CHAPTER III

DIELECTRIC PROPERTIES

3.1 Introduction

There has been a sharp increase in the number of polymer materials being investigated for possible use in microelectronic circuits. To a large extent, this has been associated with the more stringent requirements on the parameters and reliability of micro integrated circuits. Dielectric constant and dielectric loss of a polymer are some of the important factors in the design of devices. Further, the behaviour of these quantities as a function of temperature and frequency gives significant information about the chemical and physical state of the polymer. Because of their increasing use in device fabrication, conducting polymers warrant much attention and their dielectric properties have been investigated by many workers [1-11]. PPY and Pani-EB are two of the promising representatives of the wide group of the conducting polymers. Some investigations have been carried out on the dielectric properties of PPY [12-13] thin films. However no such work has been carried out on acid Pani and PPY/Pani-EB blend films. As the works done on the dielectric properties of PPY and Pani-EB films are very limited, further investigation in this line seems to be essential. Hence a study has been carried out on the dielectric properties of Pani-EB, lightly doped acid Pani, lightly doped PPY and PPY/Pani-EB blend

films. A brief theory is given followed by the experimental details and a discussion on the results.

3.2. General theory of dielectrics

3.2.1. Complex dielectric constant (ϵ^*) and dielectric loss (tanδ)

The capacitance C (Farads) of a parallel plate capacitor, neglecting edge effects is given by

$$C = \epsilon' \epsilon_0 \, A/d \qquad \text{...............} \quad (3.1)$$

where A is the area of the electrodes (m^2), d is the thickness (nm), ϵ' is the relative permittivity and ϵ_0 is the permittivity of free space (8.85 x 10^{-12} Fm^{-1}). When an alternating electric field E (= E_0 cos ωt) is applied to a dielectric, the displacement or dielectric flux density D is related to the field E as,

$$D = \epsilon E \qquad \text{......................} \quad (3.2)$$

where ϵ is the permittivity of the medium. Therefore under an a.c. field, displacement can be written as,

$$D = D_0 \cos(\omega t - \delta) = D_1 \cos \omega t + D_2 \sin \omega t \qquad \text{........} \quad (3.3)$$

where δ is the phase angle and $D_1 = D_o \cos\delta$ and $D_2 = D_o \sin\delta$.

For most dielectrics, D_o is proportional to E_o, but the ratio D_o/E_o is generally frequency dependent. Hence we introduce two frequency dependent components ϵ' and ϵ'', real and imaginary parts of the dielectric permittivity, which are given by

$$\epsilon'(\omega) = D_1/E_o = (D_o/E_o)\cos\delta \qquad \dots\dots\dots\dots (3.4)$$

$$\epsilon''(\omega) = D_2/E_o = (D_o/E_o)\sin\delta \qquad \dots\dots\dots\dots (3.5)$$

It is convenient to combine these two into a single complex dielectric permittivity as,

$$\epsilon^* = \epsilon' - j\epsilon'' \qquad \dots\dots\dots\dots\dots (3.6)$$

where $j\epsilon''$ is the component associated with the resistive vector.

The relation between D and E, both expressed as complex quantities, is then simply,

$$D = \epsilon^* E_o\, e^{i\omega t} \qquad \dots\dots\dots\dots\dots (3.7)$$

from equations (3.4) and (3.5),

$$\tan\delta = \epsilon''/\epsilon'(\omega) \, , \, 0 \leq \delta \leq \pi/2 \qquad \ldots\ldots\ldots\ldots \quad (3.8)$$

Since both ϵ' and ϵ'' are frequency dependent, the phase angle δ is also frequency dependent. Tan δ is called as the loss factor.

3.2.2. Polarization

The storage capacity of a capacitor is increased by the introduction of a dielectric material between the two plates. Neutralization of the charge at the electrode surfaces is responsible for this effect. The electrostatic dipoles in the medium are aligned under the influence of the applied field. This process of producing relative displacement of bound charges in dielectric by an external dielectric field is known as polarization.

The polarizability (α) of a dielectric is a measure of the extent to which electric dipoles are formed by the atoms and molecules. The dipoles may arise due to a variety of mechanisms, any or all of which will contribute to the value of α [14]. They are (i) The electronic polarizability (α_e) in which the negative electron charge cloud of an atom is displaced with respect to the ionic core, (ii) Atomic polarizability, in which, for example, a pair of atoms forms a dipole. The polarizability, may arise by displacement (α_a) of the atoms relative to each other (distortional) or by rotation of the dipoles (α_d) about an axis through the line joining them (orientational), (iii) Interfacial polarizability (α_i), in which charges (ions or

electrons) migrate through the material under the influence of the applied field. If they are trapped by, and accumulate at defects or discontinuities, they induce an image charge on the electrode and give rise to a dipole moment.

Considering the above described mechanisms, (i) and (ii) will apply whether the material is in the bulk or the thin film form. The third mechanism is very often observed in thin films, partly because, thin films generally have a high density of carrier - trapping defects and partly because, in thin films, the electrode/insulator dominates the electrical behaviour. Trapping of charges at this interface is a common feature of dielectric polymer thin films. Hence the total polarizability of the system is the sum of the individual polarizabilities, i.e.,

$$\alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_i \qquad\qquad \dots\dots\dots\dots (3.9)$$

3.2.3. Relaxation

Relaxation is a process which applies to linear systems where a polarization and an electric field are proportional to one another in equilibrium. The lag between field and polarization implies an irreversible degradation of free energy to heat. The dielectric flux density D, resulting from an applied alternating field E, would differ in phase from E. This is due to the inertia of the polarization which, when the frequency becomes

high enough, cannot follow the field variation giving rise to a "relaxation" of the measured permittivity. This behavior may be stated by an equation of the type,

$$\epsilon_r(\omega) = \epsilon_\infty + \int \alpha(t) \exp(j\omega t)\, dt \qquad \dots\dots\dots (3.10)$$

where $\epsilon_r(\omega)$ is the relative permittivity at ω ($= 2\pi f$), ϵ_∞ is the value of permittivity at infinite frequency which is a constant and $\alpha(t)$ is a sort of decay factor accounting for the lagging of polarization behind the applied field. Most of the relaxations can be described by means of Debye equations.

Debye proposed an exponential form for the decay factor,

$$\alpha(t) = \alpha(o)\, e^{-t/\tau} \qquad \dots\dots\dots\dots (3.11)$$

where τ is a relaxation time characteristic of the dielectric, which may be a function of the temperature but not of time. Substituting this in the above equation,

$$\epsilon_r(\omega) = \epsilon_\infty + \int \alpha(o)\, \exp^{(j\omega - 1/\tau)t}\, dt \qquad \dots\dots\dots (3.12)$$

Cole and Cole [15] showed that the above equation (3.12) should be replaced by the more general expression,

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$$\epsilon' - j\epsilon'' = \epsilon_\infty + \cfrac{\epsilon_s - \epsilon_\infty}{1 - (j\omega\tau_a)^{1-\beta}} \qquad \ldots\ldots\ldots\ldots (3.13)$$

where τ_a is the mean relaxation time and β is a constant of value between 0 and 1. If the results are plotted in an argand diagram, the points still lie on a circle, but its center is depressed below the ϵ' axis. If the radius of the circle is drawn between the points $(\epsilon_\infty, 0)$, where ϵ_∞ is the value of permittivity at infinite frequency and 0 is the center of the circle, the angle between the radius and ϵ' axis is equal to $\beta\pi/2$. β may be expressed as a spreading factor of the actual relaxation time about the mean value τ_a. There is no molecular interpretation for this factor, but it is useful in analyzing a complicated relaxation spectrum.

3.2.4. Temperature coefficient of capacitance and permittivity

Dielectrics are used at all temperatures and the temperature variation of capacitance is hence crucial. An important parameter used to indicate the variation of capacitance with temperature is the temperature coefficient of capacitance (TCC) that is defined by,

$$TCC = \cfrac{1}{C} \cfrac{dC}{dT} \qquad \ldots\ldots\ldots\ldots (3.14)$$

where T is the temperature and C is the capacitance. The temperature

coefficient of permittivity, a factor used to estimate changes in the permittivity of a material with changes in its temperature is defined as

$$TCP = \frac{1}{\epsilon} \frac{d\epsilon}{dT} \qquad \text{............... (3.15)}$$

TCP is an important practical figure for assessing the expected behaviour of thin film circuits. The relation between TCC and TCP has the form

$$TCC = TCP + \alpha \qquad \text{.................... (3.16)}$$

where α is the linear expansion coefficient of the material used as the dielectric in the capacitor. The TCC and TCP are usually expressed in parts per million (ppm) per degree Celsius. Neglecting changes in the linear dimensions of a specimen with temperature changes, TCC and TCP of the specimen may be equal in magnitude.

3.2.5. Frequency dependent behaviour of dielectric constant and dielectric loss in thin films

The dielectric constant ϵ' and the loss factor $\tan \delta$ are not absolute constants for an actual dielectric. Both these constants depend on many factors, namely the temperature, the frequency, the magnitude of the alternating voltage, the humidity of air, etc. The frequency dependence of $\tan\delta$ in thin films is a very important factor. Usually the dielectric

constant decreases with increasing frequency. At very low frequencies, the dipoles are oriented by the electric field without time lag. In this case the orientation of the dipoles is not accompanied by any loss of energy and hence tan δ is very low. At very high frequencies the dipoles are not able to follow the variations of the field, whereas the normal agitation is still present. The loss factor of thin film dielectrics shows a general behaviour of increasing loss at very high frequencies with a wide minimum in the intermediate range, as a result of superposition of various loss mechanisms.

The loss minimum observed in many cases [16-21] was explained by Goswami and Goswami [22]. The capacitance element was assumed to comprise (i) an inherent capacity element (C) unaffected by frequency and temperature, (ii) a discrete resistance element (R) due to the dielectric film in parallel with C and (iii) a series resistance (r) due to lead lengths etc. It was assumed that while R would be affected by temperature due to the exponential factor in the relation

$$R = R_o \exp(\Delta E/kT) \qquad \text{.................... (3.17)}$$

the lead resistance r would be more or less of constant value. In general R would be >> r. A mathematical analysis of the equivalent circuit leads to several conclusions.

The series capacitance and the loss factor (tanδ) were obtained as

$$C_s = \frac{1+\omega^2 R^2 C^2}{\omega^2 R^2 C} = (1+D^2)C \qquad \ldots\ldots (3.18)$$

and

$$\tan\delta = 1/\omega RC + r/\omega R^2 C + \omega rC = D(1+r/R) + \omega rC \qquad \ldots\ldots (3.19)$$

where D = 1/ωRC.

The loss minimum would be observed at a frequency given by

$$\omega_{min} = \sqrt{1/rRC^2} \qquad \ldots\ldots (3.20)$$

when $\omega R^2 C >> r$ or r/R<<1 that is true for all cases.

Equation (3.19) now reduces to

$$\tan\delta = 1/\omega RC + \omega rC = D + \omega rC \qquad \ldots\ldots (3.21)$$

when ω is small, 1/ωRC >> ωrC, then

$$\tan\delta = 1/\omega RC = D \qquad \ldots\ldots (3.22)$$

when ω is large, 1/ωRC is generally << ωrC and hence

$$\tan\delta = \omega rC \qquad \dots\dots\dots (3.23)$$

Thus equations (3.22) and (3.23) predict a condition when the loss factor will be inversely proportional to R or directly proportional to ω. It is observed from equation (3.20) that ω_{min} is determined by $(1/rRC^2)^{1/2}$. Since R would considerably increase with the lowering of temperature, r remaining practically unchanged, ω_{min} will also be lower at lower temperatures. Thus the shift of ω_{min} would be shifted to a lower frequency at lower temperature and vice-versa. In a similar way, the variation of $\tan\delta$ with temperature could be explained.

The effect of temperature on capacitance was obtained from equation (3.18) which could be rewritten as

$$C_s - 1/\omega^2 R^2 C + C = (1 + D^2)C \qquad \dots\dots (3.24)$$

If however $1/\omega^2 R^2 C \ll C$ or $D^2 \ll 1$, then

$$C_s = C \qquad \dots\dots\dots (3.25)$$

This condition can be realized in a capacitance system either by increasing R, i.e., by lowering the temperature or by raising ω. A suitable combination of these factors along with an appropriate value of C will lead to the frequency independent capacitance.

The equivalent parallel capacitance (C_P) and series capacitance (C_s) are connected by the relations

$$C_p = C_s/1+D^2 \quad \text{and}$$

$$C_s = C_p(1+Q^2)/Q^2$$

where D is the loss factor and Q is the quality factor. The loss factor is given by

$$\tan\delta = \tan\delta_f \times f/1000$$

where $\tan\delta_f$ is the loss measured at any arbitrary frequency [f (kHz)].

3.2.6. Activation energy

Simmons [23] suggested that it is possible to determine the activation energy from the capacitance versus frequency curves. This is accomplished by plotting $\log\omega$ versus T^{-1} for any constant capacitance, or specifically

$$\omega = AR_o^{-1} \exp(-\Delta E/kT) \quad \dots\dots\dots\dots (3.26)$$

where A is a constant whose magnitude depends on the particular chosen value of constant capacitance. A plot of $\log\omega$ or $\log f$ ($\omega = 2\pi f$) against inverse absolute temperature for any constant capacitance will result in a

linear plot with slope $(-\Delta E/kT)$. Thus the activation energy can be calculated.

3.3. Measurements

The measurement of series capacitance (C) and loss factor (tan δ) of a number of metal-polymer-metal (MPM) sandwich structures formed in the present study were carried out under a rotary vacuum in the frequency range 10 kHz to 10 MHz at various temperatures. Vacuum evaporated aluminium and gold thin films were used as the metal electrodes. The polymers used in the MPM sandwich structures were emeraldine base polyaniline, lightly doped (methylsulfonic acid) polyaniline, lightly doped ($FeCl_3$) polypyrrole and PPY/Pani-EB blend films.

A Hewlett-Packard digital LCR meter (4275A) was used to measure the C and tan δ values of the MPM structure. A copper-constantan thermocouple was used to measure the temperature. The r.m.s. voltage applied across the film capacitor throughout the study is 50 mV. The dielectric constant has been calculated from the measured values of capacitance, area of the capacitor (A) and the dielectric film thickness (d) using the relation

$$\epsilon' = Cd/\epsilon_o A. \qquad \dots\dots\dots\dots (3.27)$$

Since the as deposited films could contain many defects such as voids, grain boundaries, pinholes, etc., they were subjected to annealing treatment. The study of dielectric and other related physical properties of polyaniline (EB), acid doped polyaniline (x = 0.18), lightly doped polypyrrole and polypyrrole/polyaniline (EB) blend films was carried out on well-stabilized capacitors. A number of the polymer samples were subjected to the dielectric studies. Results and discussions on typical samples alone are presented in the following section.

3.4. Results and Discussion
3.4.1. Annealing

The defects present in the film represent a considerable departure from equilibrium. Application of mild heat treatment would anneal out these defects. Stabilization of these capacitors could also be achieved by repeated annealing cycles (slow heating and cooling). The stability and reproducibility in polyaniline (EB), acid doped polyaniline, polypyrrole and polypyrrole/polyaniline-EB (PPY/Pani-EB) blend thin films have been achieved after two cycles of annealing with a duration of one hour each at 323 and 333 K respectively. Figs.3.1(a-d) show the changes in capacitance with frequency for different annealing cycles for polyaniline-EB, acid doped polyaniline, polypyrrole and PPY/Pani-EB blend films of typical thicknesses 6.4 μm, 3 μm, 5.5 μm and 7 μm respectively. In all these films the capacitance values were found to decrease with repeated annealing cycles. Stable values of capacitance were found to be achieved
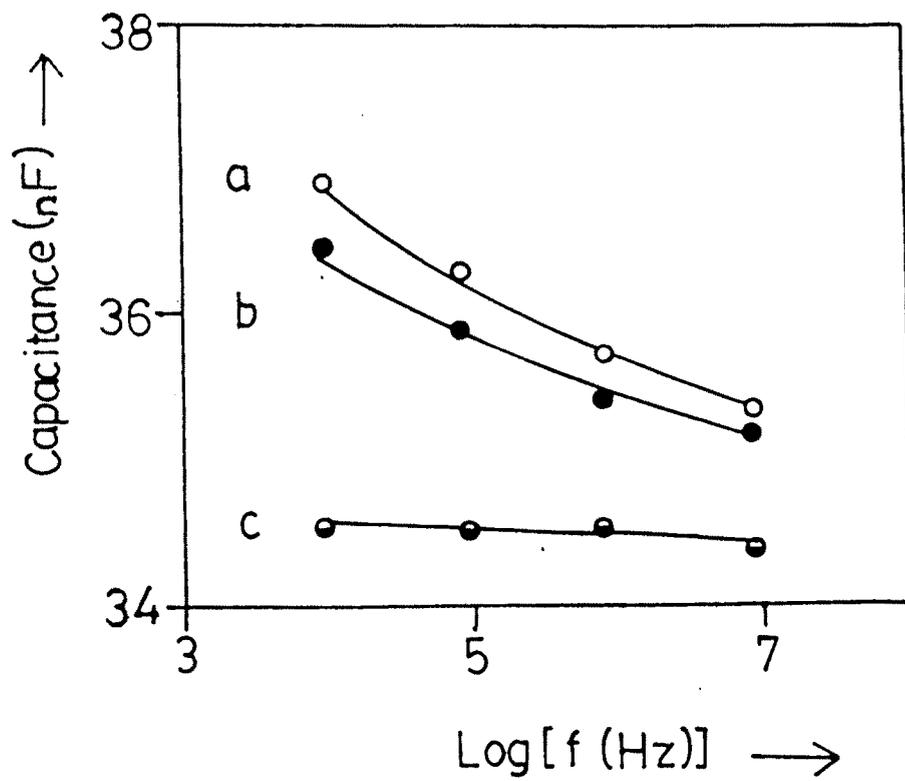
Fig. 3.1(a)   Annealing effect on capacitance of Pani-EB film
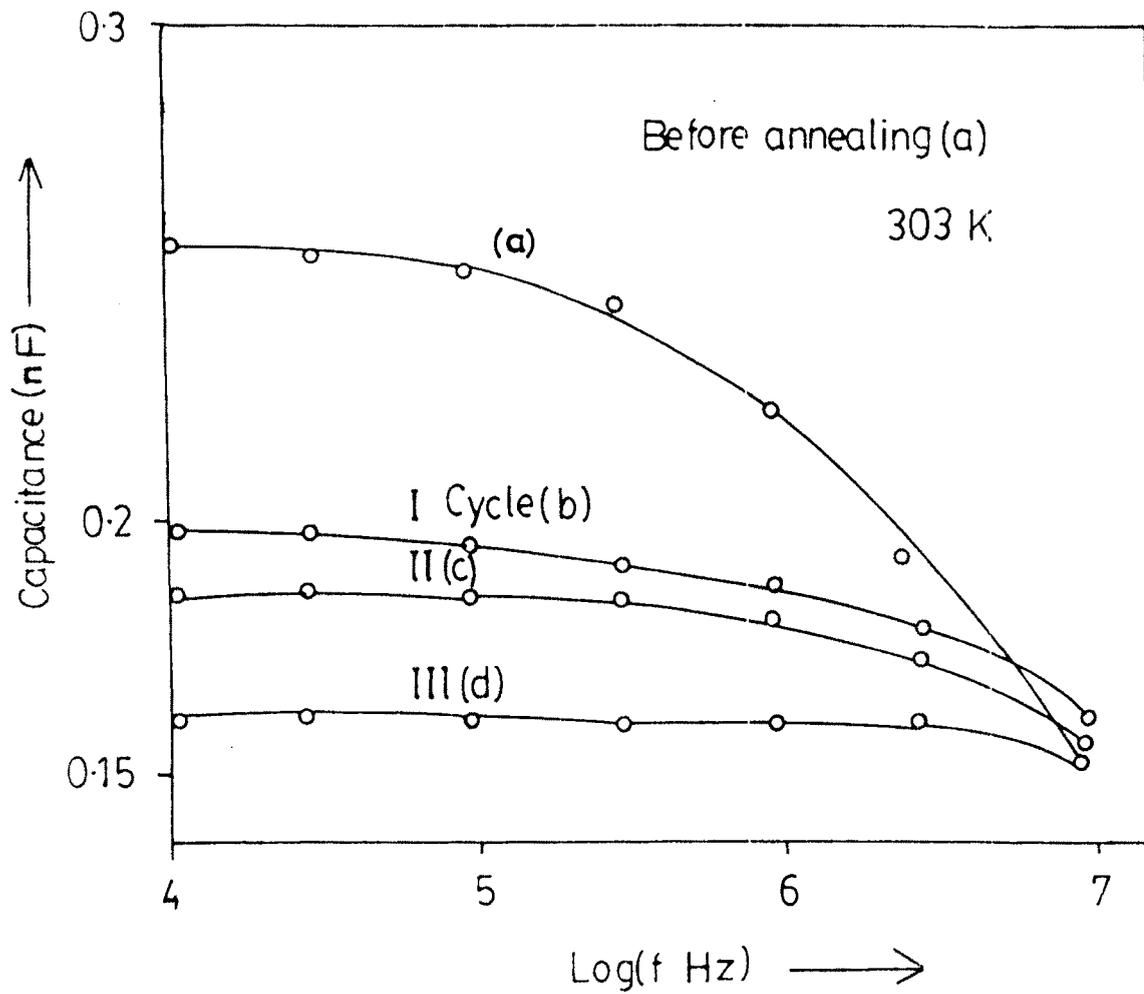
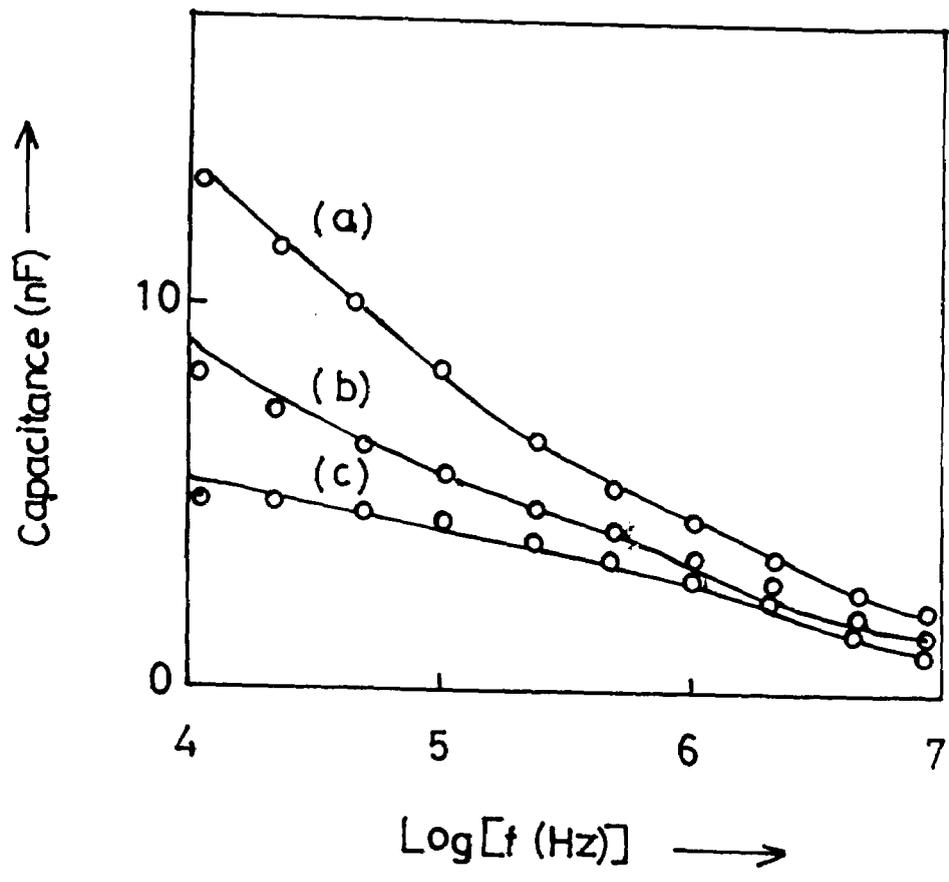Fig. 3.1(b)   Annealing effect on capacitance of Acid Pani film

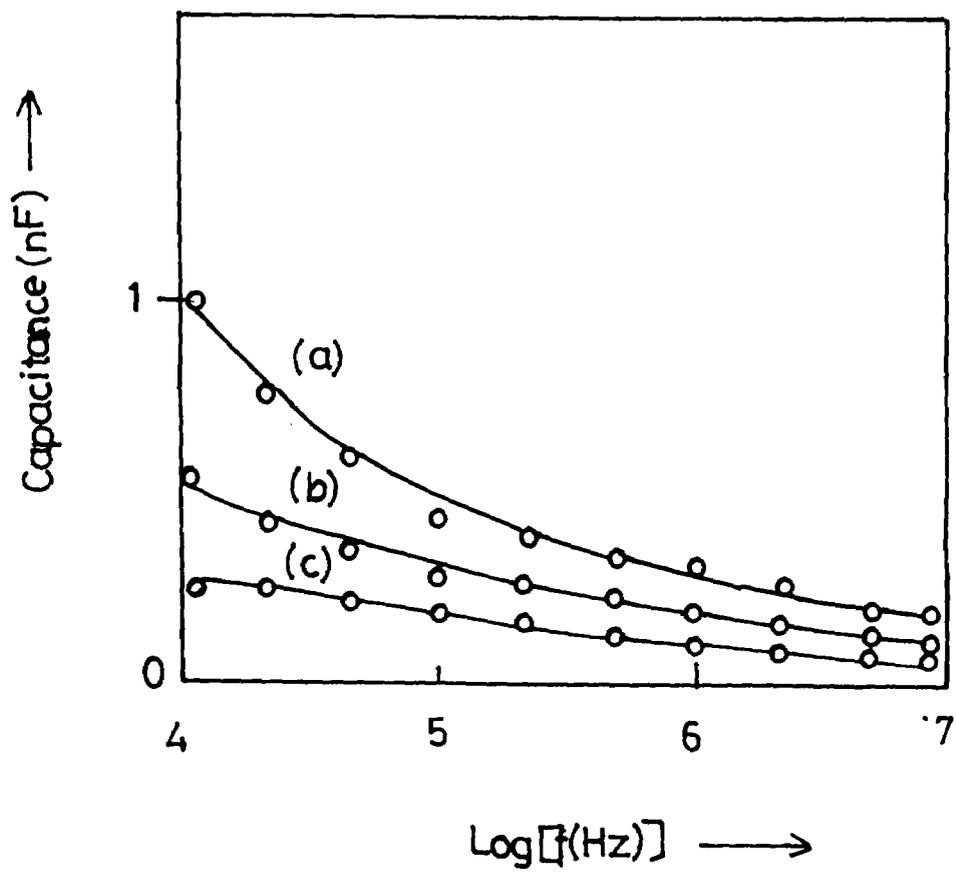Fig. 3.1(c)   Annealing effect on capacitance of PPY film

Fig. 3.1(d)   Annealing effect on capacitance of PPY/Pani-EB blend film

after two cycles of annealing.

Freshly deposited films, as mentioned earlier, have many defects and impurities such as voids, grain boundaries, dislocations, stresses, inhomogeneity, etc. The annealing process reduces many of the above defects and further improves the dielectric properties. This is because annealing is a process related with stress relief and local structural rearrangements [24] of polymer chains. Cycle after cycle, the defects are reduced gradually and each atom occupies a stable position in the interior of the film until the dielectric parameters attain a stable value.

3.4.2. Frequency dependence of capacitance

The dielectric behaviour of the polymer is determined by charge distribution and also statistical thermal motion of polar groups. The variation of capacitance (C) with frequency in the range 10 kHz to 10 MHz for different MPM capacitors are shown in Fig 3.2 (a-d).

Fig 3.2(a) shows the capacitance variation of the Pani-EB film. It is seen that for temperatures below 383 K, the capacitance decreases very gradually with increasing frequency (f). But at higher temperatures, the decrease in C with the increase of frequency is very predominant.

The capacitance of the acid doped Pani films vary in a different
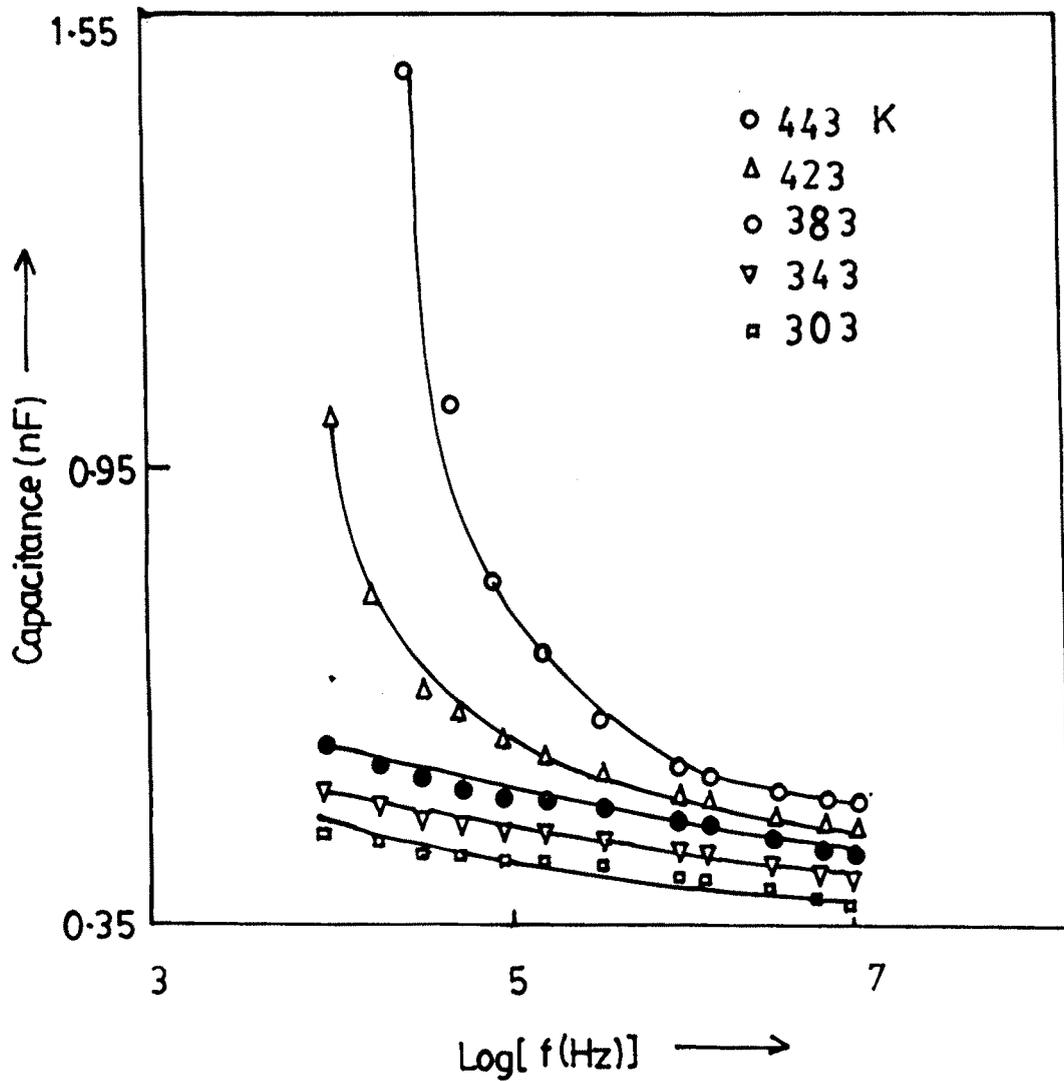
Fig. 3.2(a) Capacitance versus frequency for different temperatures of Pani-EB film
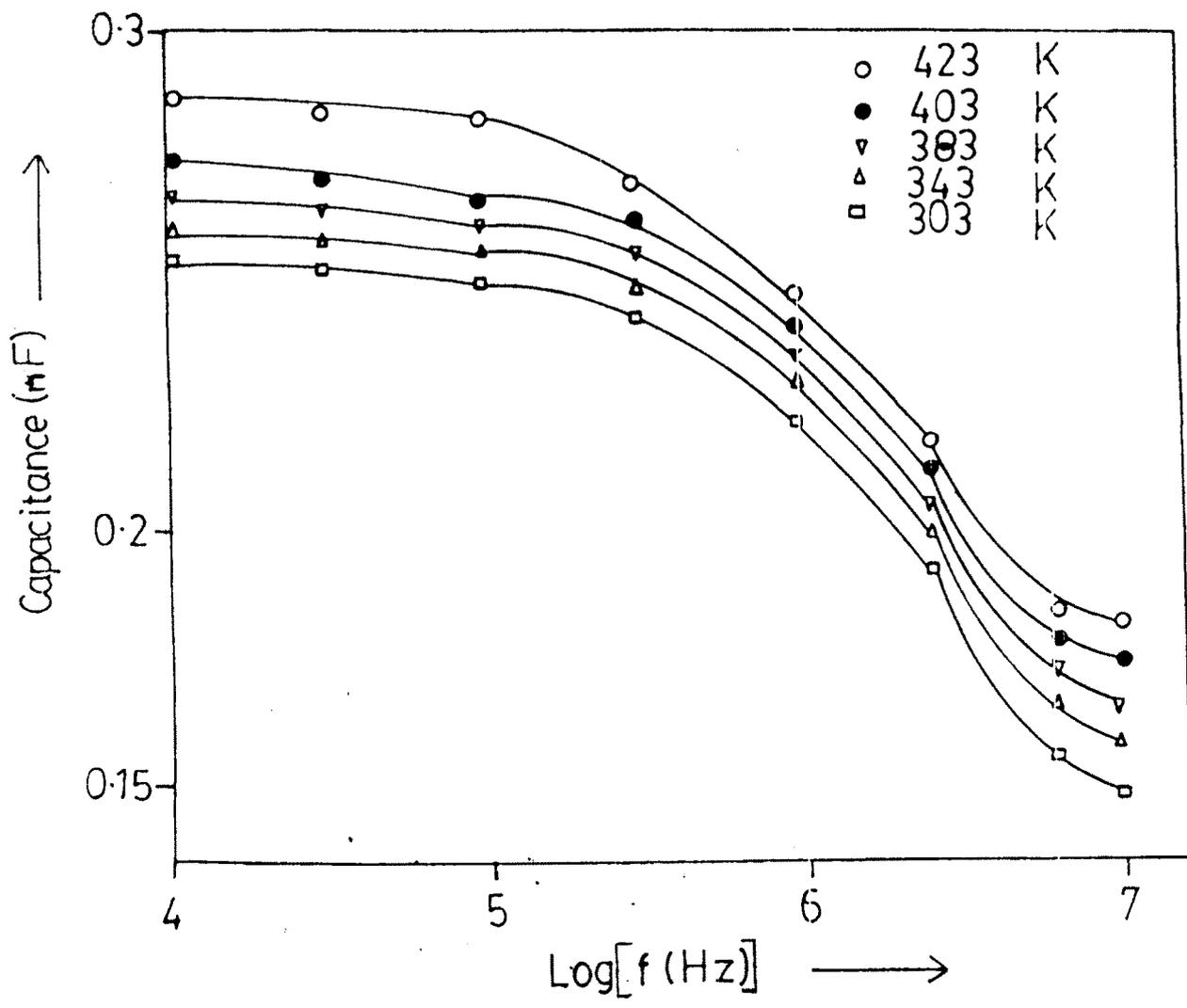
**Fig. 3.2(b) Capacitance versus frequency   for different temperatures of
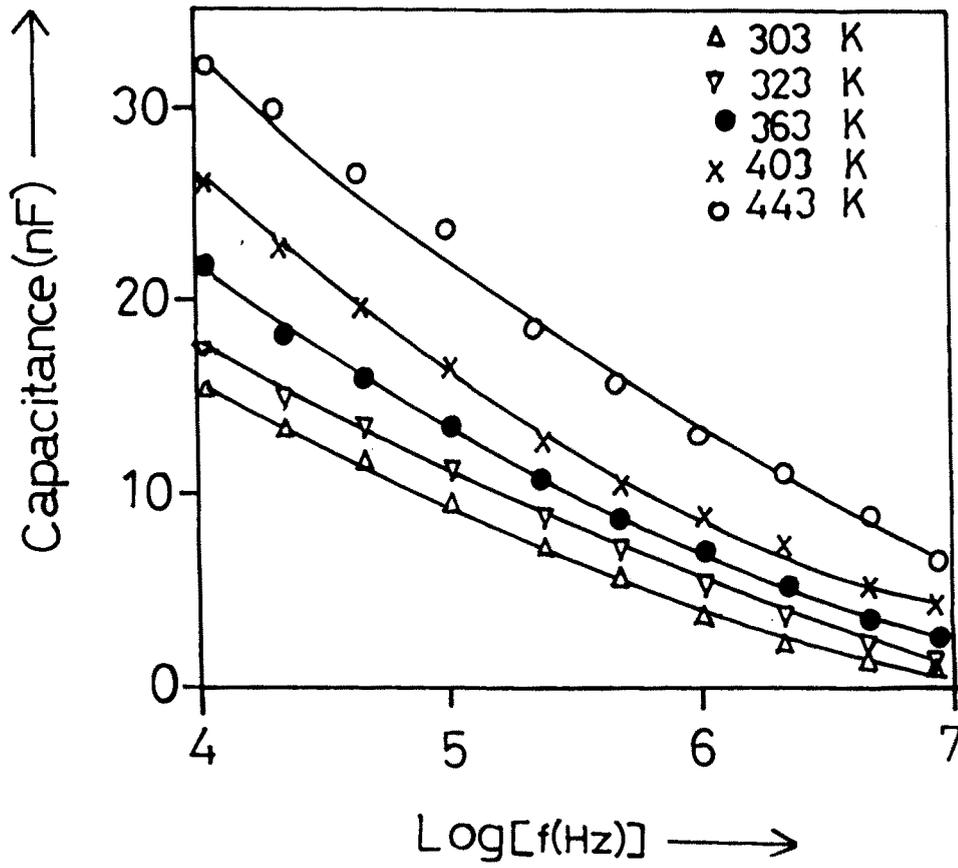Acid doped Pani film**

Fig. 3.2(c) Capacitance versus frequency for different temperatures of
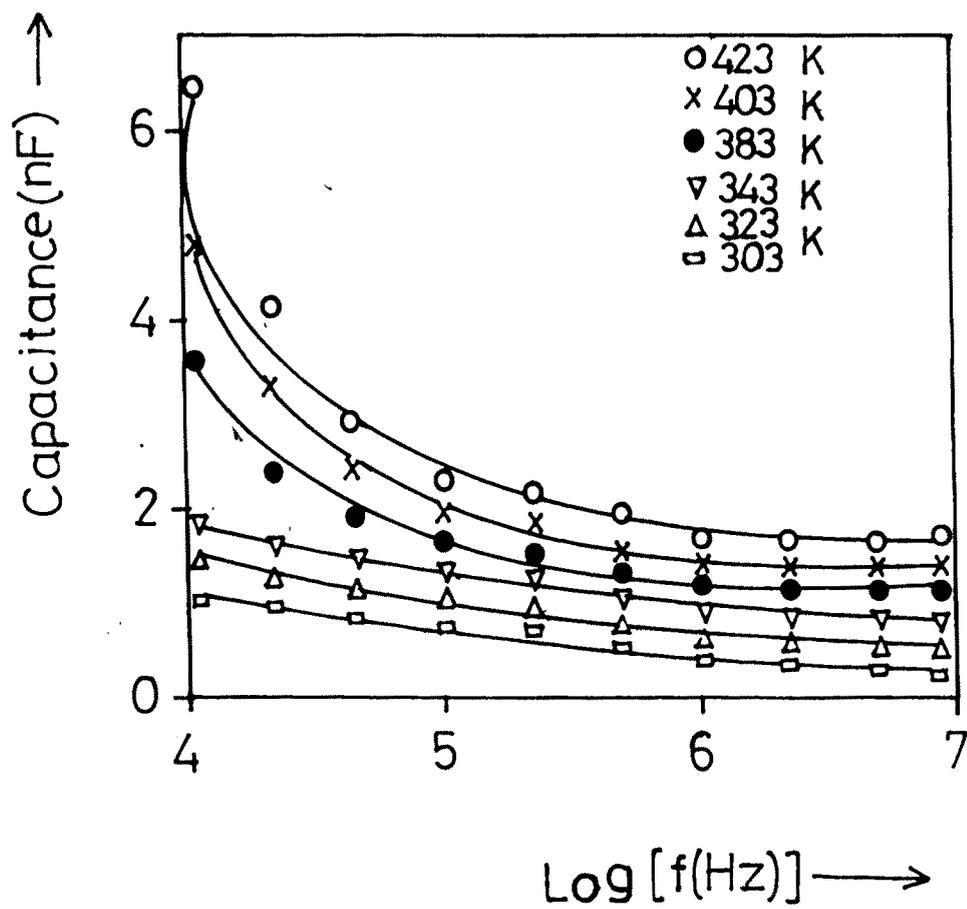PPY film

Fig. 3.2(d)   Capacitance versus frequency for different temperatures of
              PPY / Pani-EB blend film

manner [Fig. 3.2(b)]. The C is almost invarient with frequency till 300 kHz and decreases rapidly for further increase in frequency throughout the temperature range studied.

In PPY films, the capacitance decreases continuously form the lower to the higher frequencies for all the temperatures [Fig.3.2(c)]. The capacitance of the PPY/Pani-EB blend film shows an intermediate behaviour between the Pani-EB and PPY films as seen in Fig.3.2(d).

3.4.3 Frequency dependence of dielectric loss (tan δ) and dielectric constant (ϵ')

The dielectric loss of Pani-EB films Fig.3.3(a) vary very similarly as the capacitance of these films.

In acid doped Pani films, the loss decreases very gradually with increasing frequency for all the temperatures [Fig.3.3(b)]. As in the capacitance studies, the variation of dielectric loss of PPY/Pani-EB blend [Fig.3.3(d)] films is in an intermediate way to PPY and Pani-EB films.

But in PPY films [Fig.3.3(c)], a completely different behaviour of the dielectric loss is observed. The dielectric loss initially decreases very slightly with increase of frequency and after 100 kHz, it increases predominantly with increasing frequency.
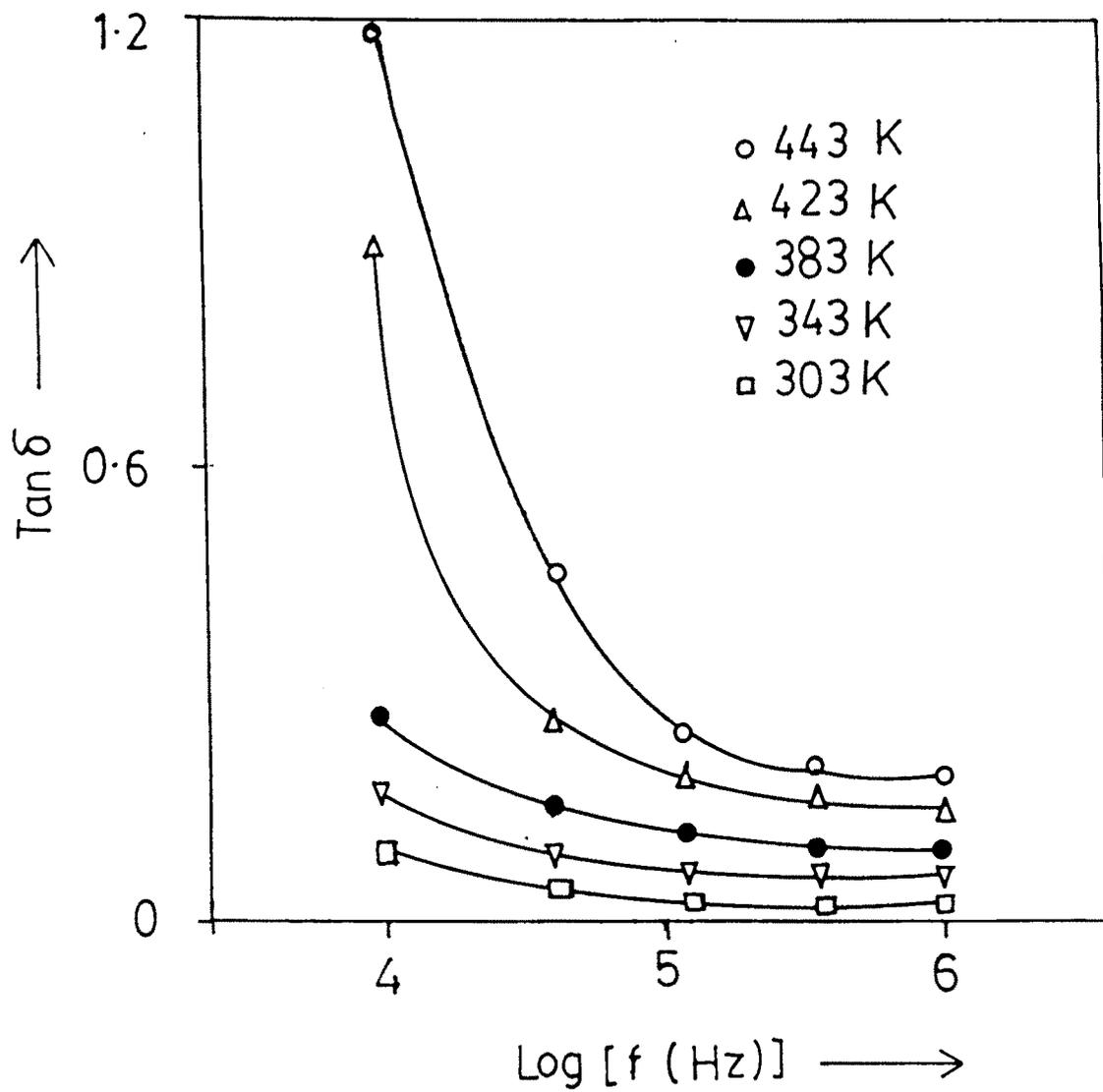
Fig. 3.3(a)   Variation of tan δ with frequency of Pani-EB film

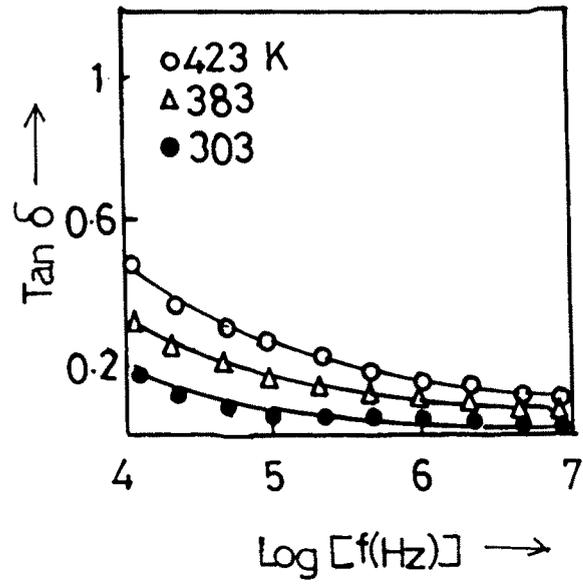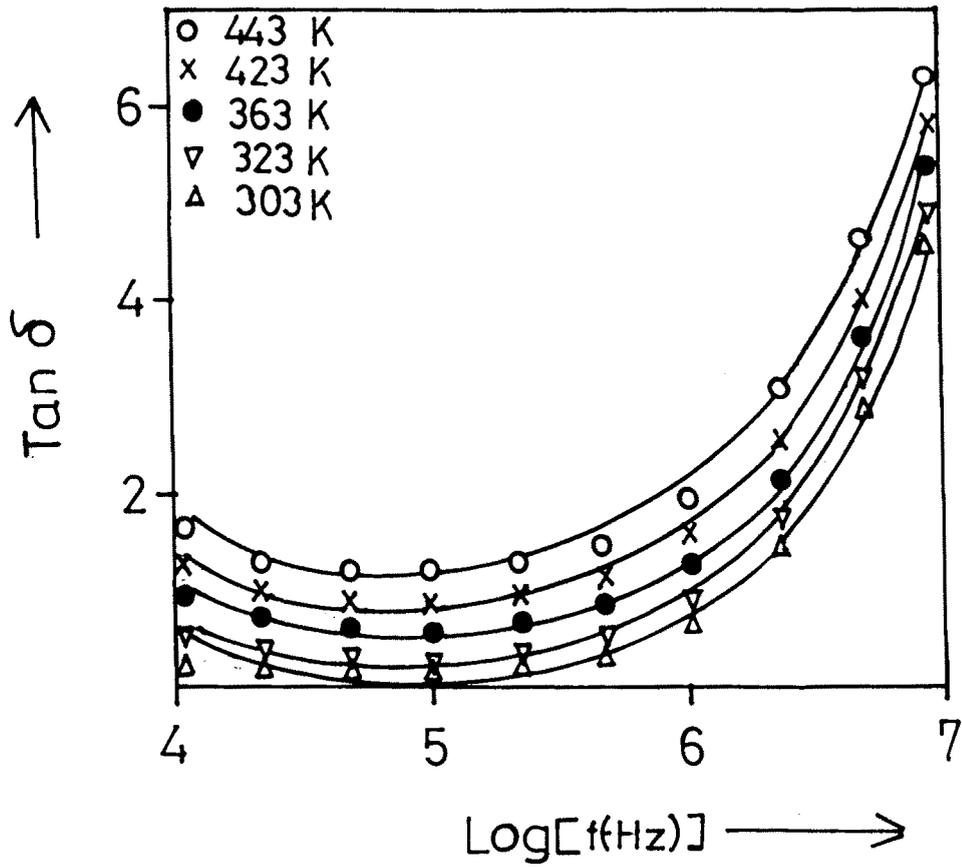Fig. 3.3(b)   Variation of tan δ with frequency of Acid doped Pani film
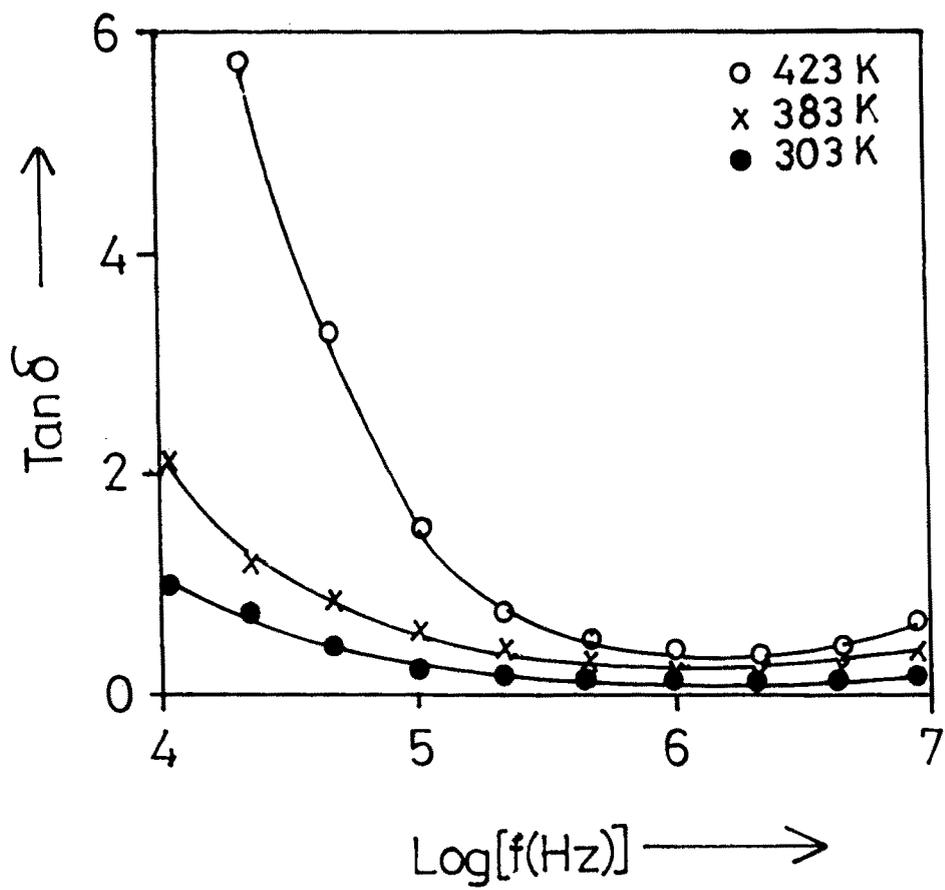
Fig. 3.3(c)   Variation of tan δ with frequency of PPY film

Fig. 3.3(d)   Variation of tan δ with frequency of PPY/Pani-EB film

Fig.3.4 (a-d) shows the variation of the real part of the dielectric constant ϵ' of the polymer films under study with the increase in frequency. The variation of ϵ' is very much similar to that of the capacitance of these films with frequency.

3.4.4 Variation of capacitance with temperature

Fig.3.5 (a-d) shows the variation of capacitance of the polymer films with temperature. Almost a completely temperature independent behaviour of the capacitance is observed for all the four polymer films at low frequencies. Only at higher frequencies, the capacitance increases with the increase of temperature for Pani-EB, PPY and PPY/Pani-EB blend films. But in acid Pani films, no such increase is seen. The dielectric constant of these films behave very similarly as the capacitance of all these films.

The temperature coefficient of capacitance is calculated from the relation TCC = $1/C(dC/dT)$. Similarly, by the plotting permittivity against temperature, the temperature coefficient of permittivity (TCP) is calculated from the relation TCP = $1/\epsilon \ (d\epsilon/dT)$ adopting the procedure reported earlier [23]. The linear expansion coefficient (α) is also evaluated from the relation,

$$\alpha = TCC - TCP$$

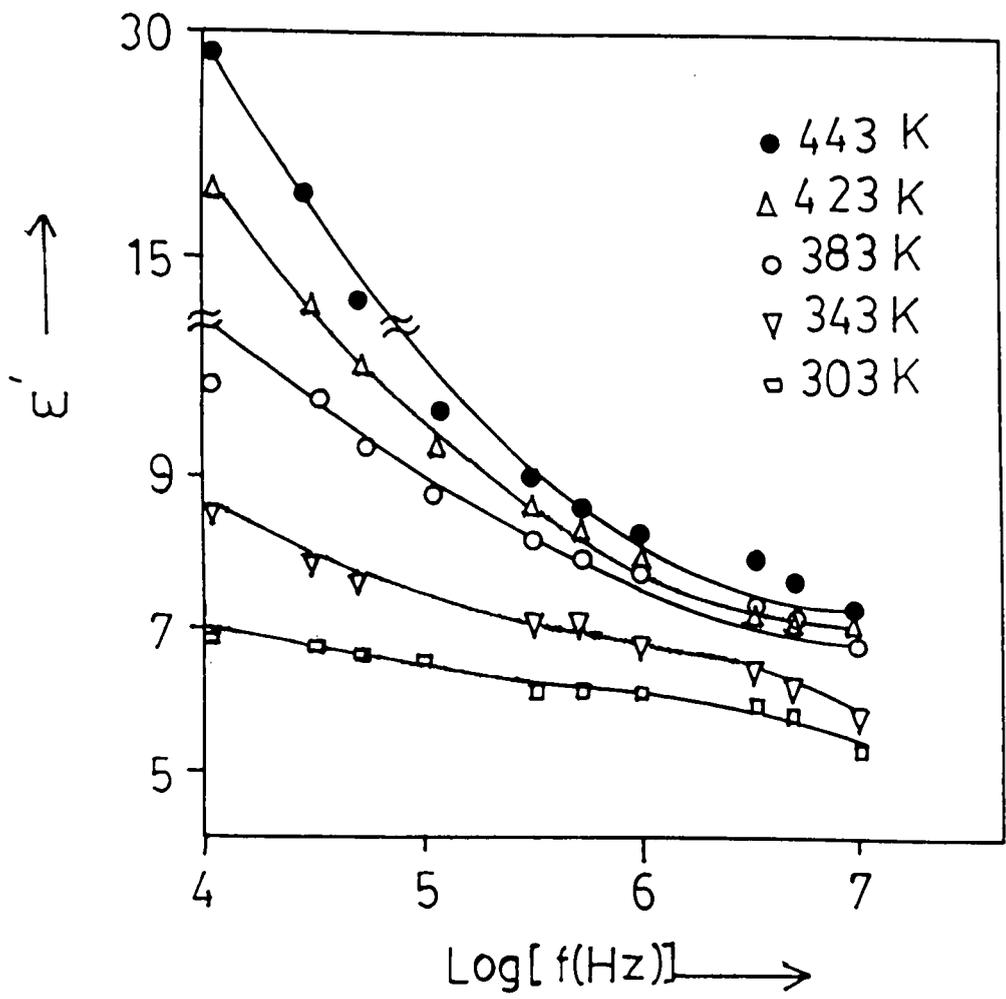The calculated values of TCC, TCP and α are given in the Tables 3.1.

Fig. 3.4(a)   Plot between dielectric constant with frequency of Pani-EB film
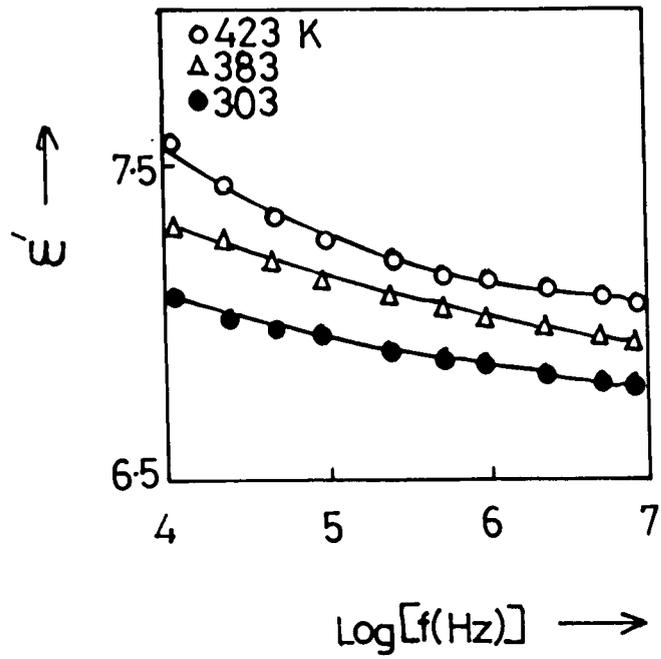
Fig. 3.4(b) Plot between dielectric constant with frequency of Acid doped
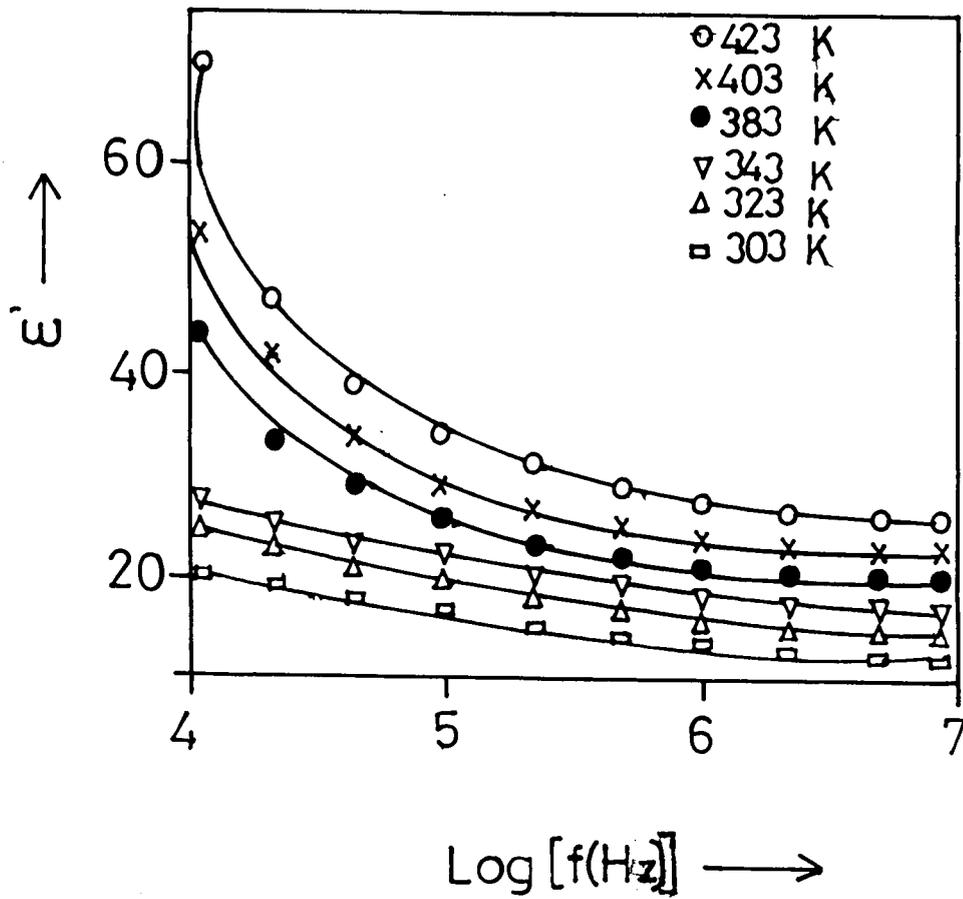Pani film

Fig. 3.4(c)   Plot between dielectric constant with frequency of PPY film
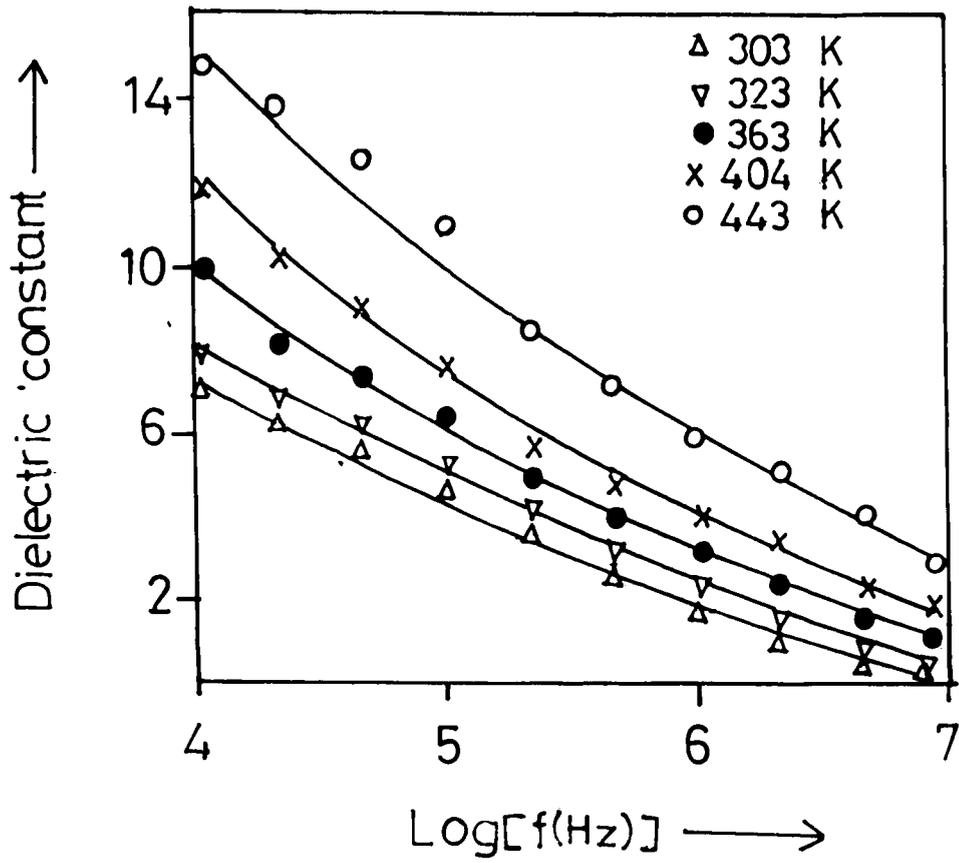
Fig. 3.4(d) Plot between dielectric constant with frequency of
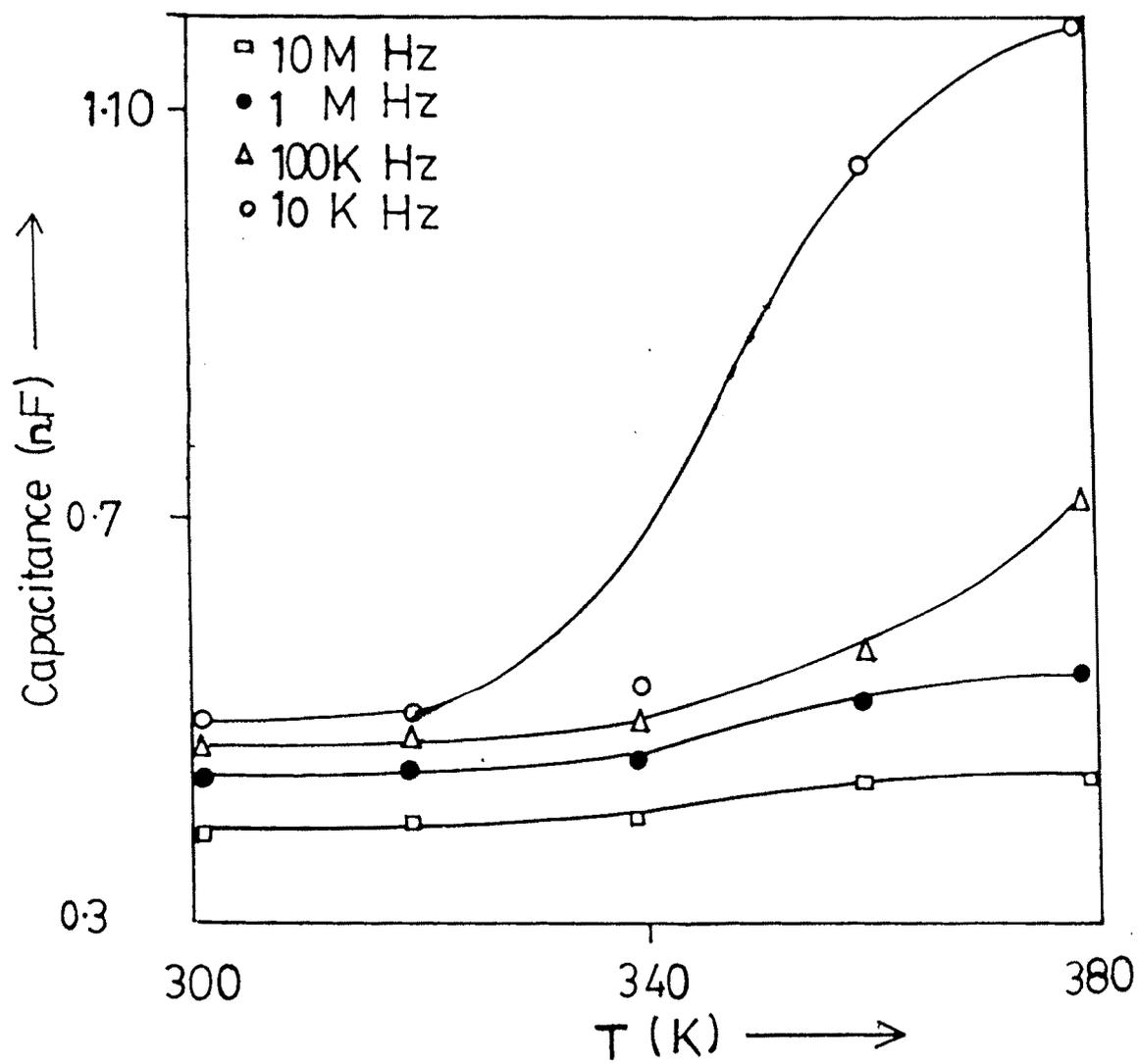PPY/Pani-EB film

Fig. 3.5(a)   Temperature dependence of capacitance of Pani-EB film
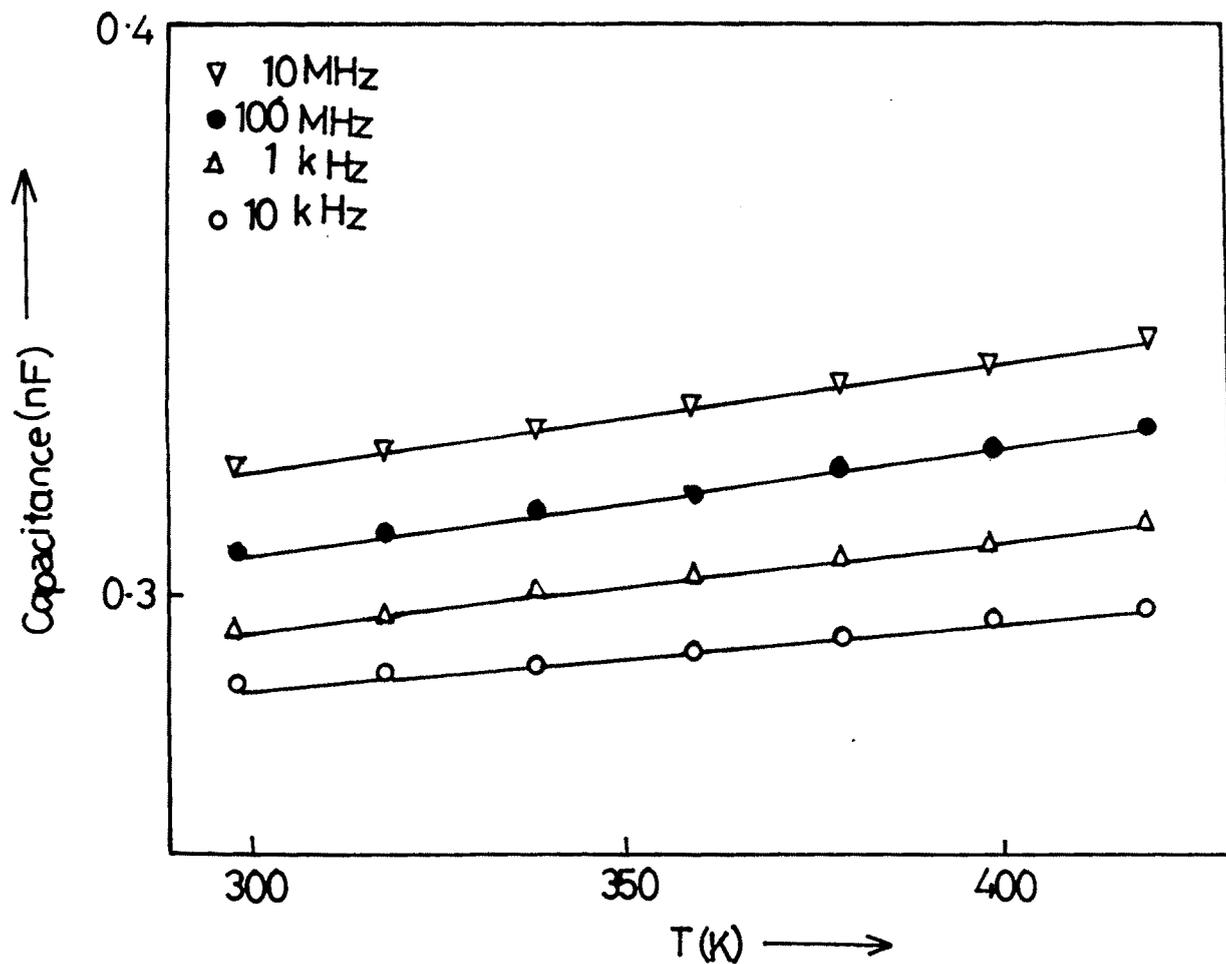
Fig. 3.5(b) Temperature dependence of capacitance of Acid doped
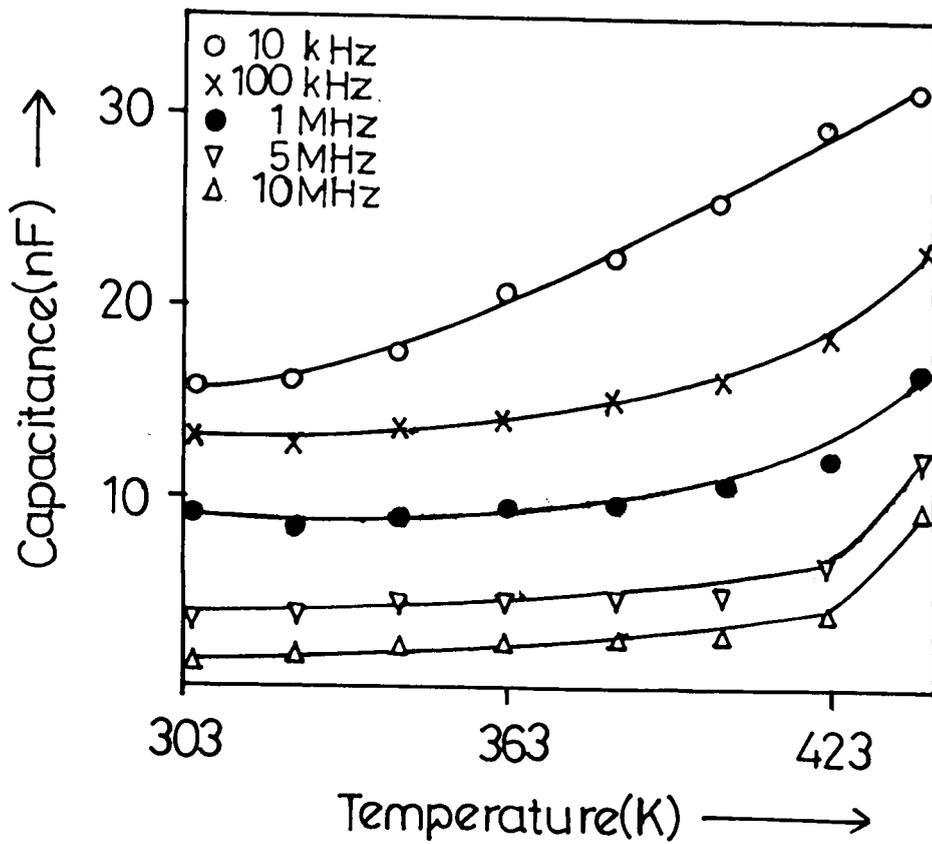   Pani film

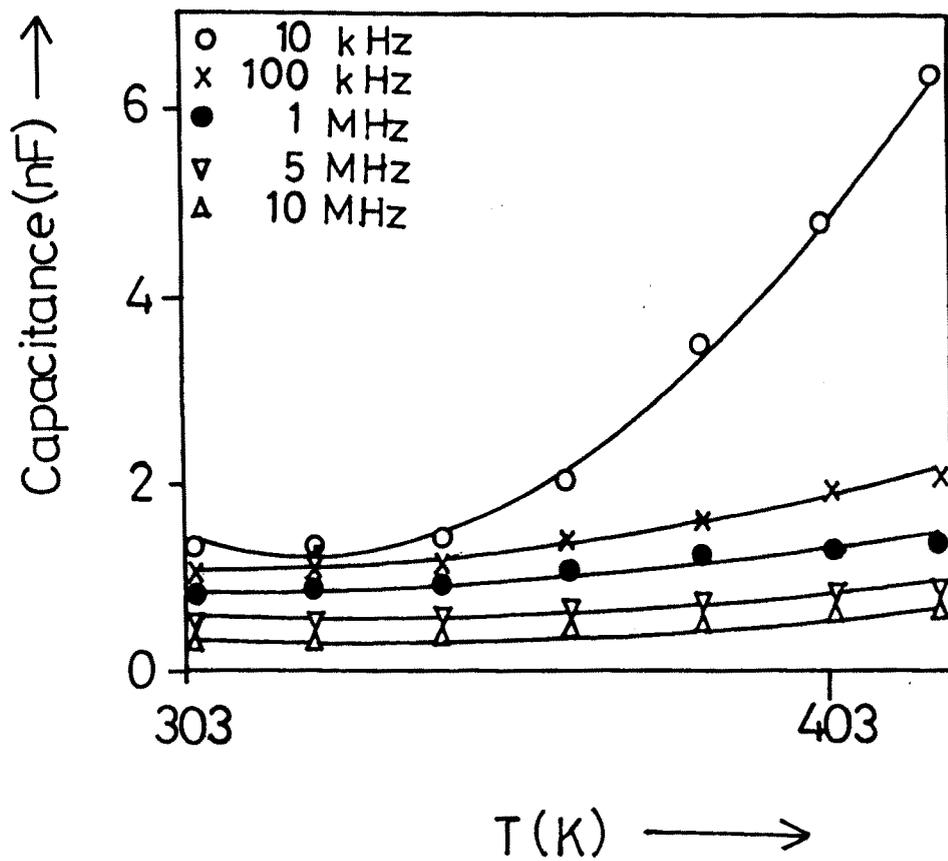Fig. 3.5(c)   Temperature dependence of capacitance of PPY film

Fig. 3.5(d)   Temperature dependence of capacitance of PPY/Pani-EB
blend film

The values of TCC and TCP at 100 kHz are low for all the films whereas they are high for PPY/Pani-EB blend films.

3.5 Discussion

Qualitatively the variation of capacitance and dielectric constants appear similar to those of other insulating materials [25-27]. But quantitatively the data are quit different from those reported for any insulator. The origin of dielectric response of undoped and lightly doped polyaniline and polypyrrole are of interest especially in the context of the role of polaron and bipolaron defect state in these systems. A Cole-Cole analysis [28-30] of the real and imaginary parts of ε, shows the absence of contact effects in these systems. The high frequency and room temperature dielectric constants measured for Pani-EB are in agreement with the results reported elsewhere [31,32].

In the case of lightly doped polyaniline films, the increase in the magnitude of the dielectric constant with frequency and its temperature independent behaviour reveal that it is the sum of the dielectric response of the backbone emeraldine base polymer plus a term related to the contribution of isolated polarons and bipolarons formed in these doped polymers.

The increase in capacitance and dielectric constant at low frequencies and

high temperatures indicate the presence of second independent relaxation process. For emeraldine base, the characteristic frequency of this process is thermally activated with a thermal activation energy. This shows that the low frequency dielectric process is the charge hopping between allowed sites in the polymer.

The variation of capacitance and dielectric constant with frequency and temperature [Figs.3.2 & 3.4] show the existence of Debye type [33] of dispersion in these films. This Debye type of dispersion may be due to the following three reasons

(i)   Maxwell-Wagner polarization due to the presence of in homogeneities [34]

(ii)   the electrode polarization due to the surface barriers [35] and

(iii) true bulk effect.

Polyaniline EB, lightly doped polyaniline, polypyrrole and PPY/Pani-EB are all predominantly amorphous in nature. Hence it may be concluded that the dielectric dispersion in these films is not due to the presence of inhomogeneities.

Also, it is seen that from the experimental data the dielectric constants is almost independent of thickness at higher thickness range. This indicates that the dielectric dispersion in these films may not be due to surface

barrier and electrode poalrization. Hence it is observed that the dielectric dispersion may be a bulk property of the polymers under study. The dielectric dispersion is not characterised by a single relaxations time exists in these films.

Table 3.1 The value of TCC, TCP and α at 100 kHz

Polymer Films	TCC	TCP	α
Pani-EB	0.0038	0.0013	0.0025
Acid Pani	0.0043	0.0030	0.0013
PPY	0.0092	0.0072	0.002
PPY/Pani-EB	0.0189	0.0141	0.0048

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