Effect of IR Radiation on the Dielectric Properties of Salicylic Acid Doped Poly-blend Thin Films of PS and PMMA.

Vidhale S.G., Belsare N.G., A.S.Wadatkar

Abstract

 Polystyrene (PS) and polymetyl methacrylate (PM-MA) were prepared by solution polymerization method. The thin films of 1:1 PS-PMMA poly blend system of pure and doped with 1%,3%,5%,7%,9% Salicylic Acid(SA) were prepared by using isothermal evaporation technique .The measurement of AC conductivity ,Dielectric Constant (εr) for all above samples have been carried out within the temperature range: 323K-363K and at frequencies in the range of 1kHz-1mHz.The results reveal that the AC Conductivity and Dielectric Constant were strongly affected by the IR radiations. It has been observed that the value of AC Conductivity decreases with the increase in time of exposure to IR radiation. Whereas dielectric constant decreases with increase in the exposure time of IR radiation. The sample was characterized by XRD, SEM and FTIR.

Key words: - PS-Polystyrene, PMMA-polymethyl methacrylate, SA-Salicylic acid, IR- Infrared radiation.

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S.G.Vidhale is currently working as Research Student at Department of Physics,

 Vidyabharati Mahavidyalaya, Amravati (M.S.) 444602 India

*Corresponding author e-mail: shilpavidhale20@gmail.com

*Corresponding author Phone: +917212662740 (Mobile +918983087071)

1. INTRODUCTION:- Ionizing radiation found to be widely applicable in modifying the structure and properties of polymers, and can be used to tailor the performance of either bulk materials or surfaces [1].It has been fifty years since researchers first began exposing polymeric materials to ionizing radiation, and reporting the occurrence of cross linking and other useful effects .Today , a substantial commercial industry is in place based on processing of polymers with radiation .Innovation in this field has by no means ended; important new products made possible through radiation technology continue to enter marketplace , and exciting new innovation in the application of radiation to macromolecular materials are under exploration at research institution around the world .In this paper we have presented our findings on the effect of IR radiation on the dielectric properties of salicylic acid doped poly blend thin films of PS and PMMA.

2.Experimental:- The two polymers i.e.(Polystyrene) and PMMA(Polymethyle methacrylate) were synthesized by solution polymerization method[2] (Qureshi et al., 2007) and taken in the ratio 1:1 and dissolved in common solvent (THF)

Tetrahydrofuran .Then the poly-blend films of PS-PMMA pure and doped with salicylic acid in different weight percentage (1%,3%,5%,7%,9%) were prepared by isothermal evaporation technique [3], [4], [5], [6], [7].Further the dried films were sandwiched between silver coins for better electrode contact .The thickness of the film was measured by digimatic micrometer (Mitutoyo Corporation, Japan).

These films were exposed to IR radiation for 5 minutes and 10 minutes .Then the film was kept between the electrodes of specially designed sample holder. The AC frequencies were applied (in the range1kHz-1MHz) across the sample by using the 4284 A precision LCR meter (model no 4284)(20Hz-1MHz) supplied by Agilent Technologies ,Singapore and the corresponding Dielectric constant (εr),AC conductivity were measured in the temperature range 323 K -363K . From the dielectric data, the values of AC Conductivity of the samples were calculated by using the relation [8].

$$\sigma_{ac\,=} \; f \, \varepsilon_r \, \tan \delta / 1.8 \times 10^{10} \qquad\qquad 1$$

where, f – frequency applied in Hz

ε_r – Dielectric Constant at frequency f

tan δ - Dielectric loss tangent.

3. Results and Discussion:-

The Results of the present study have been presented in the form of graphs as under

1. Variation of Dielectric constant with frequency at different constant temperatures for 1:1PSPMMA SA (0) (UNEXPOSED) sample

2. Variation of dielectric constant with temperature for a) 0 min exposure b) 5 min exposure c) 10 min exposure for 1:1 PSPMMA (0) sample.

3. Variation of dielectric constant with % of doping a) At different constant frequencies b)For increasing time of exposure to IR radiation at constant frequency 1Mhz and constant temperature 343K.

4. Variation of log of conductivity a) With log of frequency at different constant temperatures for 1:1PSPMMA SA(0)(0 MIN IR) b)With for 0 min, 5 min, 10 min expose to IR radiation at 343K at 1MHz f) c) Variation of conductivity with $10^3/T$.

5. Temperature dependence of the frequency exponent s at constant temperature.

6. Temperature dependence of the value β for 1:1PSPMMA SA (0) (UNEXPOSED) sample

7 .FTIR spectra for 1:1PSPMMA SA (0)

8 .XRD spectra for 1:1 PSPMMA (a) 0% SA (b) 3%SA (c) 9%SA before irradiation

9. XRD spectra for 1:1 PSPMMA (a) after irradiation (b) before irradiation

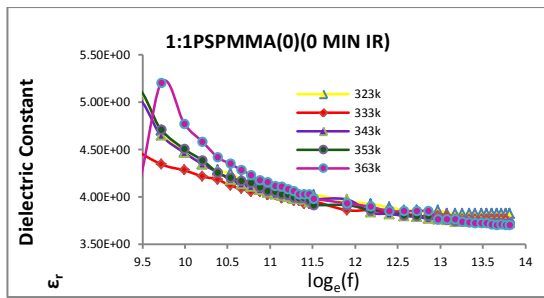10 .SEM a) for 1:1PSPMMA SA (0) b) for 1:1PSPMMA SA (3) c) for 1:1PSPMMA SA (9)

For economy of space, only select representative graphs from our study have been included in the manuscript; however the results and discussion refer to the entire study.

3.1 Prominent findings

The prominent findings of the present work can be summarised as follows,

- The dielectric constant (ε_r),
  i) Increases with the increase of temperature (fig.1).
  ii) Decreases with the increase of frequency (figs. 1&2a, b, c).
  iii) Decreases with the increase of weight percentage of doping Salicylic Acid (figs. 3a & 3b).
  iv) Decreases with increase in time of exposure to IR radiation.(fig 2b,2c & fig 3b)

- AC conductivity
  i) Increases with increase in frequencies (fig.4a&b)
  ii) Decreases with increase in percentage of doping (fig. 4b)
  iii) Decreases with increase in time of exposure to IR radiation (fig .4b)
 v) Decreases gradually with increase in temperature (fig 4a and 4c).

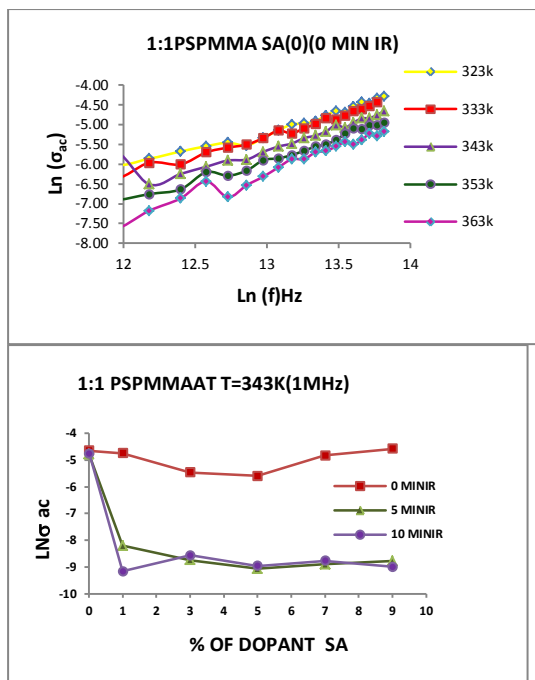### 3.1.1:- Effect of temperature and Frequency on dielectric constant before and after irradiation.

Fig 1.Variation of Dielectric constant with frequency at different constant temperatures for 1:1PSPMMA SA (0) (0 MIN IR).
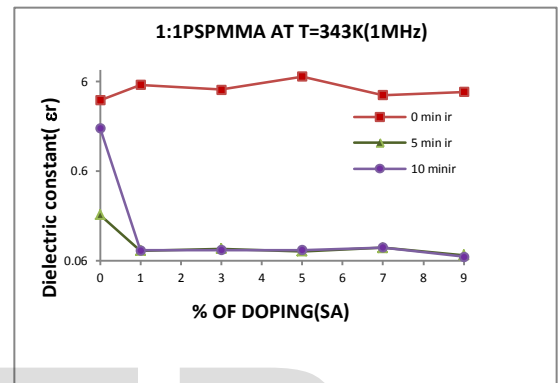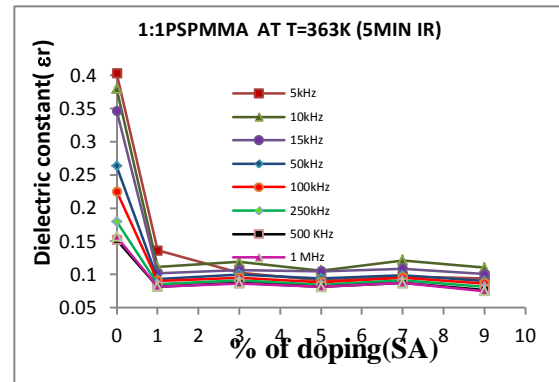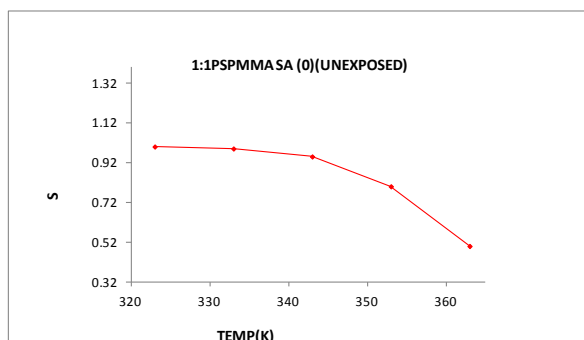

Fig 3. Variation of dielectric constant with % of doping a)At different constant frequencies b)For increasing time of exposure to IR radiation at constant frequency 1mHz and at constant temperature 343 K.
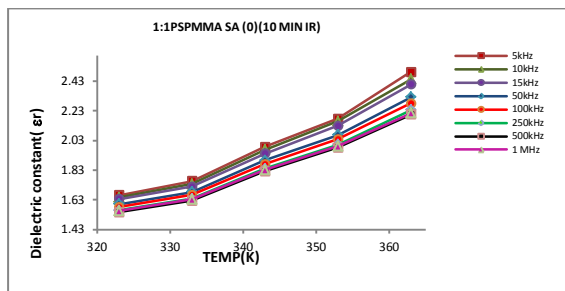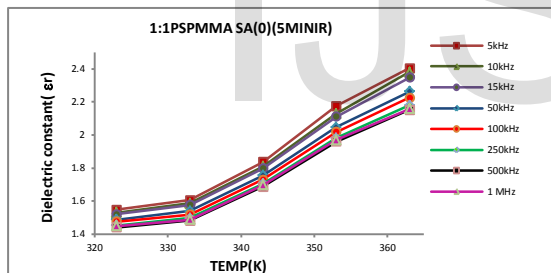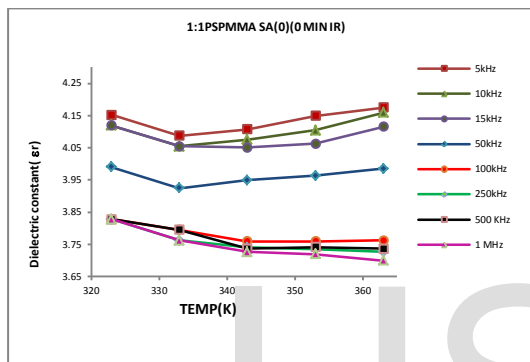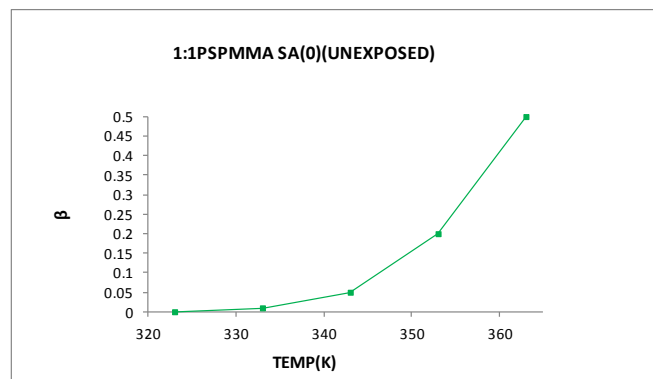

Fig 2.Variation of dielectric constant with temperature for a) 0 min exposure b)5 min exposure c)10 min exposure.

Fig 5.Temperature dependence of the frequency exponent s at constant temperature.

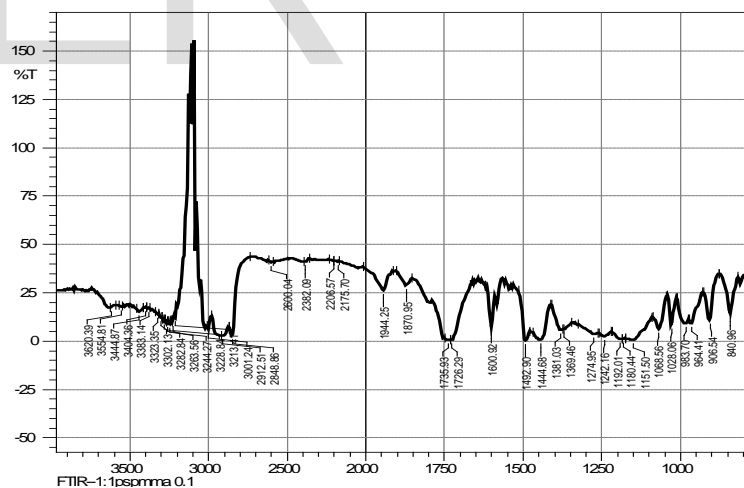**Fig 6. Temperature dependence of the value β for 1:1PSPMMA SA (0) (UNEXPOSED) sample**

Figure 4:- Variation of log of conductivity a) With log of frequency at different constant temperatures for 1:1PSPMMA SA(0)(0 MIN IR) b)With for 0 min, 5 min, 10 min expose to IR radiation at 343K at 1MHz f) c) Variation of conductivity with 10³/T.
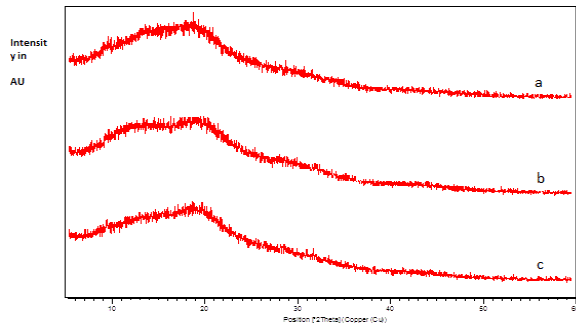

Figure 7:- a) FTIR spectra for 1:1PSPMMA SA (0)

Figure 8:- XRD spectra for 1:1 PSPMMA (a) 0% SA (b) 3%SA (c) 9%SA before irradiation
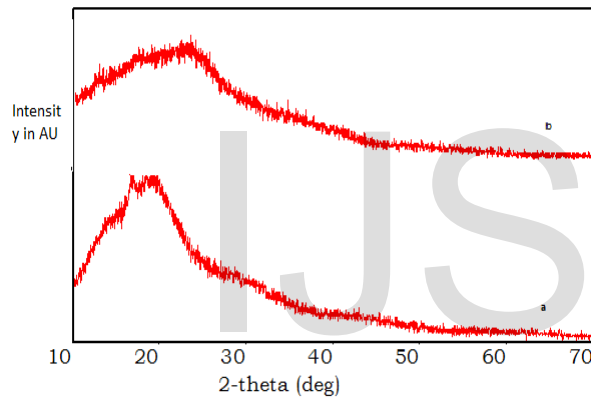
Figure 9:- XRD spectra for 1:1 PSPMMA SA (0)

(a) after irradiation (b) before irradiation
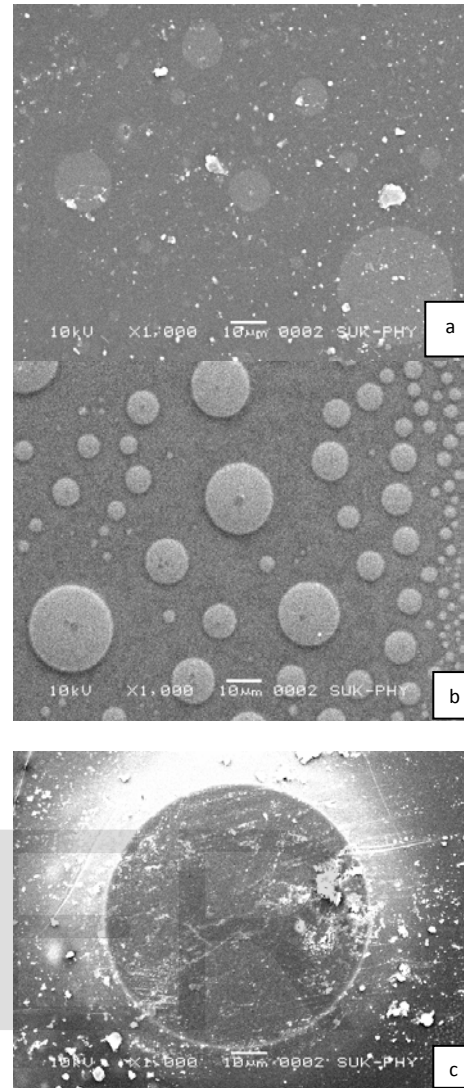
Figure 10:- SEM a) for 1:1PSPMMA SA (0) b) for 1:1PSPMMA SA (3) c) for 1:1PSPMMA SA (9)

From fig. 1 it can be observed that dielectric constant gets increases with temperature and decreases with increase in frequencies. This can be explaining as among the two polymers used to form a blend system, PS is non-polar polymer while PMMA is a weakly polar polymer [9]. The introduction of polar polymer into non polar one is reported to reduce its resistance [10], [11] and hence increases the dielectric constant. The motion possibly occurring in amorphous materials in the order of increasing temperature are

side chain motion, motion of two four carbon moieties in the main chain (The Schatzki Crunk Shaft Effect), motion of moieties containing hetero atoms in polymer chain, motion of segments containing 50-100 backbone atoms (corresponding to Tg) and motion of the entire chain as a unit [12]. These motions are responsible for the freeing of charge carriers and assisting the orientation of polar species as per the variation in the direction of applied AC electric field of constant frequency. The total polarization of the sample arises from the electronic polarization, atomic or ionic polarization and orientation polarization .Among these three contributions; orientation polarization is greatly assisted by the increase of temperature. As a result of this, increase in dielectric constant is noticed with the increase of temperature as shown in fig 1. This result is in agreement with those reported in the literature [13], [14], [15] .The microscopic behaviour of the dielectric material under the influence of a periodic (AC) electric field can be understood from the polarization which constitutes a dielectric or which is introduce during its preparation .These may be extra nuclear electrons and positively charged impurities, charged molecular species etc. The oppositely charge species having equal and opposite charges with a reasonable bond (Attractive force between them) form a dipole. This dipole under an applied electric field may undergo special or rotational displacement which may be reflected in the macroscopic behavior of the dielectric. The polarization effect is dependent on the nature of the dipoles and the frequency of the applied electric field.

As stated earlier ,under the static electric field or the AC field of low frequency, the net polarization of the sample is contributed by electronic polarization ,atomic polarization and orientation polarization .As the frequency is increased, the orientation polarization becomes unable to follow the field variation at higher frequency .As a result the dielectric constant decreases with increase of frequency as shown in fig 1and fig 2a[13], [14] ,[15] .After irradiation (fig.2b,2c,3b), the value of dielectric constant gets decreased and the rate at which the dielectric constant decreases also becomes higher with the increase in time of exposure. This can be explained as, the bonds between the atoms in many polymers have dissociation energies that are very similar to the quantum energy capable of breaking the bonds in the polymer chain to generate a cascade of reaction, oxygen radicals, hydro peroxide units, carbonyl group formation, chain cleavage, and even phenyl group cleave reaction .As a result the polarization groups may get reduced and dielectric constant gets decreased [16]. From fig 3a and 3b it is clear that the value of dielectric constant decreases with increasing percentage of doping. This can be explained as PS and PMMA are said to form a pair of compatible polymers. The compatibility exists within a particular percentage of mixing .The introduction of salicylic acid as a doping in the blend of PS and PMMA may lead to weak bonds density in the investigated compositions .This can respond to an ac electric fields much easily than the stronger bonds existing within PS and PMMA poly blends .Such weakening of bond

density is responsible for in decrease of dielectric constant.

3.1.2:- Effect of temperature and Frequency on AC conductivity before and after irradiation:-

From fig 4a it is clear that ac conductivity increases with frequency and it can be explained as a feature common to almost all amorphous semiconductor and some other disordered system is that the ac conductivity $\sigma_{ac}(\omega)$ increases with increasing frequency according to the power law relation .

$$\sigma_{ac}(\omega) = \sigma_{total} - \sigma_{dc} = A\omega^{s} ,$$
(1)

Where ω is the angular frequency, A is a constant, $s \leq 1$ is the frequency exponent, σ_{tot} is the measured total conductivity and σ_{dc} is the dc electrical conductivity. From fig 4a it is clear that $\sigma_{ac}(\omega)$ increases with frequency at any fixed temperature according to Eq. (1).Values of the frequency exponent s have been calculated from the slope of straight line of fig. 4a and are plotted as a function of temperature as shown in fig. 5.As can be seen, $s \leq 1$ and decreases with increasing temperature [17].Therefore the correlated barrier hopping (CBH) model [18] has been extensively applied to most amorphous semiconductors. This is in good agreement with obtained results, so the frequency dependence of $\sigma_{ac}(\omega)$ can be explained in terms of CBH model. The expression for s derived on the basis of this

model proposed by Elliott and Long [17], [19] can be written as

$$\beta = 1 - s = 6kT/W_m$$
(2)

Where k is Boltzmann constant, T is the temperature in K and W_m is the maximum barrier height which is the energy required to take two electrons from D^- state to the conduction band in the absence of D^+ centres .To determine the value of W_m the parameter β is plotted as a function of temperature as shown in fig 6.The value of W_m can be calculated from the slope of the obtained straight line and is equal to 0.03eV.It is known that the value of W_m is related to the optical band gap [20].The obtained value of W_m is expected to be equal to $E_g /4$ (0.75eV) [21] which is in agreement with calculated one. Activation energy is calculated from the graph of log σ_{ac} Vs $10^3/T$, and found $E_a = 0.13$ eV Figure 4a and 4c shows the variation of conductivity in the polymer blend (PSPMMA) with temperature in the range of 323K-363K. A decrease of conductivity was observed with increasing temperature. These phenomena can be explained by the fact that, thermal lattice vibration perturbs the quasi-free movement of electrons, thus scattering between electrons and phonon may occur [22].From fig 4b it is observed that the value of conductivity decreases with increase in time of exposure to IR radiation .This can be explain by the mechanism of free radical formation along the polymer backbone via chain scission. It is assumed that when free radical formation is the dominating

event during irradiation at particular total dose, the conductivity would decrease due to defects (interruptions) being formed in the electrical pathway through the sample [23] .As a result; the interchain polaron migration is much less efficient, creating a barrier to charge transport [24]. So with increase in the time of exposure of IR radiation conductivity decreases. Also the reason for decreasing conductivity is the presence of oxygen during irradiation and when the samples were taken out of the exposure vessel and move into an air (oxygen) environment for testing[25].From fig 4b it can be observed that the value of conductivity gets decreases with increase in percentage of doping as compared to undoped ,both for unexposed and exposed samples.We can explained it as the decrement of conductivity is due to the addition of SA contribute to the over crowed of the ionic dopants thus reduces the number of charge carriers further gives limitation of the mobility of ions [26]. The FTIR spectra of 1:1PSPMMA(0) shows the presence of C=O stretching at 1735 cm^{-1},C-O stretching at 1068.56 cm^{-1},CH3 bend at 1381.03 cm^{-1} and CH2 bend at 1492.90 cm^{-1} for the PMMA unit. Also the presence of stretching at1600.92cm^{-1} and 3001 cm^{-1} indicates the presence of aromatic C=C stretching and aromatic C-H stretching respectively. The peak at 750cm^{-1} 1698cm^{-1} are the two peak monosubstitution pattern peak, which is the characteristic peak indicates the monosubstituted aromatic ring .The absence of C=C stretching at 1650 cm^{-1} confirms the absence of vinylene group and formation of blend as shown in fig.7.The XRD spectra

of   1:1PSPMMA   SA   (0),1:1PSPMMA SA(3),1:1PSPMMA SA(9) reveals the amorphousness of the sample before irradiation as shown in fig 8 a, b ,c and XRD spectra after irradiation is also shows the amorphousness of the sample, as shown in fig 9a, b .The Scanning Electron Microscope (SEM) photographs are shown in fig. 10 a), b),c) for sample 1:1PSPMMA (0), 1:1 PSPMMA (3), 1:1 PSPMMA (9).The SEM photographs provide the presence of spherulites. There exists the boundary between the spherulites which shows the existence of amorphous nature. The spherulites also show the surface roughness that may be related to the crystalline fraction of the material. The results reveal the decrease in crystalline or increase in amorphous phase with the increase with the increase in the percentage of doping salicylic Acid. These observations are in agreement with the interpretations of XRD spectra as shown in fig. 8 a), b),c) and 9a) ,b).

4:- Conclusion: - The conductivity of 1:1PSPMMA system increases with frequency and decreases with increase in doping percentage and independent of temperature before irradiation and after irradiation.AC conductivity decreases with the increase in time of exposure to IR radiation. This can be explaining by the mechanism of free radical formation along the polymer backbone via chain scission. The value of dielectric constant increases with increase of temperature and decreases with increase in percentage of dopant (SA),Increase in frequency and increase in time of exposure to IR radiation. After irradiation the

rate of decreasing the dielectric constant value increases**.**SEM images and XRD spectra reveals the amorphousness of sample. An FTIR spectrum confirms the formation of blending. So this blended system can be used for capacitors, batteries and radiation sensors. The communication revolution (Microsystems operating at 1 V) and the technological thrust toward portable ,high circuit density , and low power electronic Microsystems ,have necessitated the use of low dielectric constant as the interval dielectric material, As dielectric constant get decreases after exposure to IR radiation,

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