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DIELECTRIC PROPERTIES OF ATACTIC AND ISOTACTIC POLYSTYRENE

BY

THADDEUS F. KROPLINSKI

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

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ABSTRACT

The purpose of this investigation was to determine the dielectric constant and dissipation factor of atactic and isotactic polystyrene at 25°C and at frequencies of 0.1, 1.0, 10, and 100 kilocycles per second. In addition, the effects of molecular weight and crystallinity on the dielectric properties of polystyrene was also studied.

Polystyrene slabs of uniform thickness were prepared by molding the polymer under heat and pressure. The isotactic polystyrene slabs were annealed at 175°C for various lengths of time to achieve varying degrees of crystallinity.

The molded polystyrene slabs were fitted with circular aluminum foil electrodes to form a three terminal guarded electrode system. The electrical measurements were made using a variable capacitor in conjunction with a General Radio Impedance Comparitor. The capacitance and dissipation factor of the specimen was measured by using the variable capacitor as the standard to balance the impedance difference of the specimen.

It was found that the dielectric constant and dissipation factor of atactic polystyrene is independent of molecular weight within the range of 224,000 to 337,000. For very low molecular weight, 13,000, the dielectric constant increased.

The isotactic polystyrene was found to have a higher dielectric constant than the atactic polystyrene. This increase was attributed

to the stereoregularity of the isotactic polymer resulting in less dipole-dipole cancellation. Increasing the degree of crystallinity by annealing resulted in a decrease in dielectric constant indicating that the relaxation takes place essentially in the amorphous phase. The dissipation factor of the isotactic polystyrene decreased with increasing frequency indicating the possibility of a maximum loss peak at a frequency lower than 0.1 kilocycles.

The dissipation factor and dielectric constant of atactic and isotactic polystyrene were found to be relatively low indicating a very low dipole moment per repeat unit or low polarity for polystyrene.

APPROVAL OF THESIS

DIELECTRIC PROPERTIES OF ATACTIC AND ISOTACTIC POLYSTYRENE

BY

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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I - INTRODUCTION

The use of plastics in the electrical industry has grown considerably in the past twenty-five years. With electronic components being made smaller and more compact, the requirements of the plastics such as low temperature flexibility, hydrolytic stability, moisture vapor permeability, heat distortion temperature, and dielectric properties have become increasingly more demanding. As a result, extensive literature has been published on the properties of polymeric materials. Much of this work, however, has been directed toward finding suitable materials for the manufacture of insulators and capacitors. Of greater interest are the investigations where the objective has been to relate these properties to molecular and inter-molecular structure.

The object of this investigation was to measure the dielectric properties of atactic and isotactic polystyrene, and to study the effects of molecular weight and crystallinity on these properties.

II - LITERATURE REVIEW

The literature review for the study was divided into five parts: Polystyrene, crystallinity, crystalline isotactic polystyrene, dielectric behavior of polymers, and dielectric properties of polystyrene.

Polystyrene

Because of its outstanding electrical insulation properties characterized by its very low dielectric loss at all frequencies, its small dielectric permeability, and its very high resistance to water, polystyrene is a valuable electrical insulation material especially for the manufacture of high frequency components and long distance cables.

The monomer, styrene (vinylbenzene, phenylethylene) is used in the production of polystyrene. On an industrial scale, styrene is produced by the action of ethylene on benzene in the presence of aluminum chloride (11). The ethylbenzene formed undergoes dehydration to form the styrene monomer. The structure of styrene and polystyrene are given in Figure 1, page 3.

Styrene is a colorless liquid with a boiling point of 145.2°C, and is easily polymerized even at room temperature. In order to prevent undesirable polymerization, inhibitors such as hydroquinone are added to the styrene. This activity of styrene is explained by the unbalanced nature of the molecule due to the phenyl group on the ethylene bond(21).

The polymerization of styrene is a chain reaction which proceeds readily by all known methods of polymerization with the formation of a water-white polymer of high clarity(12). In practice the block polymerization and the emulsion polymerization methods are usually used. Styrene is polymerized on an industrial scale in the presence of initiators, such as organic peroxide compounds and persulphates.

To prepare block polystyrene, the monomer is mixed with the initiator (0.1 - 0.5% based on the weight of styrene) and poured into molds. The monomer is slowly converted into solid polymer by

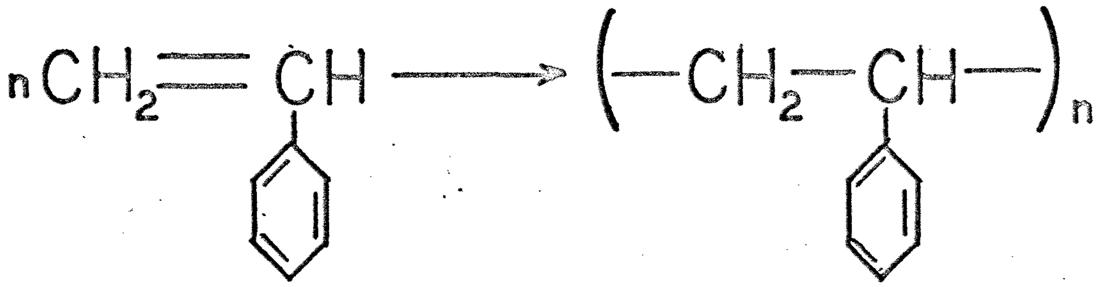

FIG. 1. POLYMERIZATION OF STYRENE

heating to 60 - 80°C. Polystyrene obtained by block polymerization always contains residual monomer and low molecular weight products which lead to a reduction in the thermostability and aging properties. Polystyrene intended for further treatment such as extrusion is crushed into fine pieces and the residual monomer can be removed by drying under vacuum. In the production of polystyrene intended for use in the electrical industry, the block polymerization is carried out without the use of initiators as these could cause deterioration of the dielectric properties.

To carry out the polymerization by emulsion polymerization, an emulsion of styrene in water is made by means of emulsifiers such as sulphonated fatty alcohols. The initiator, hydrogen peroxide or potassium persulphate, is dissolved in water and added to the emulsion. The styrene must have been freed from inhibitor by washing with an aqueous solution of alkali. Polymerization takes place in two to three hours at 85 - 90°C. The polystyrene is then precipitated as a fine powder, and then washed and dried under vacuum. Emulsion polystyrene may be contaminated by electrolytes due to incomplete removal of the emulsifiers, and the acids and salts used to precipitate the polymer. It is therefore not suitable for use as a high frequency dielectric.

Properties of Polystyrene

Polystyrene is an outstanding insulating material characterized by a very low dielectric loss at all frequencies up to a temperature of about 80°C at which point it softens. Its dipole moment is small, 0.20D(5,15,31), which accounts for its excellent dielectric properties. It is a linear polymer, available commercially only in the atactic amorphous form. Isotactic polystyrene can be prepared by use of the Ziegler-Natta catalysts, but offers little advantage in properties and it is not available commercially. Polystyrene is relatively inert chemically, and is resistant to alkalis, halide acids, and oxidizing and reducing agents(7). Its optical properties - color, clarity, and transparency, are excellent, and its high refractive index (1.60) makes it useful for plastic optical components. Polystyrene is readily attacked by a large variety of solvents. It has poor outdoor weathering stability; it turns yellow and crazes on exposure. Its tensile strength reaches about 8000 psi, but it is brittle and has a relatively low heat distortion temperature of 82 - 88°C.

Crystallinity

Most crystalline polymers contain an amorphous phase and a crystalline phase as evidenced by their corresponding diffuse and sharp X-ray patterns(6). The occurrence of both types of X-ray patterns is evidence that ordered and disordered regions coexist in most crystalline polymers. Crystalline polymers are made up of molecules which are chemically and geometrically regular in structure and whose polymer segments are capable of parallel alignment.

Increasing the degree of crystallinity in a polymer results in(23) an increase in density and tensile strength and a decrease in solubility, optical clarity, and gas permeability. Even a small amount of crystallinity in a polymer restricts the motion of the polymer molecules and results in an increase in the relaxation time of the polymer. Above the melting point crystallinity in the polymer disappears and its properties at these temperatures are the same as those of the corresponding amorphous polymer.

Crystalline Isotactic Polystyrene

For many years, it was believed that polymers such as polystyrene could not be crystallized. This conviction was due to the fact that polystyrene was an atactic polymer. The styrene monomer adds to the chain in such a way that the phenyl group occurs at random on either side of the polymer chain. As a result, the bulky phenyl group cannot fit into any crystalline lattice. By using an organometallic stereo-specific catalyst in the polymerization, isotactic polystyrene results in which the phenyl groups always appear on the same side of the polymer chain. As a result, the chain is very regular, and the phenyl groups can be packed into a crystal lattice. Isotactic polystyrene has a melting range of 240 - 250°C and exhibits a glass transition at 90°C, as does the amorphous atactic polystyrene(25).

Dielectric Behavior of Polymers

When an electric field acts on a polymer, it causes small displacements of electrons relative to nuclei and causes changes in the relative positions of atoms and groups. These displacements produce an electric moment in the molecule which persists as long as the electric field acts. The magnitude of this induced moment is proportional to the intensity of the electric field.

The electric center of gravity of negative charge in some molecules is not the same as the positive charge center of gravity. Such molecules have a permanent dipole moment which exists without the presence of an electric field. Polymers which possess permanent dipoles spend more time with their dipoles oriented in the direction of an applied field than with their dipoles oriented in other directions. The extent of this orientation is proportional to the field strength, to the square of the dipole moment, and inversely proportional to the temperature(24). Polymers containing permanent dipoles can store more energy under the influence of an electric field than those with only induced dipoles.

The ratio of the quantity of energy that can be stored in a capacitor containing a given material to the quantity of energy that can be stored if the material was replaced by a vacuum is called the dielectric constant of the material(24). Materials without permanent dipoles store little energy and have low dielectric constants. The dielectric constant is frequency and temperature dependent because a finite length of time is required for response to the electric field. The length of time required depends on whether the group set in motion by the applied field is an electron, small molecule, a pendent polar group, or a segment of a long polymer chain. The displacement of an electron is fast and reversible even at high frequencies, but the displacement of large polar groups requires more time and is reversible only if the frequency is slow enough to permit the polar group to respond completely to one pulse of the field before the reverse pulse is applied. When a polar polymer is excited by a low-frequency field, the dipoles become oriented with the field and the dielectric constant is high. As the frequency is increased, the dipoles have less and less time to become oriented and the dielectric constant drops. Finally, when the frequency becomes so high that the polar groups can no longer follow the field, the dielectric constant drops drastically and the polymer is said to show dispersion. Depending upon how the dipole is attached to the polymer will determine the number of dispersions the polymer exhibits.

At frequencies at which dispersion occurs, only part of the electrical energy is stored and the rest is dissipated as heat. This introduces the complex dielectric constant(24), e^*:

$$e^* = e' - ie''$$

where $i = \sqrt{-1}$. The electrical energy stored per cycle is proportional to e', the real part; the energy lost is proportional to e'', the imaginary part.

The ratio of e''/e' is called the loss tangent, $\tan\delta$, where δ is the compliment of the angle between the applied voltage and the current through a capacitor containing the dielectric(29). $\mathrm{Tan}\,\delta$ is also called the dissipation factor, and $\mathrm{Sin}\,\delta$ the power factor. e'' is sometimes called the loss factor. When the $\mathrm{Tan}\,\delta$ exhibits a maximum, dispersion occurs at that particular frequency. Dielectric relaxation is the cause of dispersion in which the dielectric constant decreases with increasing frequency(29). It is the lag in dipole orientation behind an alternating electric field. Polymers have a distribution of relaxation time which complicates equations derived to predict frequencies of maximum dielectric loss and dispersion.

Dielectric Properties of Polystyrene

Very little thorough work has been done on the dielectric properties of polystyrene. It is characterized by a very low dielectric loss at all frequencies, and it has a low dielectric constant due to its low polarity. Baker, et al(5) and Broens and Muller(15) calculated the dipole moment per repeat unit of polystyrene using Onsager's equation(26). Both calculations gave a result of 0.20 Debye units. Work and Treku(31) calculated the dipole moment of solid polystyrene and obtained a value of 0.26 Debye at 130°C. Krigbaum and Roig(19) measured the dielectric constant of atactic and isotactic polystyrene in toluene solutions. By plotting the molar polarization against the polymer concentration they calculated the dipole moment of the atactic and isotactic polystyrene to be 0.36 and 0.43 Debye units, respectively.

Broens and Muller(15) measured the dielectric loss of amorphous polystyrene at 0.179 - 316 kilocycles per second and found it to be less than 0.001 up to 100°C. The dielectric constant decreased from 2.55 to 2.51 between 0 and 100°C. Above 100°C a dispersion region was noted which was shown to correspond to an energy of activation of 78.8K cal. This somewhat large value was attributed to the chain stiffness. Polystyrene is generally considered to have only one dispersion region but Broens and Muller(15) found an indication of a small dispersion region at 10°C. Adamec(1) reported a beta relaxation in atactic polystyrene with its maximum at -3 or -17°C, respectively for frequencies of 1.0 to 0.1 kilocycles.

Baker, et al(5) studied atactic polystyrene, crosslinked atactic polystyrene (6% divinylbenzene), and atactic polystyrene plasticized with diphenyl. It was found that the crosslinked material gave an alpha relaxation at a higher temperature than regular atactic polystyrene, and the plasticized material gave the relaxation at a lower temperature than the regular atactic polystyrene. Saito and Nakajima(28) studied the dielectric alpha relaxation in polystyrene in the frequency range of 0.0001 to 10^6 cycles per second, with results similar to those above.

III - EXPERIMENTAL

The experimental section of the investigation contains the purpose of the investigation, plan of the investigation, a listing of the materials and apparatus used, the method of procedure, and the results.

PURPOSE OF THE INVESTIGATION

The purpose of the investigation was to determine the dielectric properties of atactic and isotactic polystyrene at 25°C and at frequencies of 0.1, 1.0, 10, and 100 kilocycles per second. In addition, the effects of molecular weight and crystallinity on the dielectric properties of polystyrene were to be studied.

PLAN OF EXPERIMENTATION

The plan of experimentation followed in the investigation consisted of preparing molded slabs of the various polystyrene polymers, preparing the molded polymer slabs for electrical measurements, measuring the dielectric constant and dissipation factor of the polymers, determining the viscosity average molecular weight and the density of the polystyrene polymers, and presentation of the data and results.

Preparation of Molded Samples

The polystyrene was molded into slabs about 30 mils thick by compressing the polymer between two polished steel plates at a temperature of 185°C under a ram force of 20,000 psi for about three minutes. The molded samples were then cooled in the mold under pressure. The isotactic polystyrene slabs were then annealed at 175°C for 0, 3, 6, and 24 hours.

Preparation of Molded Samples for Electrical Measurements

The molded polystyrene samples were prepared for electrical measurements by fitting the slabs with aluminum foil electrodes. To ensure good electrical contact, silicone grease was used to adhere the electrodes to the polymer slabs. A three terminal guarded parallel plate electrode system was used for making the dielectric measurements.

Dielectric Measurements

The capacitance and dissipation factor were measured using a General Radio 1422-D Precision Capacitor having a range of 35-115 ± 0.1 Pf and 100-1150 ± 0.6 Pf, and a General Radio Type 1605-A Impedance Comparator having frequency ranges of 0.1, 1.0, 10, and 100 kilocycles per second, ± 3%. The capacitance and dissipation factor of the specimen was measured using the variable capacitor as the standard to balance the impedance difference of the specimen. The capacitance of the specimen was read from the variable capacitor, and the dissipation factor was read as the phase angle difference recorded by the impedance comparator after the bridge had been balanced.

Molecular Weight Determination

The viscosity average molecular weights of the atactic polystyrene samples were determined by intrinsic viscosity measurements using a Cannon-Fenske Size 50 Viscometer.

Determination of Polymer Density

The density at 23 C of the molded polystyrene samples was determined by the standard water displacement method(4).

Presentation of Data and Results

The experimentally determined dielectric constant, dissipation factor, density and molecular weight of the various polystyrene polymers obtained during the investigation are presented in tabular form. The experimental data for the investigation are presented in tabular form in the appendix.

MATERIALS

This section contains the materials used in the investigation.

Aluminum Foil

Thickness 0.008 inches. Manufactured by Reynolds Metals Company, Richmond, Virginia.

Used to ensure good electrical content between the brass electrodes and the molded polystyrene slabs.

Benzene

Fisher Certified ACS. Obtained from Fisher Scientific Company, Springfield, New Jersey.

Used to prepare solutions of polystyrene for molecular weight determination.

Hexane

Commercial Grade. Obtained from American Mineral Spirits Company, Plainfield, New Jersey.

Used to clean molded polystyrene slabs.

Methyl Ethyl Ketone

99% Anhydrous Grade. Obtained from Union Carbide Corporation, Chemicals and Plastics Division, Bound Brook, New Jersey.

Used as solvent for Soxhlet extraction of isotactic polystyrene.

Methylene Chloride

Commercial Grade. Obtained from Union Carbide Corporation, Chemicals and Plastics Division, Bound Brook, New Jersey.

Used as solvent for degreasing the aluminum foil electrodes.

Polystyrene - Atactic

Dow PS-2, Dow 666-U-26-7, Dow 678-26-7, Dow 685-26-7. Obtained from The Dow Chemical Company, Midland, Michigan.

Used to prepare the molded samples to atactic polystyrene for measuring dielectric properties.

Polystyrene - Atactic

Monsanto's Lustrex® 55-2020 and Lustrex® 101-2020. Obtained from

Monsanto Chemical Company, Indian Orchard, Massachusetts.

Used to prepare molded samples of atactic polystyrene for measuring dielectric properties.

Polystyrene - Isotactic

Dow EP-1340-128 isotactic polystyrene. Obtained from The Dow Chemical Company, Midland, Michigan.

Used to prepare molded samples of isotactic polystyrene for measuring dielectric properties.

Silicone Release Agent

Dow Corning Type 20. Manufactured by The Dow Chemical Corporation, Midland, Michigan.

Used to adhere the aluminum foil electrodes to the molded polystyrene slabs.

Toluene

Fisher Certified ACS. Obtained from Fisher Scientific Company, Springfield, New Jersey.

Used to prepare solutions of polystyrene for molecular weight determination.

Water Distilled

Obtained from The Baker Castor Oil Company's laboratory.

Used for determining the densities of the molded polystyrene slabs.

APPARATUS

This section is a listing of the apparatus used in the investigation.

Balance

Analytical, damped, 0 to 500 grams capacity, 0.0001 gram subdivision, model number 80-180, serial number 2132541. Manufactured by Seederer Kohlbusch, Incorporated, Jersey City, New Jersey.

Used to weigh the molded polystyrene for determining density.

Constant Temperature Bath

10 Gallon Aquaria tank. Obtained from Scientific Glass Apparatus Company, Incorporated, Bloomfield, New Jersey.

Used to provide a constant temperature bath for determining the viscosities of the polystyrene solutions.

Electrodes

Circular brass guarded electrode and guard electrode. Rectangular brass electrode. Manufacturer unknown, obtained from The Baker Castor Oil Company, Electrical Testing Laboratory.

Used for measuring capacitance and dissipation factor of polystyrene slabs.

Flask - Volumetric

Six, 100-milliliter capacity. Obtained from Fisher Scientific Company, Springfield, New Jersey.

Used to prepare polystyrene solutions for viscosity determination.

Heater Immersion

115 volts A.C., 300 watts. Obtained from Fisher Scientific Company, Springfield, New Jersey.

Used as heating source for the constant temperature bath.

Impedance Comparator

Type 1605-A. Manufactured by General Radio Company, West Concord, Massachusetts.

Used to measure the capacitance and dissipation factor of the molded polystyrene specimens.

Lightnin® Mixer

Model V-12, 110 volts, 1000 rpm. Manufactured by Mixing Equipment Company, Incorporated, Rochester, New York.

Used to maintain uniform temperature in constant temperature bath.

Powerstat®

Variable Transformer, Type VS3PN16B, 120 volts, 10 amps. Manufactured by The Superior Electric Company, Bristol, Connecticut.

Used to regulate speed of the Lightnin Mixer.

Press

Hydraulic Laboratory Press. Model Number 150-C. Manufactured by Fred S. Carver, Incorporated, Summit, New Jersey.

Used to mold polystyrene slabs.

Thermometer

Mercury in glass, range -10 to 50°C, total immersion. Obtained from Scientific Glass Apparatus, Bloomfield, New Jersey.

Used to measure temperature of constant temperature bath.

Thickness Gauge

One degree equal to 0.0001 inches. Manufactured by Randall and Stickney, Waltham, Massachusetts.

Used to measure the thickness of the molded polystyrene slabs.

Variable Precision Capacitor

Type 1422-D, range 35-115 Pf and 100-1150 Pf. Manufactured by General Radio Company, West Concord, Massachusetts.

Used as standard for balancing the Impedance Comparitor.

Viscometer

Cannon-Fenske, size number 50. Obtained from Scientific Glass Apparatus, Bloomfield, New Jersey.

Used to measure viscosity of pplystyrene solutions for determining molecular weight.

METHOD OF PROCEDURE

The method of procedure followed in the investigation is outlined on the following pages. The procedure is divided into, preparation of molded samples of atactic and isotactic polystyrene, preparation of molded samples for electrical measurements, dielectric measurements, and the performance of analytical tests.

Preparation of Molded Samples of Atactic Polystyrene

The polystyrene beads were molded into 6 inch squares having a thickness of 40 to 50 mils. The molding cycle consisted of heating the polymer to a temperature of about 185°C between two polished steel plates for about 5 minutes. The specimen was then compressed using a Carver Laboratory Press under a ram force of 20,000 psi for about 3 minutes. The sample was then cooled in the mold under pressure, and the molded samples were then examined for cracks or air bubbles.

Preparation of Molded Samples of Isotactic Polystyrene

The isotactic polystyrene, lot EP-1340-128 received from the Dow Chemical Company, had a viscosity average molecular weight of 515,000. The polymer, as received, contained approximately 15% of an atactic fraction which was removed by Soxhlet extraction using methyl ethyl ketone. Extraction time was 30 hours and a weight loss of 15% was observed. The extracted polymer was dried for 16 hours at 110°C to remove the solvent. The removal of other impurities, such as dirt and catalyst residue was attempted by dissolving the polymer in toluene and precipitating in methanol. This procedure, however, was not satisfactory as the isotactic polystyrene was only soluble at a concentration of 1-2%. The polymer was reported to contain about 70 ppm of Ti, 400 ppm Al, 200 ppm halogens as chloride and bromide. The dried isotactic polymer was molded into 6 inch squares having a thickness of 45-55 mils. The same molding procedure was used as described above in preparing the atactic polystyrene samples. The molded samples of isotactic polystyrene were annealed at 175°C for 0, 3, 6, and 24 hours in a forced draft oven between polished steel plates. After annealing for 6 hours at 175°C, the crystallinity should have been in the range of 35%.

Preparation of Molded Samples for Electrical Measurements

A guarded parallel-plate electrode system (three terminal) was used for making the dielectric measurements and is illustrated in Figure II, page 21. The fringing and stray capacitance at the edge of the guarded electrode was practically eliminated by the addition of the guard electrode. The test specimen extended two inches and the guard electrode extended about one inch beyond the guarded electrode. The guard gap was 1/32 inch wide. By constructing the electrodes in this manner, the field distribution in the guarded area was the same as when vacuum or air was the dielectric and the ratio of the two capacitances is the dielectric constant. The guard terminal was connected to a guard terminal on the measuring circuit.

A sample calculation for the effective area of the guarded electrode is given on page 47 of the appendix.

Aluminum foil, 0.008 inches thick, was used as the electrode material to ensure good electrical contact with the rigid electrodes and the specimen. The aluminum foil was applied to the specimen with Dow Corning #20 Silicone Grease. The foil was first degreased with methylene chloride and then coated with a thin coating of the silicone grease. The foil was then placed over the specimen and the excess grease was squeezed out using a rubber squeegee. The foil was then cut down to the exact size of the rigid electrodes using a finely ground blade, and the excess grease was then wiped from the specimen using hexane solvent. The rigid electrodes were made of polished brass ground plane and parallel to ± 0.0001 inch.

Dielectric Measurements

The thickness of the samples was measured using a Randall and Stickney Thickness Gauge having an accuracy of ± 0.0001 inch. Several readings were taken over the entire electrode area and the average thickness was found to be uniform within ± 1%. The thickness of the aluminum foil was then subtracted from the overall thickness giving the actual sample thickness. This value was then used in calculating the capacitance of the cell in vacuum (or air).

All samples to be tested were conditioned at least 24 hours at 25°C.

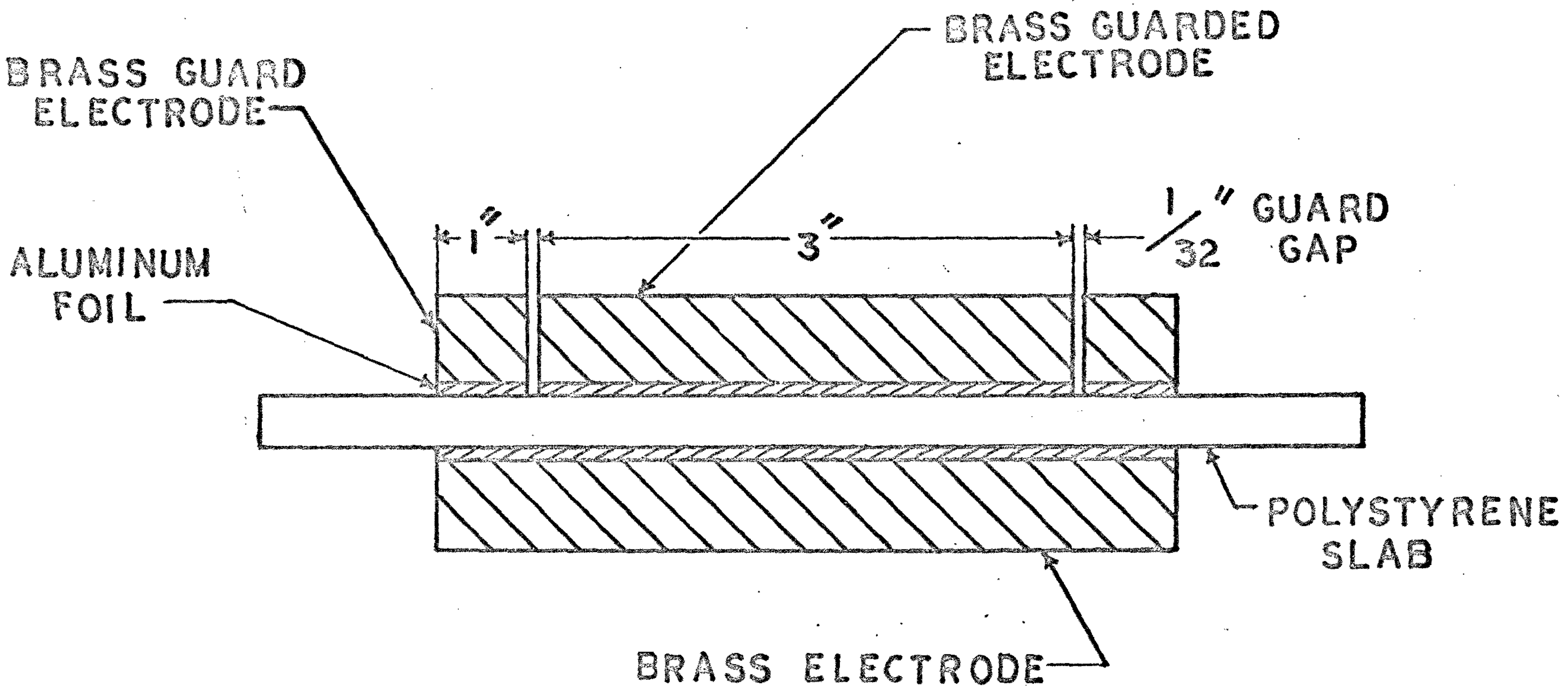

FIG.II.ELECTRODE SYSTEM

Capacitance and dissipation factor measurements were made using a General Radio 1422-D Precision Variable Capacitor (35-115 ± 0.1 Pf - 100-1150 ± 0.6 Pf range), and a General Radio Type 1605-A Impedance Comparator having frequency ranges of 0.1, 1.0, 10, and 100 kilocycles per second, ± 3%.

The impedance comparator is basically a special, self-contained bridge measurement system, consisting of a signal source, a bridge, and a detecting circuit. The bridge consists of two external impedances to be compared and two highly precise unity ratio arms equal to within one part in 10^6. The accuracy of the impedance measurement, therefore, depends largely on the precision of the external standard(18).

The capacitance and dissipation factor of the specimen was measured by using the variable capacitor as the standard to balance the impedance difference of the specimen. The capacitance of the specimen was read from the variable capacitor, and the dissipation factor was read as the phase angle difference recorded by the impedance comparator after the bridge had been balanced. The accuracy of the phase angle difference or dissipation factor was 3% of full scale or 0.003% for the 0.01 radians scale used in the measurements.

To eliminate any errors due to ground and lead capacitance, the capacitor containing the specimen was placed in a shielded cabinet during the dielectric measurements.

The dielectric constant of the specimen was calculated using the following equation:

$$D.C = \frac{C_s}{C_v}$$

Where: D.C. = dielectric constant of the polystyrene at 25°C

C_s = capacitance of the capacitor with polystyrene as the dielectric at 25°C

C_v = capacitance of the capacitor with air as the dielectric at 25°C

C_v was calculated from the geometry of the capacitor after corrections were made for the increased size of the diameter of the guarded electrode due to the guard gap correction.

Sample calculations are given on page 48 of the appendix.

Analytical Tests

The analytical procedures used in determining the polymer densities and molecular weights are outlined on the following pages.

Molecular Weight Determination

In order to study the effects of molecular weight on the dielectric properties of the atactic polystyrene, their viscosity average molecular weights were determined. The intrinsic viscosities of the samples were determined following the standard procedure using a Cannon Fenske Size 50 viscometer.

The viscosity average molecular weight was determined by using the equation:

$$[\eta] = KM^a$$

Where: M = viscosity average molecular weight

$[\eta]$ = the intrinsic viscosity

K, a = Constants of the polystyrene solvent system used.

The constants K and a, used to calculate the molecular weight of the Dow PS2, were obtained from D.C. Pepper(27). Here the solvent used was benzene at 25 C. With the higher molecular weight samples, however, the results obtained using benzene as the solvent yielded poor extrapolation data. Toluene was then used as the solvent and the values of K and a at 30°C were obtained from S. N. Chinai, et al(17).

Determination of Polymer Density

The density of the various polystyrene samples at 23°C was determined using the standard water displacement method(4). The samples used in the density determinations were taken from the molded samples used in measuring the dielectric properties.

RESULTS

The results obtained from the investigation are presented in the following section.

Dielectric Prpperties of Atactic Polystyrene at 25°C

The experimentally determined values of the dielectric constant and dissipation factor of the atactic polystyrene samples at the various frequencies are presented in Table I, page 26.

Dielectric Properties of Isotactic Polystyrene at 25°C

The experimentally determined values of the dielectric constant and dissipation factor of the isotactic polystyrene samples at the various frequencies are presented in Table II, page 27.

Molecular Weight Determination of Atactic Polystyrene

The experimentally determined values of the intrinsic viscosities of the atactic polystyrene are listed in Table III, page 28.

Also listed in Table III are solvents, temperatures, and K and a constants used in the determination of the intrinsic viscosities.

The viscosity average molecular weights of the atactic polystyrene, calculated from the experimentally determined intrinsic viscosities, are listed in Table IV, page 29.

A sample calculation of the viscosity average molecular weight is given on page 50 of the appendix.

Determination of the Polymer Densities of the Atactic and Isotactic Polystyrene at 23°C

The experimentally determined values of the densities of the atactic and isotactic polystyrene at 23°C are listed in Table V, page 30, and Table VI, page 31, respectively.

Table I

Experimental Values of the Dielectric Constant and Dissipation Factor of Atactic Polystyrene at 25°C

Sample	Frequency Kilocycles	C_v(a) MMf	C_s(b) MMf	E(c)	D(d)
Dow PS-2 Polystyrene	0.1	48.89	135.1	2.765	0.0001
	1	48.89	135.1	2.765	0.0001
	10	48.89	135.1	2.765	0.0001
	100	48.89	135.1	2.765	0.0001
Dow 678-26-7 Polystyrene	0.1	41.45	108.3	2.613	0.0001
	1	41.45	108.3	2.613	0.0001
	10	41.45	108.3	2.613	0.0005
	100	41.45	107.9	2.603	0.004
Dow 666U26-7 Polystyrene	0.1	42.42	110.6	2.607	0.0001
	1	42.42	110.6	2.607	0.0001
	10	42.42	110.6	2.607	0.0005
	100	42.42	110.2	2.598	0.005
Monsanto 55-2020 Polystyrene	0.1	39.1	101.3	2.591	0.0001
	1	39.1	101.3	2.591	0.0001
	10	39.1	101.3	2.591	0.0004
	100	39.1	101.2	2.588	0.005
Monsanto 101-2020 Polystyrene	0.1	34.2	88.9	2.599	0.0001
	1	34.2	88.9	2.599	0.0001
	10	34.2	88.9	2.599	0.0005
	100	34.2	88.7	2.594	0.003
Dow 685-26-7 Polystyrene	0.1	41.61	108.2	2.600	0.0001
	1	41.61	108.2	2.600	0.0001
	10	41.61	108.2	2.600	0.0005
	100	41.61	107.9	2.593	0.0045

(a) C_v = Calculated capacitance of cell in vacuum.

(b) C_s = Measured capacitance of cell with polystyrene as the dielectric at 25°C.

(c) E = Dielectric constant of the polystyrene at 25°C.

(d) D = Dissipation factor of the polystyrene at 25°C.

Table II

Experimental Values of Dielectric Constant and Dissipation Factor of Dow EP-1340-128 Isotactic Polystyrene at 25°C

Annealing Time at 175°C	Frequency Kilocycles	C_v [(a)] MMf	C_s [(b)] MMf	E[(c)]	D[(d)]
0 hours	0.1	33.49	91.60	2.735	0.0005
	1	33.49	91.42	2.730	0.00045
	10	33.49	91.34	2.727	0.0003
	100	33.49	91.34	2.727	0.0002
3 hours	0.1	35.25	93.90	2.664	0.0002
	1	35.25	93.85	2.662	0.0002
	10	35.25	93.80	2.661	0.00015
	100	35.25	93.77	2.660	0.0001
6 hours	0.1	31.03	83.36	2.686	0.0001
	1	31.03	83.33	2.685	0.0001
	10	31.03	83.31	2.685	0.0001
	100	31.03	83.31	2.685	0.00005
24 hours	0.1	34.87	91.67	2.629	0.0002
	1	34.87	91.66	2.626	0.0002
	10	34.87	91.62	2.627	0.0001
	100	34.87	91.62	2.627	0.0001

(a) C_v = Calculated capacitance of cell in vacuum.

(b) C_s = Measured capacitance of cell with polystyrene as dielectric at 25°C.

(c) E = Dielectric constant of the polystyrene at 25°C.

(d) D = Dissipation factor of the polystyrene at 25°C.

Table III

Values of Intrinsic Viscosities of the Atactic Polystyrene Determined by Solution Viscosity Measurements

Sample	Solvent	Temperature	K	a	(N)
Dow PS-2	Benzene	25°C	2.27×10^{-4}	0.72	0.208
Dow 666-U-26-7	Toluene	30°C	9.2×10^{-5}	0.72	0.752
Dow 678-26-7	Toluene	30°C	9.2×10^{-5}	0.72	0.655
Dow 685-26-7	Toluene	30°C	9.2×10^{-5}	0.72	0.878
Monsanto 55-2020	Toluene	30°C	9.2×10^{-5}	0.72	0.778
Monsanto 101-2020	Toluene	30°C	9.2×10^{-5}	0.72	0.862

Table IV

Values of Viscosity Average Molecular Weights of the Atactic Polystyrene Calculated from Intrinsic Viscosities

Sample	Molecular Weight
Dow PS-2	13,000
Dow 666-U-26-7	272,000
Dow 678-26-7	224,000
Dow 685-26-7	337,000
Monsanto 55-2020	285,000
Monsanto 101-2020	328,000

Table V

Experimental Values of the Densities of the Atactic Polystyrene at 23°C

Sample	Density - g/cm^3
Dow PS-2	1.0534
Dow 666-U-26-7	1.0454
Dow 678-26-7	1.0454
Dow 685-26-7	1.0474
Monsanto 55-2020	1.0434
Monsanto 101-2020	1.0454

Table VI

Experimental Values of the Densities of the Isotactic Polystyrene at 23°C

Dow EP-1340-128 Polystyrene	Density - g/cm^3
No Annealing	1.0543
3 hours Annealing at 175°C	1.0663
6 hours Annealing at 175°C	1.0733
24 hours Annealing at 175°C	1.0733

IV - DISCUSSION

This section contains the discussion of the sample preparation, dielectric measurements and the elimination of stray capacitance, results of the investigation, recommendations, and the limitations imposed on the investigation.

Sample Preparation

The principle problem encountered in preparing the molded samples of polystyrene was the exclusion of air bubbles from the specimens. After repeated attempts to prepare bubble-free specimens, the following procedure was found to be successful.

1. Initially, silicone grease was applied to the polished steel plates to aid in removing the molded sample from the mold. It was found that the silicone grease caused air bubbles to occur in the sample and the silicone grease was omitted. It was found that on cooling the molded samples, they pulled away from the mold and were easily removed without any release agent.

2. In addition to bubbles appearing in the molded samples, the presence of air bubbles between the aluminum foil electrodes and the polystyrene also presented a problem. These bubbles were eliminated by coating both the aluminum foil and the polystyrene with the silicone grease. The excess grease was then squeezed out with a small rubber squeegee. The surface of the sample was then cleaned with hexane to remove the excess silicone grease.

Dielectric Measurements and the Elimination of Stray Capacitance

In addition to the direct interelectrode capacitance measured by the variable capacitor, the system also includes(3):

Ce = fringing or edge capacitance.

Cg = ground capacitance of the outside face of each electrode.

C_L = capacitance between connecting leads.

C g = capacitance of the leads to ground.

C e = capacitance between the leads and the electrodes.

By using the three-terminal guarded electrode system, all of these stray capacitances except the lead capacitance, C_L , and the edge capacitance, Ce, are eliminated as a source of error. The lead capacitance was made negligibly small by using leads as short as possible. At the frequencies used in this investigation, the error due to C_L is then negligible. The error due to edge capacitance, Ce, was eliminated by correcting for the increased effective area of the guarded electrode. The effective area of the guarded electrode is increased by about half the area of the guard gap.

After each measurement at each frequency, the impedance comparator was recalibrated to eliminate any possible error due to drifting. In addition, the instrument was hooked up to a separate power line to eliminate any sudden voltage drop which could affect the measurements.

Dielectric Properties of Atactic Polystyrene at 25 C and the Effect of Molecular Weight

As can be seen from the data in Table I, page 26, the value of the dielectric constant for the high molecular weight polystyrene (224,000 - 328,000) ranges from a low of 2.59 to a high of 2.61 for a frequency range of 0.1 to 100 kilocycles per second. The dissipation factor ranges from a low of 0.0001 at 0.1 kilocycles/second to a high of 0.005 at 100 kilocycles/second. These values are in good agreement with literature values(13,16,20).

The low dielectric constant and dissipation factor is as would be expected for a linear, nearly non-polar polymer. As can be seen from its structure, the dipole moment of polystyrene should be small and similar per repeat unit, to that of toluene, which has been reported to be 0.30 Debye units(30). This low polarity is responsible for the excellent dielectric properties of polystyrene. As can be seen by examining the literature values of the dielectric properties of the more polar polychlorostyrenes, the dielectric constant increases with increasing polarity. Poly-2,6-dichlorostyrene, poly-2,5-dichlorostyrene, and poly-3,4-dichlorostyrene have dielectric constants of 2.75, 2.62, and 4.0 respectively(14). Baker, et al(5) and Broens and Muller(15) calculated the dipole moment per repeat unit of atactic polystyrene using Onsager's equation(26). Both calculations gave a result of 0.20 Debye units. The slightly smaller value than that of toluene was attributed to the compensating effect of the coupling of the closely spaced dipoles.

The dielectric constant of the high molecular weight polystyrene samples remained constant over the frequency range of 0.1 to 10 kilocycles/second, and decreased very slightly at 100 kilocycles/second to an average of 0.007. This would indicate an extremely small orientation polarization which also is in agreement with what one would expect from the nearly non-polar structure of polystyrene and its low dipole moment. The orientation polarization is probably due to partial rotation of the phenyl group about its carbon axis and restricted rotation about the ethylene group.

The dielectric constant of the lowest molecular weight atactic polystyrene, Dow PS-2 with a molecular weight of 13,000 was found to be significantly higher than that of the higher molecular weight samples, 2,765 vs. 2.60. The dissipation factor, on the other hand, maintained the very low value of 0.0001 throughout the frequency range of 0.1 to 100 kilocycles/second. Since decreasing the molecular weight of the polymer results in an increased number of chain ends, it seems likely that some extraneous dipoles located at the chain ends is responsible for the increased dielectric constant. These extraneous dipoles may be due to oxidation of the polymer during polymerization or during the molding operation. Similar results were observed for low molecular weight polyethylene(8) and it was concluded that extraneous dipoles, probably carbonyl groups formed by oxidation, were responsible for an observed increase in dielectric loss. The lack of any increase in dissipation factor can be explained by the increased mobility of the lower molecular weight polystyrene molecules. The maximum frequency used in this investigation was only 100 kilocycles and it is possible that, due to the increased mobility of the polymer molecules, a higher frequency would be required to observe any increased dielectric loss. This reasoning would also account for the lack of dispersion observed for the dielectric constant of the low molecular weight polystyrene as compared to the high molecular weight samples.

Examination of the measured densities of the atactic polystyrene, Table V, page 30, indicates a higher density for the low molecular weight Dow PS-2 polystyrene, than that of the higher molecular weight samples, 1.0534 vs. 1.045, respectively. This is difficult to explain. In general, lowering the molecular weight of a polymer tends to increase the molar free volume which would lower the density and glass transition temperature of the polymer(22). Each end group is a flaw in the polymer and causes inefficient packing of the polymer molecules. It may be possible, however, that because of the stiffness of the polystyrene molecule, due to the bulky phenyl group, the lower molecular weight polystyrene molecules are more mobile and have less polymer entanglements thereby allowing for tighter packing.

The Effects of Crystallization on the Dielectric Properties of Polystyrene

The results of the measured dielectric properties of amorphous atactic polystyrene and crystalline isotactic polystyrene are listed in Table I, page 26, and Table II, page 27, respectively. As can be seen, the dielectric constant for the isotactic polystyrene is greater than that of the amorphous atactic polystyrene. This is in agreement with what one would expect. The dipoles in the isotactic polystyrene, by definition, are all on the same side of the polystyrene molecule.

Because of this stereoregularity of the polymer chain, there is presumably considerably less dipole-dipole cancellation or coupling, and as a result the dielectric constant is increased.

As the percent crystallinity, or the annealing time, is increased, the dielectric constant decreases from 2.735 for no annealing to 2.629 for 24 hours, annealing at 175 C. The intermediate 6 hours annealed sample was somewhat out of line with this trend in that its dielectric constant was 2.685 as compared to 2.664 for the 3 hours annealed sample. The slight increase in dielectric constant was probably due to oxidation during annealing. This general decrease in dielectric constant with increasing crystallinity or annealing is also in agreement with what one would expect. As the percent crystallinity is increased, more and more of the amorphous phase of the polystyrene is associated with or incorporated into the crystalline phase and the mobility of the dipoles, or their ability to orient in or follow the electric field is greatly hindered. As a result, the dielectric constant decreases in value. The values of the dissipation factor for the crystalline isotactic polystyrene samples were in general, slightly higher than those of the amorphous atactic polystyrene at the frequency of 0.1 kilocycles. It is important to note, however, that contrary to the results obtained for the atactic polystyrene, the values for the dissipation factor of the isotactic polystyrene decreased with increasing frequency. It appears that the loss peak of the isotactic polystyrene occurs at a lower frequency than that of the atactic polymer due to the dipoles being closely associated with or incorporated into the crystalline region. This would restrict the motion of the dipoles causing the relaxation or loss peak to occur at a lower frequency or higher temperature.

Similar results were obtained for polyethylene(9) where a loss peak at 0°C for high pressure polyethylene was shifted to a higher temperature for the more crystalline low pressure polyethylene. As the percent crystallinity increases, the relaxation or loss peak occurs at a lower frequency due to the increasing number of dipoles being incorporated into the crystalline phase resulting in a decrease in dielectric constant and dissipation factor over the frequencies used in this investigation.

Examination of the density data for the amorphous atactic and crystalline isotactic polystyrene samples, Table V, page 30, and Table VI, page 31, indicates a higher density for the isotactic polystyrene. This confirms the presence of crystallites in the isotactic polymer and also confirms the increasing crystallinity with increased annealing time. The density value for the low molecular weight atactic polystyrene, Dow PS-2, is an exception, and as discussed earlier, the improved mobility of the lower molecular weight material may make molecular packing and allignment easier. This would account for its density being very close to the non-annealed isotactic polystyrene.

RECOMMENDATIONS

On the basis of this investigation, the following recommendations are suggested for future study of the dielectric properties of atactic and isotactic polystyrene.

Temperature and Frequency Range

Since polymer relaxation is temperature and frequency dependent, it is recommended that the dielectric constant and dissipation factor of polystyrene be studied over a wider frequency and temperature range than that used in this investigation. Extending the temperature and frequency range would give a more complete picture of the relaxations characteristic of polystyrene. Extending the frequency range, for example, would show the maximum loss peak of the isotactic polystyrene. Under this investigation it appeared that the maximum loss occurred at a frequency lower than 100 cycles per second.

Plots of dielectric loss and dissipation factor versus temperature or frequency could be made, and from these the activation energies of the relaxation process observed could be calculated.

Isotactic Polystyrene

It is suggested that future investigations include isotactic polystyrene of various molecular weights and degrees of crystallinity. Under the present investigation the isotactic polystyrene had a molecular weight of 515,000 and a maximum crystallinity of 35%.

Effects of Oxidation

Since the observed increase in the dielectric constant of the low molecular weight atactic polystyrene, Dow PS-2, was attributed to possible oxidation of the polymer, it is recommended that future investigations study the effect of enforced oxidation on the dielectric properties of polystyrene. The degree of oxidation should be verified by such means as infrared spectroscopy.

LIMITATIONS

This section contains the limitations imposed upon this investigation.

Atactic Polystyrene

Six atactic polystyrene polymers were evaluated in this investigation: Dow Chemical Company's Dow PS-2, Dow 666-U-26-7, Dow 678-26-7, Dow 685-26-7, Monsanto's Lustrex® 55-2020, and Lustrex® 101-2020.

Isotactic Polystyrene

Dow Chemical Company's isotactic polystyrene EP-1340-128 was evaluated after 0, 3, 6, and 24 hours annealing at 175°C. The maximum crystallization was reported as 35%.

Molding Conditions

The specimens were prepared by molding the polystyrene between two polished steel plates under a ram force of 20,000 psi for 3 minutes.

Frequency Range

The dielectric properties were measured at frequencies of 0.1, 1.0, 10 and 100 kilocycles per second.

Temperature

The dielectric properties were measured at 25°C.

V - CONCLUSIONS

The conclusions resulting from the present investigation are:

1. The dielectric constant and dissipation factor for atactic polystyrene of varying molecular weight were determined at 25°C for the frequencies of 0.1, 1.0, 10 and 100 kilocycles per second.

2. The dielectric constant and dissipation factor of atactic polystyrene, for this frequency and temperature range, are independent of the molecular weight for high molecular weight polystyrene ranging from 224,000 to 337,000. For very low molecular weight, 13,000, the dielectric constant appears to increase.

3. The dielectric constant of the high molecular weight atactic polystyrene exhibits a very slight drop, and the dissipation factor increases slightly at 100 kilocycles indicating a very low orientation polarization.

4. The dielectric constant and dissipation factor of the low molecular weight atactic polystyrene remained constant over the entire frequency range.

5. The dielectric constant and dissipation factor of isotactic polystyrene having various degrees of crystallinity were determined at 25°C for the frequencies of 0.1, 1.0, 10 and 100 kilocycles per second.

6. Isotactic polystyrene has a higher dielectric constant than atactic polystyrene, presumably due to the decrease in the dipole - dipole

coupling or cancellation in the isotactic polymer chains.

7. Increasing the degree of crystallinity in isotactic polystyrene results in a decrease in the dielectric constant indicating that the relaxation takes place essentially in the amorphous phase.

8. The dissipation factor of isotactic polystyrene decreases with increasing frequency indicating the possibility of a maximum loss peak at a frequency lower than 0.1 kilocycles.

9. The dissipation factor and dielectric constant of atactic and isotactic polystyrene are very low indicating a very low dipole moment per repeat unit or low polarity of polystyrene.

VI - SUMMARY

The purpose of this investigation was to determine the dielectric properties of atactic and isotactic polystyrene at 25°C at frequencies of 0.1, 1.0, 10 and 100 kilocycles per second.

The effect of molecular weight on the dielectric properties of atactic polystyrene was investigated and it was found that the dielectric constant and dissipation factor are independent of molecular weight for high molecular weights in the range of 224,000 to 337,000. For very low molecular weight polystyrene, 13,000, the dielectric constant increased and no dielectric dispersion was observed. It was also observed that the density of the low molecular weight polystyrene was slightly higher than that of the high molecular weight atactic polystyrene, 1.0534 vs. 1.0454 average respectively. This value was extremely close to that of the non-annealed isotactic polystyrene (1.0543) suggesting that the increased mobility of the very low molecular weight polystyrene chain resulted in tighter packing.

The effects of crystallization on the dielectric properties of polystyrene was also studied. It was found that the dielectric constant of the isotactic polystyrene was greater than that of the atactic polymer, and it was concluded that this increase was due to the decrease in dipole-dipole cancellation. It was also observed that the dissipation factor of the crystalline isotactic polystyrene decreased with increasing frequency suggesting that the maximum loss peak occurred at a frequency lower than 100 cycles per second. Increasing the degree of crystallinity of the isotactic polystyrene by annealing at 175°C for various periods of time resulted in a decrease in dielectric constant. It was concluded that the relaxation process takes place in the amorphous phase of the polymer since a linear relationship was observed for decrease in dielectric constant with increasing crystallinity.

APPENDIX A

Experimental Data

The data obtained from the investigation are presented in the following section.

Density of Atactic Polystyrene

The data and results for the determination of the densities of the atactic polystyrene at 23°C are presented in Table VII, page 45.

Density of Isotactic Polystyrene

The data and results for the determination of the densities of the isotactic polystyrene at 23°C are presented in Table VIII, page 46.

Table VII

Data for the Determination of the Densities of Atactic Polystyrene at 23°C

Sample	Specific Gravity	Density gm/cm^3	a (gm)	b (gm)	w (gm)
Dow PS-2	1.056	1.0534	2.2261	0.3325	0.2150
Dow 666-U-26-7	1.048	1.0454	2.4563	0.3275	0.2150
Dow 678-26-7	1.048	1.0454	1.9080	0.3024	0.2150
Dow 685-26-7	1.050	1.0474	2.6560	0.3415	0.2150
Monsanto 55-2020	1.046	1.0434	2.6109	0.3298	0.2150
Monsanto 101-2020	1.048	1.0454	2.2530	0.3182	0.2150

a = The weight of the specimen in air.

b = The weight of the specimen completely immersed and of the wire partially immersed in the water.

w = The weight of the partially immersed wire.

Table VIII

Data for the Determination of the Densities of the Isotactic Polystyrene at 23°C

Dow EP-1340	Specific Gravity	Density gm/cm^3	a (gm)	b (gm)	w (gm)
No Annealing	1.057	1.0543	2.0991	0.3282	0.215
3 hours Annealing at 175°C	1.069	1.0663	1.6478	0.3214	0.215
6 hours Annealing at 175°C	1.076	1.0733	1.6154	0.3291	0.215
24 hours Annealing at 175°C	1.075	1.0723	1.6168	0.3278	0.215

a = The weight of the specimen in air.

b = The weight of the specimen completely immersed and of the wire partially immersed in the water.

w = The weight of the partially immersed wire.

APPENDIX B

Sample Calculations

Examples of the calculations used in the investigation are presented in this section.

Determination of the Effective Area of the Guarded Electrode

The effective area of a guarded electrode is greater than its actual area by approximately half the area of the guard gap. The diameter of a circular electrode, therefore, is increased by the width of the gap. If the ratio of the gap width, g, to the electrode separations, t, is appreciable, the increase in the diameter of the guarded electrode is less than the gap width by a quantity, 2δ, called the guard gap correction.

For the electrode system used in this investigation, the guard gap correction is given by the following equation(3):

$$\frac{2\delta}{g} = \frac{1}{4}\left(\frac{\pi g}{2t}\right) - \frac{1}{96}\left(\frac{\pi g}{2t}\right)^3$$

For the Monsanto 101-2020 polystyrene molded slab:

$g = 0.03125$ inches
$t = 0.047$ inches

Substituting in the above equation:

$$\frac{2\delta}{0.03125} = \frac{1}{4}\left(\frac{3.14 \times 0.03125}{2 \times 0.0472}\right) - \frac{1}{96}\left(\frac{3.14 \times 0.03125}{2 \times 0.0472}\right)^3$$

$$\frac{2\delta}{0.03125} = 0.2598 - 0.0168$$

$$2\delta = 0.007595 \text{ inches}$$

The measured diameter of the guarded electrode is 3.0 inches.

Therefore, Effective Diameter = 3.0 + 0.03125 - 0.007595

Effective Diameter = 3.02366 inches

Determination of the Capacitance of the Electrode System in Vacuum, C_V

The capacitance of the electrode system in vacuum, C_V, is given by the equation(3):

$$C_V = \frac{EA}{4\pi t} \quad \text{electrostatic units}$$

where:

E = the dielectric constant of a vacuum
A = the area of the circular electrode
t = the distance between the circular electrodes

or: $$C_V = \frac{0.1766 d^2}{t} \quad \text{picofarads}$$

where:

d = the effective diameter of the guarded electrode

For the Monsanto 101-2020 molded polystyrene slab:

d = 3.02366 inches
t = 0.0472 inches

Substituting in the above equation:

$$C_V = \frac{0.1766\ (3.02366)^2}{0.0472}$$

$$C_V = 34.2 \text{ picofarads}$$

Determination of the Polymer Densities of the Atactic and Isotactic Polystyrene at 23°C

The density at 23°C of the polystyrene samples was determined using the standard water displacement method. The following equation was used for the determination:

$$\text{Density at } 23^{\circ}\text{C} = \frac{a}{a + w - b} \times (0.9975)$$

Where:

a = The weight of the specimen in air.

b = The weight of the specimen completely immersed and of the wire partially immersed in the water.

w = The weight of the partially immersed wire.

0.9975 = The density of water (g/cm^3) at 23°C.

Substituting the data from Table VII , page 45, for the Dow PS-2 polystyrene.

$$\text{Density at } 23^{\circ}\text{C} = \frac{2.2261}{2.2261 + 0.2150 - 0.3325} (0.9975)$$

$$\text{Density at } 23^{\circ}\text{C} = 1.0534 \text{ g/cm}^3$$

Determination of the Viscosity Average Molecular Weight

The viscosity average molecular weight of the polystyrene was determined using the following equation from Billmyer:

$$[\eta] = KM^a$$

$$\text{Log } M = \frac{\log[\eta] - \log K}{a}$$

Where:

M = The viscosity average molecular weight.

K = A constant for the polystyrene-toluene system, at 30°C, 9.2×10^{-5}.

a = A constant for the polystyrene-toluene system, at 30°C, 0.72.

$[\eta]$ = The intrinsic viscosity

Substituting the value for the intrinsic viscosity of Dow 666-U-26-7 polystyrene from Table III, page 28:

$$\text{Log } M = \frac{\log 0.752 - \log 9.2 \times 10^{-5}}{0.72}$$

$$\text{Log } M = 5.434$$

$$M = 272{,}000$$

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