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RESEARCH ARTICLE

Effect of Gamma Radiation on the A.C Electrical and Dielectric Properties of Prepared Pure and Doped Polyaniline Salt

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ABSTRACT

Purepolyaniline and doped with hydrochloric acid was prepared in different molarities at room temperature. The a.c electrical properties were stadied.AC conductivityσ_{ac} (ω), is found to vary as ω^S in the frequency range (100Hz-10MH), S< 1and decreases indicating a dominate hopping process. Thedielectric constant $\varepsilon_1$and dielectric loss ε_2 have been determined for bulk polyaniline. ε_1 decrease with the increase frequency. Electrical conductivity measurements increase with the increases both of the amount of HCl and the dose of radiation. The dielectric investigations show decrease with dose radiation.

Keywords: polyaniline, gamma radiation, electrical conductivity, dielectric constant

INTRODUCTION

Conducting polymers have received much attention due to their potential usage in several applications such as biosensor [1] electrochemical display [2] corrosion protection [3] or even rechargeable batteries [4]. Polyaniline is a type of conductingpolymer which received the most attention due to the discovery of its high electrical conductivity [5] reversible acid-base chemistry in aqueous solution, thermal and environmental stabilities and easiness of synthesis [6].Since the discovery of electrically conducting polymer by Alan MacDiarmid, Alan J. Heeger, and Hideki Shirakawa in 1976, intensive investigations have been carried out on the new generation of “synthetic metals” due to their unique combination of electronic and optical properties and processing advantages [7]. The electrical conductivity is achieved in the conjugated polymers by means of delocalized of the π-electrons that allow charge mobility along the backbone of the polymer chain. The synthesis of conducting polymers has been accomplished by oxidizing or reducing process either through chemical doping [8] or electro-chemical doping [9]. The aniline polymers have the general formula $[(\text{- B- NH-B-NH})_y(\text{-B-N =Q=N-})_{1-y}]_x$ in which B andQ denote the C_6H_4 rings in the benzenoid and quinonoid forms, respectively. Thus, the aniline polymers are basically poly (p-phenyleneamine)s, in which the intrinsic oxidation states can vary from that of fully reduced leucoemeraldine (LM y=1), through that of the 50%intrinsically oxidized prenigraniline (PNAy=0).The polymer canachieveits highly conductive state either through protonation (doping) of the aminenitrogens(=N-) in its EM oxidation state or through the oxidation of the amine nitrogens(-NH-) [10]. A numberof studies have been reported on the electrical and dielectric properties of polymericnanocomposite of PANI, as wellas,polypyrrolecomposites.The properties of these systems aresensitive to particle, inter-particle interaction and temperature.Synthesisof materials with a large dielectric is very important for the development of a new generation dynamic RAM and microelectro-mechanicalsystem. High dielectric behavior is possible for application in conductive paints, rechargeable batteries, sensors and actuator [11].The aim of this work is to study the effect of gamma rays on the electrical properties of prepared polyaniline.

Experimental work

The preparation of (PANI) is based on the oxidation of (0.2M) aniline hydrochloride with (0.25M) ammonium peroxydisulfate in aqueous medium. The pure sample was prepared in distilled water and the doped sample with different molarities of HClaquous solution (0.5M, 1M and2M). To prepared sample doped with 2M aniline hydrochlorid was dissolved in (1M) HCl in a volumetric flask to 50ml of solution, ammonium pexroywas similarly dissolved in (1M) HCl also to 50ml of solution both solutions are mixed at room temperature in a rounder, and gentlestirring to polymerize the mixture is left to rest to the next day. The (PANI) precipitate is collected on a filter and washed with three 100ml of (0.2M) HCl, and 150ml of acetone. Polyaniline (emeralidin) hydrochloride powder is dried in air for about one hour then in vacuum oven about (80 ºC) for 6 hours the average yield was (1.85)gm. The A.C electrical measurements are used to investigate polyaniline samples doped during polymerization with various molarities of HCl. The polyaniline powder was thoroughly grounded in a morter to obtain very fine particles, and then it was compressed under a pressure 10 tone in the form of a pellet. The resulting pellet has a diameter of 1.3cm and thickness of (1.88-1.79mm). To improve theelectrical contact the faces of the pellet were coated with aluminum by thermal evaporation. The LCR meter models (HP-4274A and HP-4275A) were used for the ac measurements. The sample was placed in a holder specially designed to minimize stray capacitance. The range of frequency was 100Hz - 10MHz. For the sample under investigation, the specimen capacitance C, dissipation factor D and resistance R were measured. The total conductivity was calculated from the following equation: $\sigma_t(\omega) = d/RA$, where d is the thickness of the sample and A is the cross-section area.

The ac conductivity $\sigma_{ac}(\omega)$ was calculated by using the relation: $\sigma_{ac}(\omega) = A\omega^S$where$\omega$ isangular frequency, A is a constant;S (≤ 1.0) is frequencyexponent. The dielectric constant ε_1 wascalculated from the equation: $\varepsilon_1 = Cd/A\varepsilon_o$,where $\varepsilon_o$is the permittivity of free space =8.854x10^{-14}(F/cm). The dielectric loss$\varepsilon_2$was calculated from the equation: $\varepsilon_2 = \varepsilon_1 \tan\delta$, where $\tan\delta$ is the dielectric tangent loss ($\delta = 90 - \phi$).

RESULTS AND DISCUSSION

Gamma rays (γ- radiation) imparted it is energy in the medium through various processes such as ionization and excitation of atoms, chemical bound scission, grafting, cross-linking and disintegration of molecules. Figure 2 shows the variation of the total conductivity as a function of frequency for polyaniline pure and doped withHCl (0.5, 1 and 2M) at various doses. The total conductivity can be expressed as in equation (1).

$\sigma_T(\omega) = \sigma_{dc} + \sigma_{ac}(\omega)$ ------------(1)

σ_{dc} is the dc conductivity.

At frequency independent, the conductivity is served by weakly disassociated ions by irradiation such as Cl^-, H^+ and OH^- while at frequency dependant the conductivity is served by relaxed and phonon assisted process [12].$\sigma_{ac}$is obtained by subtracting the dc conductivity from the measured total conductivity according to Eq.(1). Figure (3) shows the dependence of a.c. conductivity on frequency atvarious doses at room temperature. It is clear from the figure that $\sigma_{a.c}$ increases with the increase in frequency. The frequency exponent s can be calculated from the slope of the straight lines in figure 3, the exponent s is less than unity. The general values of s appear to be consistent with a hopping process of charge carriers (protons) between polymer chains. Figure 4 shows the variation of S values as a function of HCl M concentration and listed in Table (1).

Polyaniline can be made more conducting by protonation with an acid such as hydrochloric acid (HCl) [13]. The presence of the acid result is the protonation (increased proton concentration) of nitrogen atoms; the degree of protonation depends on the PH of the acid solution [14]. Fig.5 show the effect of HCl content on the ac conductivity at room temperature, the time of radiation at 1.20 hour in this plot indicates that the low frequency behavior is less than 10^4Hz of all the sample looks like a straight line dc conductivity dominated and then the absolute conductivity for individual sample increases as a function of frequency and the conductivity increases with increased in HCl concentration (0.5M, 1M and 2M).Figure 6 shows the variation of electrical conductivity at 100 KHz as a function of HCl concentration(protonconcentration) at various doses. Themeasurement of radiation-induced conductivity inpolymers has been developed as a technique to study theinfluence of radiation on the electrical behavior of polymeric layers used in radiation environments. Electrical conductivity of organic polymers can be significantly increased during the time that the material is exposed to a radiation flux due to the formation of transient conductive species (electrons, holes). Thespecies also known as charge carriers rapidly recombine once the irradiation is stopped with the result that the conductivity quickly decreases to near the initial value. Theabsorption of relatively high doses, however, may cause permanent changes in the conductivity [15, 16].

The dielectric constant was calculated from the measured value of capacitance C_p in the range of frequency 100Hz-10MHz. The frequency dependence of ε_1 at different doses is shown in Fig. 7. It is clear from the figure that ε_1 decreases with the increase in frequency. The variation is small at high frequencies. The decrease of ε_1 with frequency can be explained as follows: at low frequencies ε_1 for polar materials is due to the contribution of multi-component of polarizability, deformational polarization (electronic, ionic, orientation, and interfacial).When the frequency is increased, the dipole will no longer be able to rotate sufficiently rapidly. So their oscillations are lagging behind those of the field. As the frequency is further increased, the dipole will be completely unable to follow the field and the orientation stopped, so $\varepsilon_1$decreases at a higher frequency approaching a constant value due to the interfacial polarization [17].

CONCLUSION

A.C conductivity and dielectric behavior of polyaniline /HCl have been presented in this work. These are synthesized by the 'in-situ polymerization. The AC conductivity of these composites will obey the power law well above the critical frequency .The dielectric behavior of PANI shows nearly a Debye-type relaxation, because of this, there is a decrease in the dielectric constant with increase in frequency. Numbers of blends which are different in composition were exposed to gamma radiation to various doses and the effect of irradiation time and composition of polymers used in the blends on the conductivity of films were investigated by using conductivity measurements, PANI- has also been found to be very efficient in inducing conductivity in gamma-irradiated PANI. The results clearly showed that ionizing radiation is an effective tool to induce conductivity in the blends of PANI. The main mechanism behind this radiation-induced conductivity is insitu doping of PANI-base with HCl released from partner polymers and compounds by the effect of radiation.

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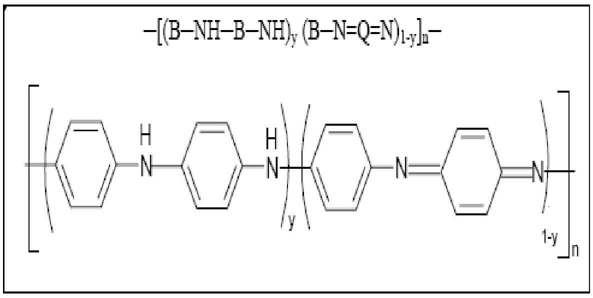
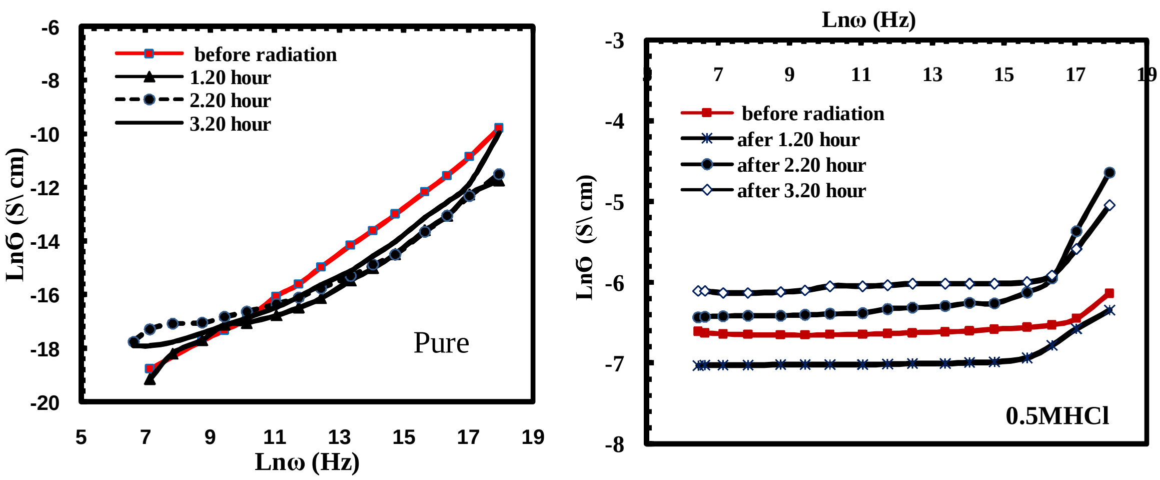


Figure 1: The structure of the polyaniline chain [10].



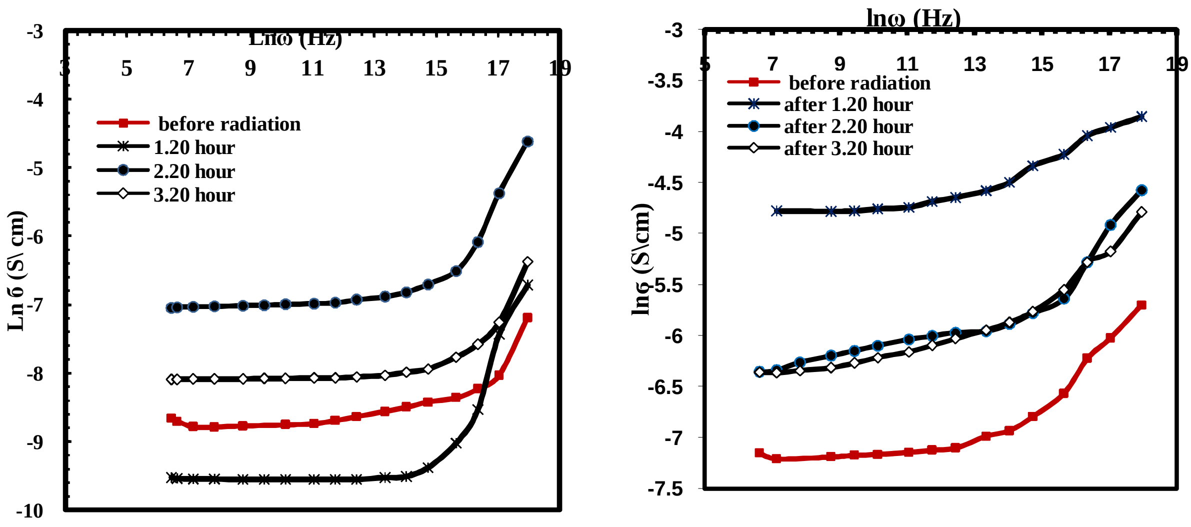
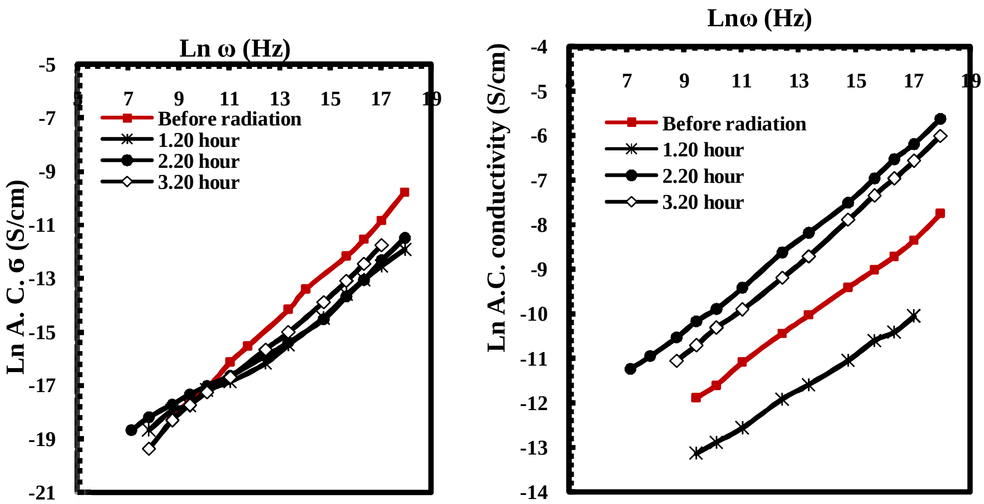


Figure2:Frequency dependence of σ_t for polyaniline pure, 0.5 M, 1M, and 2M HCl before and after radiation.



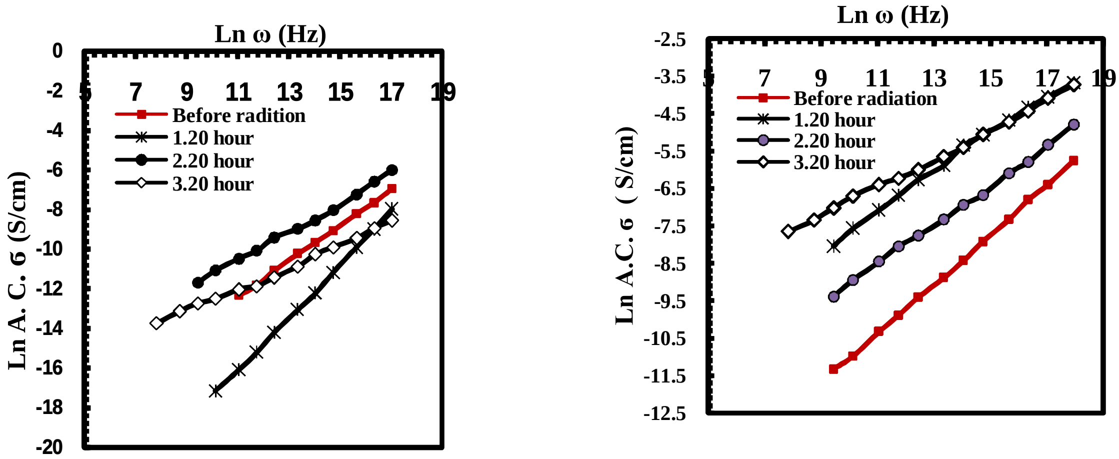


Figure 3: Variationofa.c conductivity as a function of frequency at various doses of radiation

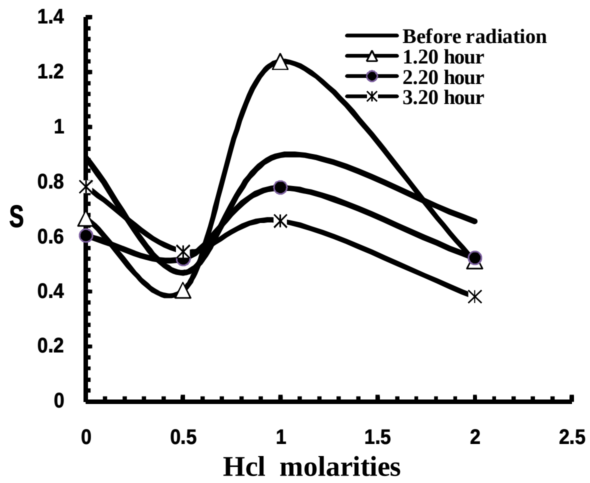


Figure 4: Variation of S with HCl Mconcentration

Table 1: The values of S

concentration HCl Mol.	Before radiation	1.20 hour	2.20 hour	3.20 hour
0	0.888	0.668	0.604	0.782
0.5	0.468	0.405	0.519	0.546
1	0.897	1.238	0.779	0.658
2	0.656	0.512	0.522	0.381

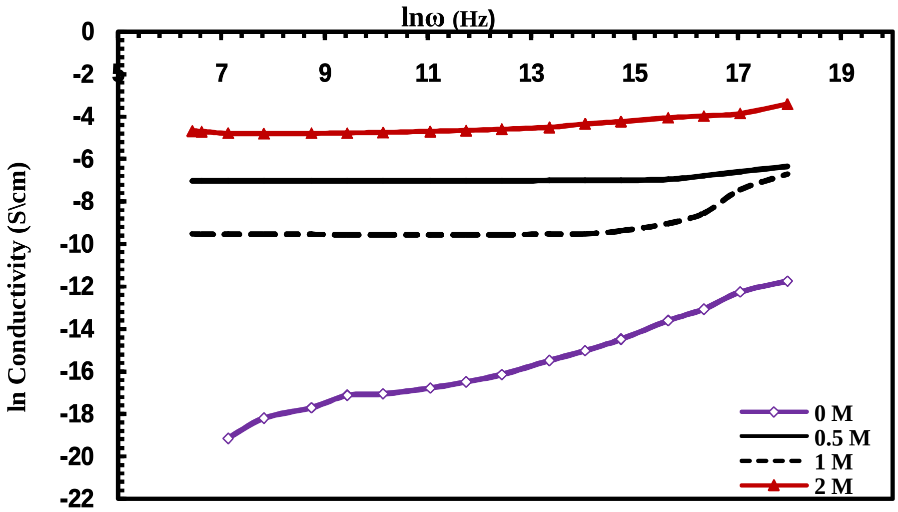


Figure 5: Variation of electrical conductivity as a function of frequency for different concentration of HCl M at time 1.20 hour.

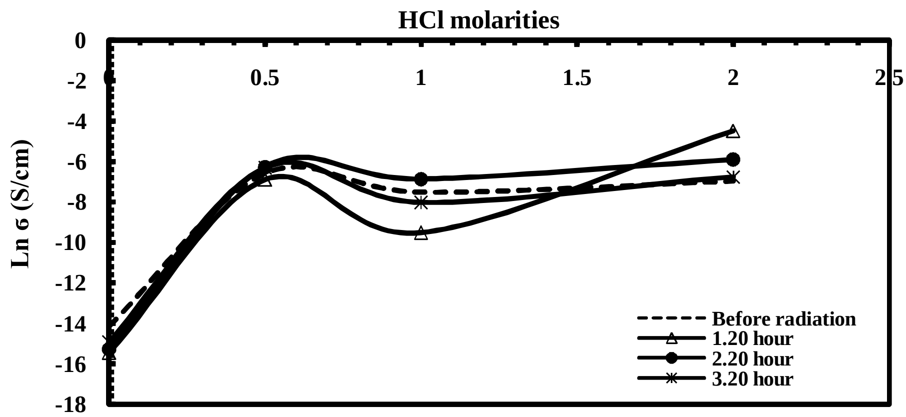


Figure 6: Variation of conductivity at100KHz as a function of HCl molarities in different doses.

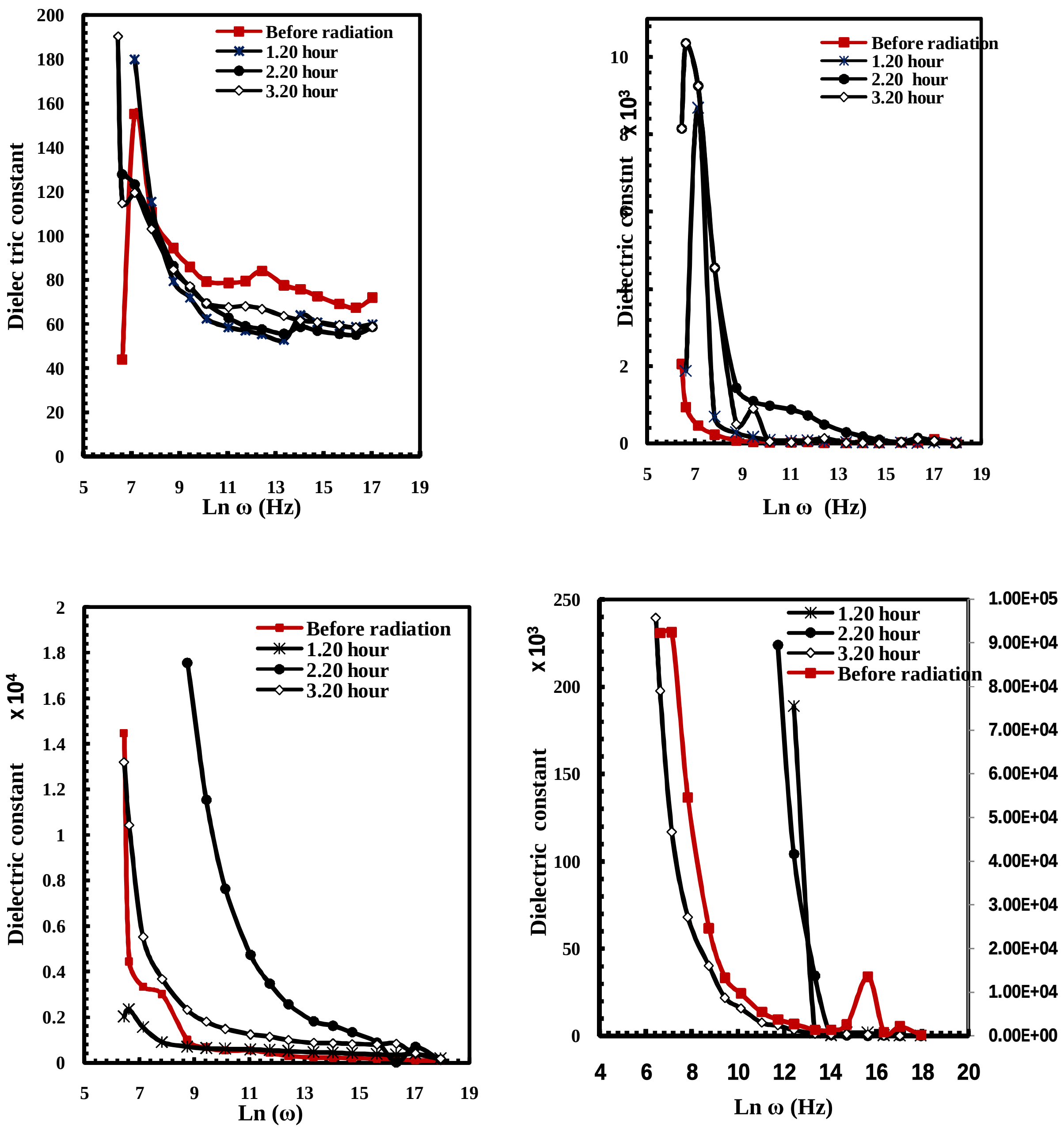


Figure 7: The variation of dielectric constant as a function of frequency.