Chapter 3

Experimental Part

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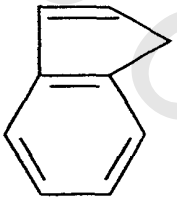
3.1. Materials:

- **Monomers:**

1. Indene (In) (Riedel-De-Haeno AG-Seelze-Hanover), was purified by distillation under pressure before use.

2. Acrylonitrile (AN) (Cambrian), was distilled at 70° C before use.

3. Acrylic acid (AA) (BDH England), was used without further purification.

Monomer	Empirical Formula	Molecular Structure
1. Indene	C_9H_{10}	
2. Acrylonitrile	C_3H_3N	CH_2=CH-CN
3. Acrylic Acid	$C_3H_4O_2$	CH_2=CH-COOH

- **Solvents:**

Dimethyle formamide DMF, Diethyle formamide, DEF (Prolabo France) were used as received without purification. Dioxane (Aldrich), petroleum ether, acetone & benzene were purified according to conventional procedures.

- **Initiators:**

4. Azobisisobutyronitrile AIBN (E.Merk), was twice recrystallized from methanole and kept in the refrigerator ready for use (m.p 104°C).

5. potassium persulphate.

6. Conc. H_2SO_4.

3.2. Preparation of the Investigated Samples

3.2.1. Homopolymerization Procedure:

Glass vials were charged with the required amounts of the monomers, together with the required amount of the initiator (AIBN) in the polymerization of acrylonitril and acrylic acid, and conc. H_2SO_4 to polymerize the indene, and dioxane or distilled water as solvents. The vials were then closed with rubber septum through which passed needle to equilibrate the pressure. The polymerization was done at 60° C in a water thermostat with

periodical shaking for a definite time. At that time, the polymerization reaction is stopped and the content is poured in the vials into a large amount of non solvent (ethyl alcohol). The precipitated polymers were purified by repercipitation and allowed to dry in oven at 50° C.

3.2.2. Copolymerization Procedure:

As chemically introduced polymerization, glass vials, were charged with the required amounts of the two comonomers (at different molar ratios) together with the suitable amount of initiator (AIBN) and the solvent (dioxane). The vials were then closed with rubber septum through which is passed a needle to equilibrate the pressure. The copolymerization was done at 60° C in a water thermostat with periodical shaking for a definite time. The copolymers of In/AN was precipitated in ethanol while the In/AA copolymers was precipitated in water. The copolymers were purified by several reprecipitations to ensure complete elimination of the unreacted monomers and homopolymers, filtered, washed, &finally dried at 50° C to constant weight.

3.3. Copolymer Characterization

Copolymers composition was calculated on the basis of nitrogen for the In/AN copolymers and carbon contents for the In/AA copolymers. The analysis was performed in the Central Micro Analytical Unit in Cairo University.

3.3.1. Reactivity Ratio Determination:

The reactivity ratio r_1 of indene and r_2 of the other monomers were calculated in this work according to the methods of Finman and Ross and Kelen and Tüdos.

3.4. Spectral Analysis:

3.4.1. Infrared Measurements:

FTIR spectroscopy was used for confirmation of the copolymers compositions.

3.4.1.1. Infrared Spectrometer

There are two major types of infrared spectrometers: Classical (dispersive) and the modern (fourier transform, or f.t). The most important difference between the modern fourier transform spectrometer and the classical type is the use of a Michelson interferometer, rather than a diffraction grating. Both types of instruments produce the same information, but they differ in resolution power. In the present work, the infrared spectrophotometer used was Mattson 1000 series LC operating. Issue I (0791) spectrophotometer.

3.4.1.2. Sample Preparation for IR Measurements:

The pressed disc potassium bromide was used for IR spectrophotometric studies of the prepared homopolymer and copolymer samples. Two mg. of each sample was carefully grinded with 198 mg of KBr to give1% concentration of fine power. The mixture was placed in a special mould; the mould was connected to an evacuating pump to remove water vapor, during the evacuation the mould pressure is applied slowly. The final pressure 10 tons held for 5 minutes and then slowly released. A disc diameter of 13 mm is finally obtained; the exact surface area for each sample was calculated. It is noticed that very careful grinding and mixing is essential to avoid band broadening and/or frequency shift of the absorption maximum.

The films were prepared for IR measurements where film thickness is 15 mm.

3.4.2. X-Ray Diffraction:

X-ray diffraction pattern of different forms have been investigated using a modern Philips diffractometer. Nickel filtered cupper radiation (λ = 1.542 °A) was used. All the diffraction patterns were examined at room temperature and under constant operating conditions (36 KV & 16 mA). The scanning rate was 1 degree (2θ/min). The studied samples were grounded to a fine powder form and mounted in appropriate aluminum folder. The X- ray diffraction pattern is essentially a plot of intensities as a

function of the angle of reflection even by the material. It is a well known fact that the angular position of reflections and their relative intensities are characteristic the structure of a crystalline sample.

Absence of any diffraction peaks in the X-ray pattern indicates the amorphous character of the sample under examination.

3.5. Thermal Analysis:

3.5.1. Thermogravimetric Analysis TGA:

Thermogravimetric analysis was performed for determining the thermal dissociation temperatures of the copolymers. Two samples of the copolymers of each system were weighted (0.1 gm of each sample) & placed in a crucible and then the crucibles were weighted containing the copolymer, and then heated in the oven at different temperatures every 10 minutes, starting with 60° C until reach 600° C. Every time the crucibles were weighted W_1. Then the weight loss Wt% calculated from the following relation:

$$Wt\ \%\ loss\ = \frac{W - W_1}{W} * 100 \qquad (3.1)$$

Where W is the weight of the sample before heating and W_1 is the weight of the sample after heating every time.

3.5.2. Differential Scanning Calorimetry DSC:

Differential Scanning Calorimetry thermogram was used to study the thermal effective that takes place during heating the sample. From the DSC thermograph of the sample under test, phase transition, could be easily detected. In the present work, the DSC thermogram of the sample, were carried out using the Japanese device Shimadzu DSC-50 figure (3.1). The samples weight was 5 mg. it was sealed inside an aluminum pan to the left where the reference sample was to the right. The measurements were carried out in an atmosphere of Nitrogen. The samples were heated from the room temperature up to near the melting point of the sample at a constant rate of 5 °/min.

3.6. Electrical Conductivity Measurements:

3.6.1. Sample Preparation:

- The sample was in the form of blocks, firstly it was molted in a cleaned Agate morter until it became in the form of powder. Then it compacted under pressure of 90 Passcal to be a compacted disk (1cm diameter) of the powdered material, for each 200 mg. of each sample.

- Some of the samples were in the form of rubber so they made in the form of film. This was achieved by dissolving the sample in a definite amount of dimethyle formamide DMF. The solution was then placed on a hot plate for 10 minutes to ensure complete dissolution. The solution was then poured onto a peter dish &dried at room temperature for several days. Finally the sample was dried in an oven at 60 °C.

3.6.2. The Sample Holder:

The sample holder used for the electrical conductivity measurement is shown in figure (3.2), it consists mainly of two copper electrodes. The upper &the lower electrodes were held in close contact with the sample, by a stainless steel spring. The two electrodes are supported on a copper frame isolated by a ceramic tile. The sample could be handled and introduced quite easily between these two electrodes. The holder was charged into a well calibrated electric oven. The oven was connected by a temperature controller to control the temperature of the oven. The temperature range of the oven is from room temperature to 700 °C.

3.6.3. Temperature Variation of the Sample:

The sample temperature was raised by means of cylindrical electrical furnace operated by variable transformer in order to control the rate of change of temperature.

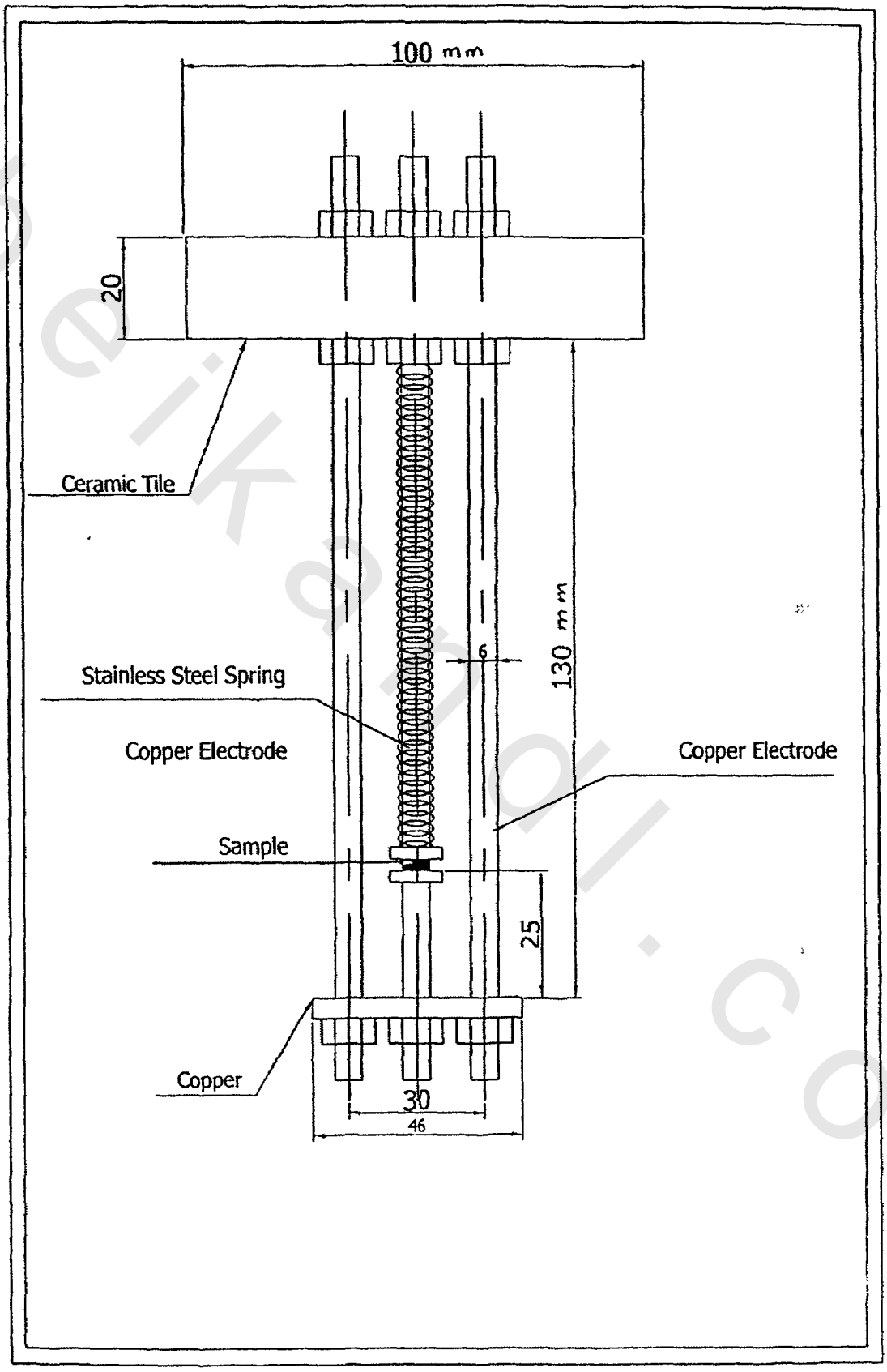


Figure (3.1): The sample holder used for conductivity measurements.

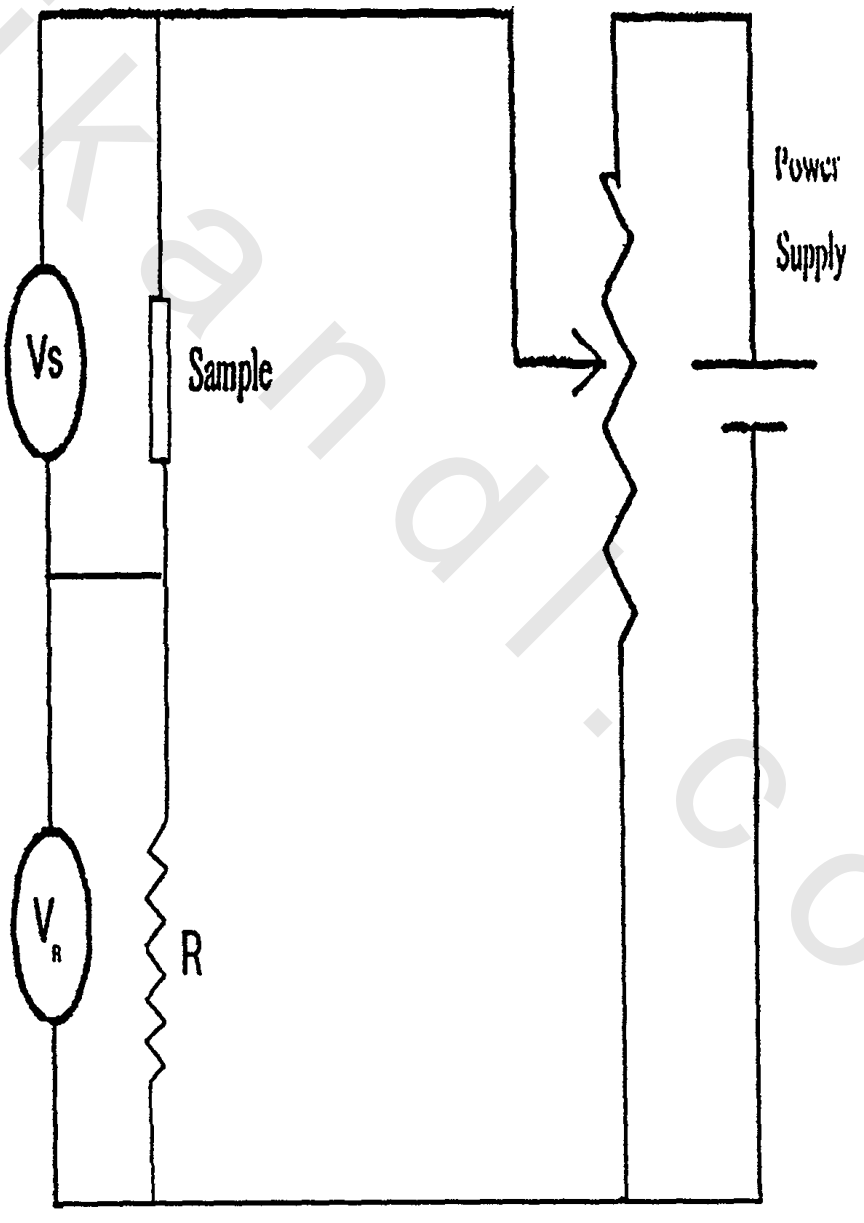


Figure (3.2): The electrical circuit used in determining the dc conductivity.

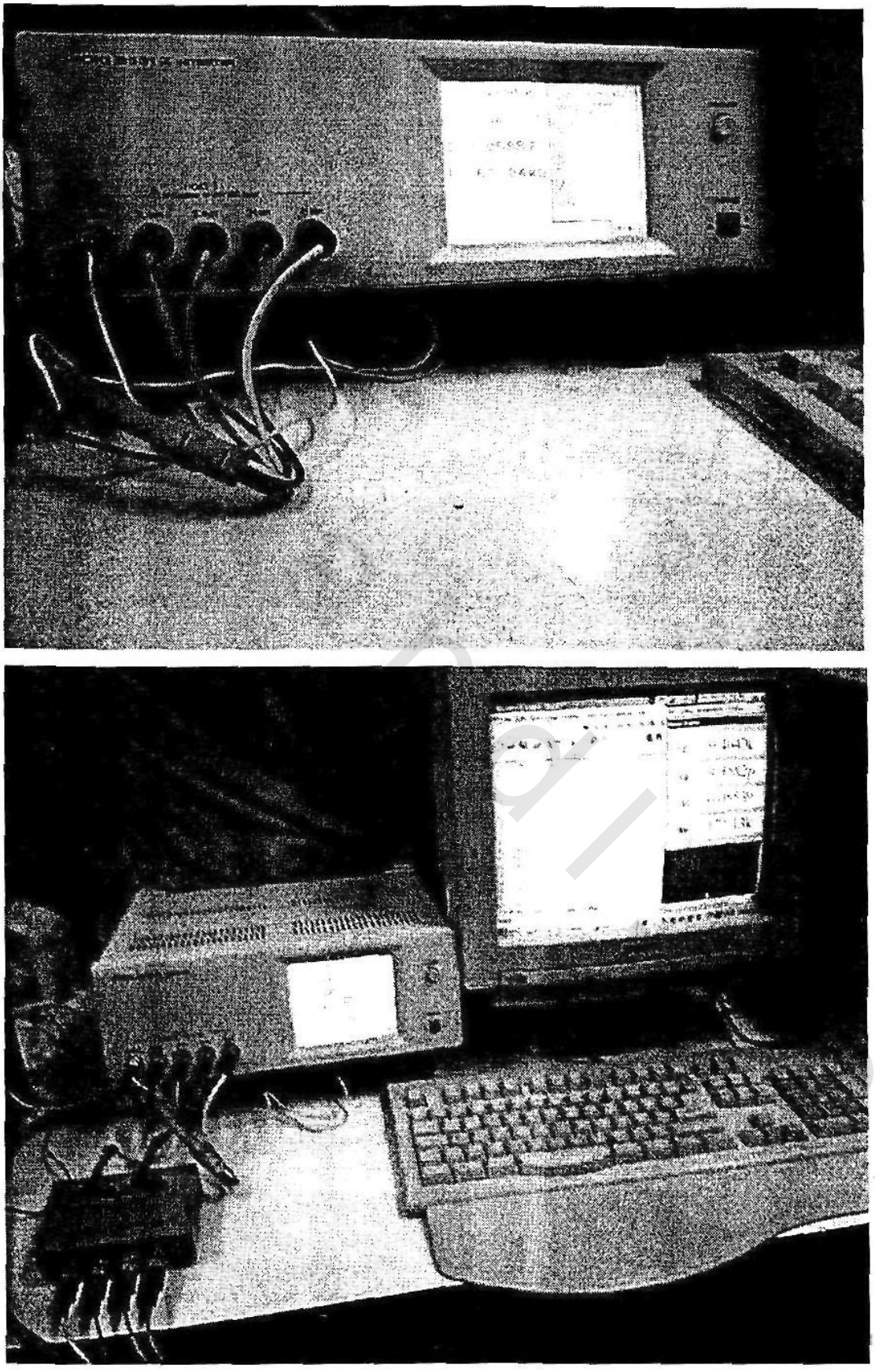


Figure (3.3): The computerized RCL bridge mode Hioki 3531 Z Hitester.

The temperature was measured using the thermocouple or thermometer which placed inside the furnace and attached to the sample. The conductivity of the samples was measured by both D.C & A.C methods.

3.6.3.1. D.C Conductivity Measurements:

The sample resistance was measured using the potential drop method using the following circuit figure (3.3).

The sample resistance was calculated as follow:

$$\frac{V_R}{R} = \frac{V_s}{R_s} \qquad (3.2)$$

$$R_s = \frac{V_s \cdot R}{V_R} \qquad (3.3)$$

Where **R** is a known value, then the resistivity of the sample was determined from the relation:

$$\rho = R_s \cdot \frac{A}{d} \qquad (3.4)$$

Where A & d are the dimensions of the disk of the sample. A = area (cm^2), d = thickness of the sample disk (cm). The D.C conductivity of the samples was measured over the temperature range of (298-443) K using the electric circuit shown above.

3.6.3.2. A.C Conductivity Measurements:

The A.C conductivity of all samples were measured over the temperature range (298-443) K in the frequency range from 100 KHz to 1 MHz using the RCL bridge mode Hioki 3531Z Hitester figure (3.4).

The bridge can be used to measure several parameters, but we use only the following parameters C_p (Parallel equivalent static capacitance), D (Loss coefficient) and R_p (Parallel equivalent resistance) to calculate the dielectric loss, dielectric constant & the conductivity of the samples.

The real part of the dielectric constant was calculated from the following relations:

$$\varepsilon' = LC/A\ \varepsilon_o \qquad (3.5)$$

where L is the thickness of the compacted disk in m, A is the area in m^2, C is the capacity in farad and $\varepsilon_o = 8.85*10^{-12}$.

The imaginary part of the dielectric constant was calculated from the formula:

$$\varepsilon'' = D \tan \delta \qquad (3.6)$$

The AC conductivity was calculated using the following relation:

$$\sigma_{ac} = \omega \varepsilon_o \varepsilon'' \qquad (3.7)$$