperature curve of the waxes appears as spurious effect, if proper precaution of maintaining thermal equilibrium inside the entire volume of the wax is not taken. This effect has also been found while studying the variation of conductivity with the field. Granier and Caillon (98) reported this effect on the application of A.C. and D.C. fields simultaneously. Polycrystalline rutile baked with a small addition of an oxide also exhibit hysteresis effect (99). Khanna and Bhawalkar ascribe this effect in Delaron plastic due to ionic conductivity(100).
(b) Electret effect in high polymers. The term electret can be precisely defined in the following words. 'An electret is a dielectric which can give rise to a sensibly permanent external electric field; in other words an electret is a dielectric which has the property of conserving the electric moments of polarisation which are produced in it by the application of high electric fields under conditions for example during the course of solidification' (101).

From the work of early workers which is summarised in a report by Gutmann (102) it can be gathered that depending upon the nature of the substances and also sometimes upon the intensity of the applied electric field, the electrets may have two completely different types of behaviour. In the case of the Carnauba wax resins mixtures, one observes immediately after the removal of the electric field a positive charge on the face pointing towards the negative electrode. This is well known classical phenomenon of the polarisation of the dielectric in an electric field. This type of charge is referred to as heterocharge. However, at the end of a period of several days, one observes a diminution of the charge which becomes zero and finally changes sign. The face which was adjacent to the positive electrode is itself positively charged and face adjacent to the negative electrode becomes
negative. This phenomenon is called charge reversal and is referred to as 'Homocharge'.

The first systematic study aimed at the classification of substances which can form electrets is due to Mikola (103). He showed that dielectrics whose conductivity is relatively high give only heterocharges, while those having low conductivity can give homocharges.

Homocharges are developed chiefly in compounds containing esters and alcohols (104) while heterocharges appear chiefly in glasses, resins and acidic compounds. Gemant (105) has confirmed that nonpolar substances, such as paraffins, do not generally form electrets. Johnson and Carr (106) have prepared electrets of sulphur. The first significant contribution using plastics for investigation of electret effect is of Wieder and Kaufmann (loc. cit.). They have shown that Plexiglas, Lucite and Nylon give lasting electrets. According to their findings, the best thermal conditions consisted in heating the Nylon at about 150°C, Perspex and Lucite at 200°C and then cooling up to room temperature in about one hour time, the electric field being held constant and switched off after total cooling.

A similarity has been found between Plexiglas and Lucite and Carnauba wax electrets so far as
electret forming current is concerned. In the case of Nylon however, the formation current differs in the shape because of higher conduction current; this in turn masks any polarisation current which might be present.

Field strengths of the order of 35 kV/cm employed during formation result in electrets having an initial net homocharge. If the field strength is in the range of 20 to 25 kV/cm, the resulting electret will have an initial heterocharge which subsequently becomes a homocharge. If the forming field is below 6 kV/cm a slowly decaying heterocharge is observed. The highest detectable charge density is limited to an order of magnitude of $10^{-9}$ Coulomb/cm$^2$ by breakdown of the surrounding air. Surface charged dielectrics prepared under a field of 55 kV/cm at room temperature exhibited a slowly decaying homocharge. The absence of elevated temperature prevented inner polarisation and thus led to a pure homocharge which decayed directly to zero. Nylon electrets in contrast to Plexiglas and Lucite have a greater activity as evidenced by the former more rapid sign reversal and attainment of steady state homocharge. This can be caused by the presence of larger inner and outer polarisation or a lower volume resistivity in the Nylon.

From these conclusions it is not very difficult to see that no overall criteria for selecting suitable
material has been established except a high volume resistivity greater than $10^{14}$ Ohms cm seems to be essential as concluded by Mikola (loc. cit.) in the case of Carnauba wax. As far as theoretical explanation of electret formation is concerned a postulate in agreement with Mikola (loc. cit.) and Gross (107), the existence of two separate decaying charge distribution of opposite polarities has been put forward. A differential in their decay rates could result in the apparent growth of the total charge density in the direction of a greater homocharge. This growth is eventually limited and an approximate steady state is reached because of air breakdown. Both polarised distribution involve the mechanism of ionic charge displacement. The alternative possibility that dipole orientation is the basis of inner polarisation appears to be unreasonable, since the maximum surface charge density obtainable in this case (assuming complete alignment with reasonable magnitude for dipole moments and dipole density) is $5 \times 10^{-6}$ Coloumb/cm$^2$. In contrast, the actual charge density due to inner polarisation was computed by integrating the displacement current-time curve and found to be $5 \times 10^{-4}$ Coloumb/cm$^2$.

Recently Baldus (108) has reported that electrets made from non polar substances like Naphthalene also, show in a well reproducible manner, the characteristic reversal
of heterocharge into a fairly permanent homocharge, contradicting the earlier conclusion that non polar substances do not show electret effect.

8. Conclusion. The work of Wieder and Kaufman (loc. cit.) has given sufficient amount of indication that plastics offer a wide variety of material of known structure to be studied extensively, keeping in view the anomalous properties of dielectrics in general and electret property in particular. In the past it has been customary to classify substances according to whether they acquire charges or exhibited no electret behaviour. Gemant has reported that non polar compounds do not generally form electrets (loc. cit.). According to later investigations (109, 110) non polar substances have been found exhibiting the electret effect under proper circumstances. The summarising report of Gutman contains explanations which partly contradict one another for the behaviour of an electret. There is an extensive agreement in that, by the assumption of a single process taking place in the dielectric, the properties mentioned can not be explained. It is with all these points in view that the present investigations on plastics have been undertaken in continuation of the work being carried on in this laboratory. Polyethylene, a non polar high polymer has been primarily chosen to understand the basic
mechanism of electret formation. Besides polyethylene a
dipolar polymer i.e. perspex has been selected to make a
comparative study so as to distinguish between the behaviour
of non polar and dipolar substances towards electret effect.
An extensive study of the electrical conduction in these materials
under the electret forming condition has been made. A X-ray
study of both these charged samples under different physical
conditions has also been made so as to establish a correlation
between internal and external behaviour of these electrified
samples. Surface charge studies has yielded a better picture
of this effect, which has been discussed in the light of the
available published work.
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