CHAPTER VII
SUMMARY AND CONCLUSIONS

ABSTRACT

All the conclusions relating to the various studies on PAN such as short-circuited current of poled and unpoled specimens, dielectric properties and mechanism of conduction are summarised in this chapter.
It has been established that plasma-polymerisation process is a useful method for preparing insulating and dielectric polymers from monomer vapours. The process is relatively economical particularly because of the efficiency of polymerisation and the optimisation of the rate of flow of the monomer. From the growth rate of polyacrylonitrile thin films prepared by plasma-polymerisation method it has been found that the rate of growth is proportional to the square of the current in the plasma tube. It is also concluded that the accelerated ions collide with monomer molecules and due to the energy transfer the monomer radicals are generated. In the polymerisation process, these radicals combine together to form the polymer chain. A special chamber has been designed to produce good, pin-hole-free and uniform polymer thin films. Using this set up, a brownish yellow coloured polymer is prepared while the chemically processed PAN is transparent. From different parametric studies at elevated temperatures, it is established that the observed properties are associated with PAN. The polymer dissolves in ethyl alcohol, acetone and dimethyl formamide showing a low order of polymerisation and low degree of cross-linking.
From the infrared studies, it is concluded that PAN is a long planar zig-zag chain molecule. It is further concluded that the forming process of plasma-polymerisation is not a controlled process resulting in the formation of amorphous polymer and it was not possible to identify the steric configuration. From the analysis of the emission spectrum of the monomer plasma and also from the structure of the resulting polymer, it is concluded that radical polymerisation is the most suitable mechanism for the formation of PAN by this method. For the termination reaction, it was not possible to confirm the mechanism from the present experimental data, but hydrogen addition and charge trapping have been put forward as the most probable processes. The additional bands of CO in the plasma spectrum and also in the infrared spectrum show the existence of the CO group as an impurity which is perhaps the characteristic of the gas phase discharge method of polymerisation. The visible ultraviolet absorption band of the polymer film shows band broadening suggesting the formation of long chain macromolecules.

A short-circuited current is generated from plasma-polymerised unpoled Al-PAN-Al thin films on heating. The current originates from the accumulation of negative trapped charges in the vicinity of the outer electrode. The preferential orientation of the dipoles due to rotation of -CN side group towards the outer electrode also contribute to the
short-circuited current. It is concluded that the charge trapping is associated with the compositional inhomogeneity in PAN films during the polymerisation process. The electrodes of dissimilar thicknesses also produce an additional contribution to the short-circuited current due to the nonuniform heating and surface strain. Since the activation energy is \( \sim 1.4 \text{ eV} \), it is concluded that the charges are formed from the covalent bonds of the carbon atoms and thus in turn suggests the trapping of charges at the tail end of the molecules. From the initial part of the optical absorption band of the polymer films, it is found that a trap level exists at \( \sim 1.7 \text{ eV} \) below the conduction band and is in agreement with the temperature activation energy. From the thermally stimulated current data, it is concluded that a preferred orientation of the dipoles is not possible at low fields (\( \sim 5 \times 10^4 \text{ V/cm} \)).

In poled Al-PAN-Al, a low temperature peak is observed in depolarisation current studies. It is concluded that the origin of the polarisation is mainly due to the orientation of dipoles associated with \(-\text{CN}\) side groups and migration of charges through microscopic distances. A partial contribution has also to be considered due to the injection of charges. The theoretically predicted total polarisation is found to be greater than the experimentally predicted one. This shows that the preferred orientation of
dipoles are restricted in PAN. Some local structure develops in PAN on high field polarisation preventing the dipoles from returning to their original position on depolarisation. From the polarisation studies, it is concluded that the electrons are trapped at the vicinity of the outer electrode due to compositional inhomogeneity. As a result an internal field of $\sim 6.2 \times 10^4$ V/cm is developed across the specimen.

For sufficiently large thicknesses ($>4000\AA$), the dielectric constant of plasma-polymerised PAN is found to be $\sim 3.4$ esu. But at lower thicknesses the dielectric constant is larger. The decrease in the value of the dielectric constant with the increase in the thickness of the film may be attributed to the structural changes due to ion bombardment during the formation of the films. From the dielectric studies it is concluded that the dipolar relaxation is widely distributed. The thermally generated trapped charges also contribute to the dielectric constant at high temperatures. From the frequency response of Al-PAN-Al capacitors in the range 20 Hz to 30 KHz, it is found that there are no changes in dielectric constant and loss factor. From the Jonscher analysis it is concluded that in the audio frequency range, Al-PAN-Al behaves as an ideal capacitor without any resonance components associated with it.
From the conductivity studies it is found that up to a field of $5 \times 10^5 \text{V/cm}$, plasma-polymerised PAN obeys Ohms law and shows a conductivity of $\sim 3 \times 10^{-18} \text{cm}^{-1}$ at room temperature. Above this field the conduction mechanism is due to Poole-Frenkel effect. The Poole-Frenkel coefficient $\beta_{PF}$ is calculated to be $3.4 \times 10^{-15} \text{cm}$ and is in good agreement with the theoretical values.

It is well known that PAN is a very good polar electret. Above experimental data also shows that PAN can store large amount of charges. The dipole orientation is constrained by the formation of local structure on high field polarisation. Hence stored energy will not be completely released on depolarisation process. But thermally released charges contribute a large depolarisation current. One of the notable features of PAN is that it has a very large dipole moment (3.4D) associated with the $-\text{CN}$ side group and as such piezoelectric and pyroelectric effects are expected. Hence further work has to be done in this direction especially on stretched polymer so as to get information regarding these properties.