

DIELECTRIC DISPERSION OF POLY(VINYL ACETATE) SOLUTIONS

by

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THIS THESIS IS AFFECTIONATELY DEDICATED TO MY GRANDFATHER

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INTRODUCTION

INTRODUCTION

The investigation of dielectric properties has provided an important approach to an understanding of the structure, size and molecular weight of high polymer molecules. (16)(9)(11).

At Virginia Polytechnic Institute, experimental work on the dielectric behavior of polymer solutions has been in progress for a number of years. Various cellulose derivatives have been investigated, and in the case of cellulose acetate and ethyl cellulose, there were indications that the dielectric dispersion and the molecular weight of the material could be correlated by a rather simple relationship. (18)(17). The cellulose derivatives are believed to have a relatively rigid "backbone" as compared to that of the vinyl compounds. The chemical constitution of these polymers should be reflected in their dielectric behavior.

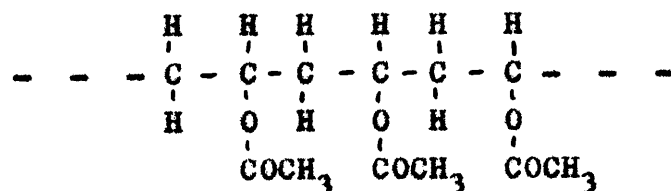
The purpose of this investigation was to study the dielectric dispersion of a vinyl type polymer and the relation of this behavior to the chemical nature of the material. The capacitance of a solution of poly(vinyl acetate) was measured at various frequencies by the bridge method. Experimental data verified the assumption that a vinyl polymer possesses greater chain flexibility than a cellulose derivative.

LITERATURE REVIEW

Historical

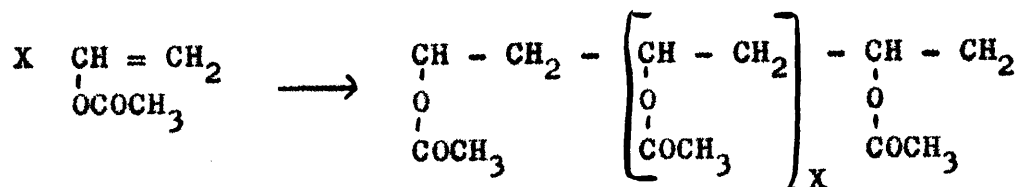
Previous to 1912, when Klatte (13) discovered poly (vinyl acetate), nothing was known about poly vinyl esters other than the poly vinyl halides.

Staudinger (20) studied the reactions of poly(vinyl acetate) and came to the conclusion that in poly vinyl derivatives a large number of vinyl groups are combined forming an unbranched, saturated carbon chain. His formula for poly (vinyl acetate) was:



The conception of as many as 50 or 100 molecules of an organic substance combining by primary valence forces into a "macromolecule" was at that time quite revolutionary but is now generally accepted. Thus, poly(vinyl acetate) has the distinction of being one of the early compounds studied which demonstrated the theory of large molecules.

Staudinger, Frey and Starck (21) represented the conversion of monomeric vinyl acetate to poly(vinyl acetate) as follows:

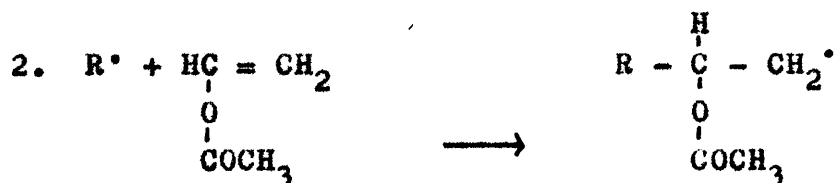
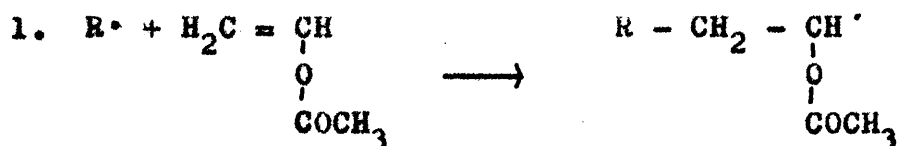


$$\text{X} = 40 - - - 100$$

Structure

The structural units of poly(vinyl acetate) are usually found in a regular head-to-tail sequence (14), and the substituent is located on alternate atoms of the chain. Evidence for this type of structure was found by Marvel and Denoon. (13).

An explanation for the predominance of the head-to-tail arrangement is based on the free radical mechanism of the growing chain. (6). The free radical (R[•]) may add to the monomer in two ways:



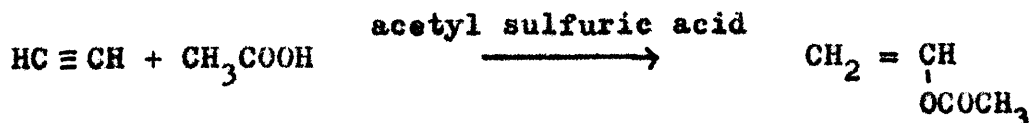
In reaction (1), the free radical is stabilized by the attached substituent(O-CO-CH₃). No such stabilization occurs in reaction (2). On this basis, Flory predicts that reaction (1) will occur in preference to reaction (2).

On examination of poly(vinyl acetate) with x-ray, no crystalline structure is shown, but halo diagrams characteristic of amorphous solids are found. (7). Staudinger and Schwalbach (22) suggested that the absence of crystallinity might be due to asymmetric carbon atoms which make diastereoisomerism possible.

Preparation

All reactions intended to form vinyl alcohol yield either acetaldehyde or ethylene oxide; therefore, vinyl acetate cannot be made by the usual esterification reaction of treating an alcohol with an acid.

Acetylene is generally used as the source of the alcohol radical:



The reaction between acetylene and acetic acid in the presence of mercuric salts or acetylsulfuric acid as a catalyst gives vinyl acetate. This method is carried out in either the liquid or gaseous states to produce vinyl acetate on a commercial scale. In the liquid process, an important condition affecting the yield is the use of highly selective catalysts. (1).

In the cold vinyl acetate does not polymerize in the absence of light, but, when illuminated, polymerization occurs rapidly. At a temperature of 100° C. or higher, the reaction takes place in the dark and is accelerated by oxygen or peroxides. In photopolymerization, oxygen acts as an inhibitor. (5).

The degree of polymerization will depend on the conditions under which the reaction occurs. Such conditions include polymerization by irradiation or by heat, and the DP is also dependent on the catalyst used, the solvent employed, and the temperature at which the reaction occurs.

Theory of Dielectric Dispersion

Before considering dielectric dispersion, it seems appropriate to mention briefly the static or low frequency dielectric constant and dipole moment. The present interpretation of the dielectric constant is based on the theory of Debye (19) with added modifications and refinements.

When two oppositely charged plates attract each other with a certain force, the effect of the material constituting the medium is measured by the dielectric constant (ϵ). The dielectric constant can be determined by measuring the capacitance of a condenser (C) with the particular medium between the plates and then repeating with air (C_0) between the plates.

$$1. \quad \epsilon = \frac{C}{C_0}$$

The relationship between the dipole moment and the dielectric constant is given by the Debye equation:

$$2. \quad P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi N}{3} \alpha_0 + \frac{4\pi N}{3} \left(\frac{\bar{\mu}^2}{3KT} \right)$$

$\bar{\mu}$ is the permanent dipole moment. (The charges in a molecule may be distributed so as to give rise to an electric dipole even when the field is absent.)

P is the molar polarization, N is Avogadro's number, M is the molecular weight, d is the density, k is the Boltzmann constant, T is the absolute temperature, and α_0 is the molecular polarizability.

It can be seen from equation (2) that the total polarization of a molecule is the sum of two terms:

1. The first is polarization resulting from distortion (P_D) which will be present for any molecule, polar or non-polar.
2. The second, due to the permanent dipole moment, is the orientation polarization (P_O).

$$3. \quad P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P_D + P_O$$

$$4. \quad P_O = \frac{4\pi}{3} N \alpha_0$$

$$5. \quad P_O = \frac{4\pi}{3} N \left(\frac{\bar{\mu}^2}{3kT} \right)$$

Substances with permanent dipole moments will usually have high dielectric constants because when the field is applied the permanent doublets are oriented with the positive end toward the negative plate and the negative end toward the positive plate. The intensity of the field within the medium is decreased as compared to that in air or a vacuum.

If the doublets are unable to orient in the field because of hinderance to free rotation, the orientation will be zero. Therefore, equation (2) can hold only if there is no restriction whatever to the movement of dipoles in the field. In the case of liquids, mutual interaction between molecules will restrict the movement of the molecules so the Debye equation is strictly applicable only in the case of gases.

When the frequency is of such a magnitude that there is an observable lag in the attainment of equilibrium between the dielectric and the externally applied field, then over a frequency range dielectric dispersion occurs. Historically,

Drude (4) first observed such dispersion in liquids with increasing frequency.

In the absence of an external field, the orientation of a polar molecule is unpredictable. If such molecules were placed in a low frequency field, then during each cycle the molecules will have time to align themselves with the field. During each reversal of the cycle, the molecules will revert gradually to the random orientation. The time required for the molecules to establish a random distribution is the relaxation time (τ). In such a case, the dielectric constant will be large.

If the frequency is increased, a point is reached where the orientation begins to lag behind the field reversals, the lag being greatest when the period of the frequency is of the same order as the relaxation time. This lag produces a decrease in molecular orientation, and the dielectric constant decreases.

At high frequencies, the Debye equation (2) does not hold but was changed by Debye to:

$$6. \quad P(\omega) = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left[\alpha_0 + \frac{\bar{\mu}^2}{3kT} \left(\frac{1}{1 + i\omega\tau} \right) \right]$$

Where τ is the relaxation time and ω is equal to 2π times the frequency in cycles per second.

If equation (6) be solved for

$$7. \quad \epsilon = \frac{1 + \frac{2d}{M} P(\omega)}{1 - \frac{d}{M} P(\omega)}$$

If ϵ_0 is the dielectric constant at low frequencies and ϵ_∞ is the dielectric constant at high frequencies, then on substituting in (6)

$$8. \quad \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \alpha_0$$

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \cdot \frac{M}{d} = \frac{4\pi}{3} N \left(\alpha_0 + \frac{\bar{z}^2}{3KT} \right)$$

Again substituting (8) in (6)

$$9. \quad P(\omega) = \frac{M}{d} \left[\frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} + \left(\frac{1}{1 + i\omega\tau} \right) \left(\frac{\epsilon_0 - 1}{\epsilon_0 + 2} - \frac{\epsilon_{\infty} - 1}{\epsilon_{\infty} + 2} \right) \right]$$

On substituting (9) in (7) there is obtained

$$10. \quad \epsilon = \frac{\frac{\epsilon_0}{\epsilon_0 + 2} + i\omega\tau \frac{\epsilon_{\infty}}{\epsilon_{\infty} + 2}}{\frac{1}{\epsilon_0 + 2} + i\omega\tau \frac{1}{\epsilon_{\infty} + 2}}$$

Equation (10) shows that the dielectric constant is made up of two components, a real and an imaginary one.

Separation of these two components gives:

11.
$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2 \tau^2}$$

$$\epsilon'' = \frac{(\epsilon_0 - \epsilon_{\infty}) \omega \tau}{1 + \omega^2 \tau^2}$$

Where $\epsilon = \epsilon' - i\epsilon''$. ϵ' is the usual dielectric constant while the imaginary component contains ϵ'' which is the loss factor. The loss factor is due to a consumption of power by the production of a component of the total current which is in phase with the applied field while the lagging occurs. This "in-phase" component of current will increase up to the point where the period of the frequency and the relaxation time are the same, whereupon it will pass through a maximum.

When the region of high frequencies is reached, the molecules will no longer have time to follow the field to any appreciable extent and the only polarization remaining is that of the electrons; the molecule as a unit makes no contribution. Thus, the dielectric constant goes from a high value ϵ_0 at low frequencies to a low value ϵ_{∞} at high frequencies. At the same time, ϵ'' goes from zero at the point where $\omega \tau = 1$ and back to zero at high frequencies.

Literature on Dielectric Dispersion of Solutions

Funt and Mason (8) made dielectric measurements on concentrated solutions of poly(vinyl acetate) in toluene at three fixed frequencies over a temperature range. They found serious discrepancies in the quantitative comparison of the results of their experimental data with the Debye theory of dielectrics. They found that only rough approximations of the molecular size could be made from the Debye theory. From small, positive values of entropy, they found indications of restricted dipole rotation. They also found a relatively narrow distribution of relaxation times.

Hammerle and Kirkwood (10) found, in a study of poly(vinyl acetate) in toluene, that ϵ'' at any frequency, f , is given reasonably well by:

$$\epsilon''_f = \epsilon''_{max} \operatorname{sech}(\alpha x)$$

where, x , is $\log \frac{f}{f_m}$ and f_m is the frequency of maximum dispersion ϵ''_m . α was found for each molecular weight, temperature and concentration by plotting $\operatorname{sech}^{-1}(\epsilon''/\epsilon''_m)$ versus x . The values of α may be used to find the maximum reduced dispersion, H_m , which compared favorably with the theoretical dispersion. Some indication was found that f_m depends upon the temperature, being inversely proportional to the viscosity of the solvent at infinite dilution of the polymer. Theoretically, f_m is inversely proportional to the square root of the molecular weight when the solution is so dilute that no polymer molecule interactions occur. In this case, the theory did not hold. The data they used consisted of measurements of the real and imaginary parts of the dielectric constant for frequencies between 2 and 18 Mc/sec.

The concentrations were from 5 to 11 gms. of polymer per 100 cm.³ of solvent, temperatures were from 235° to 262° A. and molecular weights from 2.2×10^5 to 2×10^6 were employed.

Scherer, Levi, and Hawkins (18) found that a solution of cellulose acetate in dioxane exhibited dispersion in the region between 1 and 40 KC which appeared to be related to the size of the molecule involved. They found very close agreement between the degree of polymerization found by dielectric dispersion and that determined by viscosity measurements. This work was done on 5% by weight solutions of cellulose acetate. It was found to be impossible to use lower concentrations and make satisfactory measurements with the apparatus that they used.

In later work, Scherer, Hawkins, and Levi (17) made dielectric measurements on ethyl cellulose in dioxane in which a "differential" bridge method was used. They found that solutions having concentrations between 0.1 and 0.5% could be measured satisfactorily. Their experimental results showed that the critical frequency of an ethyl cellulose solution in dioxane is related to the intrinsic viscosity by an equation of the form:

$$\text{Log}[\eta] = A + B \text{Log}(\nu_c)$$

The critical frequency could be used to evaluate the intrinsic viscosity and from this the DP (degree of polymerization) of the polymer could be calculated.

EXPERIMENTAL

Materials:

The samples of poly(vinyl acetate) used in this investigation were obtained from the Bakelite Company, South Charleston, West Virginia, and were fractionated by S. N. Chinai. (2).

The dioxane was a purified grade supplied by Fisher Scientific Company, Fairlawn, New Jersey.

The ethylene chloride was supplied by Fisher Scientific Company in a purified form and was distilled before use.

The acetone was obtained from Commercial Solvents Corporation, Newark, New Jersey, and was C.P. grade.

The toluene was supplied by Fisher Scientific Company as a reagent grade.

Equipment:

The apparatus consisted of the following components:

1. 2 variable oscillators
2. frequency counter
3. capacitance bridge
4. variable precision capacitor
5. null detector with unit power supply
6. 2 amplifiers
7. resistor decade
8. capacitance cells

The oscillator with a frequency range of 10 cycles to 100 KC. was manufactured by Heathkit (model AG-9 Audio Generator). The oscillator with a frequency range from 50 cycles to 5 megacycles was manufactured by General Radio Company. The smaller oscillator was used at frequencies below 100 KC. because it was thought to provide more stable frequencies

and it was more convenient to use.

The frequency counter was manufactured by the Hewlett-Packard Company (type 524-A). It can be used to count frequencies from 10 cycles per second to 10 megacycles per second with an accuracy of 0.03%.

The capacitance bridge was manufactured by General Radio Company (type 722-D). It is an instrument of high stability, high precision of setting, low backlash, and low dielectric losses. It has an accuracy of 0.1%.

The null detector was manufactured by General Radio Company (type 1212-A). It was designed primarily as a balance-indicator in A-C bridge measurements.

The amplifiers were built by Hermon Hoshmer Scott, Inc. (type 140-A). Each amplifier had a gain control (10 or 100) and was used to amplify the bridge signal.

The resistance decade was built by W. C. Lawrence and had a range of 1 ohm to 11,111 ohms with an arrangement for increasing this range by connecting resistors to the decade in series.

The capacitance cells were manufactured by J. C. Balsbaugh and consist of concentric nickel cylinders.

A block diagram of the apparatus is shown in Figure 1.

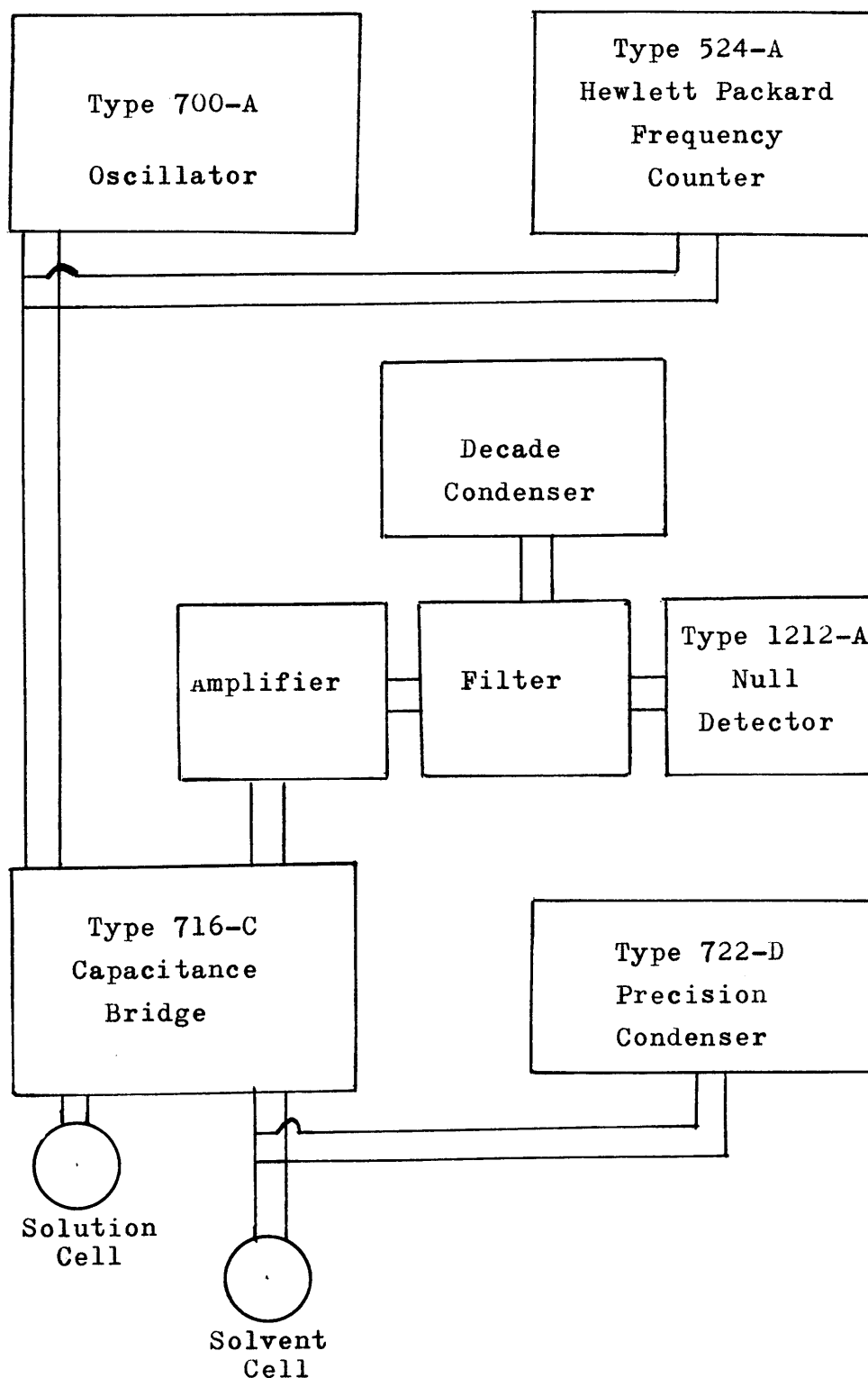


FIGURE 1
Block Diagram of Apparatus

Dispersion of Poly(vinyl Acetate) in Dioxane

In earlier (10) investigations of dielectric dispersion of solutions of cellulose acetate, it was found that the solvent used had to be of a low dielectric constant in order to make satisfactory measurements with the available equipment. Dioxane proved to be suitable for this type experiment and was, therefore, employed in this study. All of the experiments in this investigation were carried out in a room maintained at 77° F. and 50% relative humidity.

The solutions of poly(vinyl acetate) were prepared by weighing 5 gms. of polymer and dissolving in 100 ml. of dioxane.

Initial measurements of the capacitance of a 5 gm. per 100 ml. solution of poly(vinyl acetate) in dioxane showed no change over the frequency range of 400 cycles to 100 KC. The "Substitution Method" described in "Operating Instructions for Type 716C Capacitance Bridge," page 4, General Radio Company, was used.

It was then found by using the "Differential Method" that these solutions showed small differences in capacitance at various frequencies. In the "Differential Method," two 100 micromicrofarad cells were used. One cell containing the solution was placed across the "substitution" terminals of the bridge, and the second containing pure solvent was placed across the "direct" terminals in parallel with a precision condenser on the low range. The filter in parallel with the bridge output was set at the desired frequency and the oscillator output brought into resonance as indicated by a maximum on the null detector and, by using the precision condenser, a bridge balance was obtained and recorded.

The bridge condenser was set at a fixed value. The leads from the cells were disconnected from the bridge and "cell out" readings were obtained over the entire frequency range. "Cell in" readings were then obtained over the frequency range with the leads connected to the bridge. The difference between the "cell in" and "cell out" readings gave ΔC .

Figure 2 illustrates a typical curve obtained when ΔC was plotted against log frequency. The initial drop in capacitance (A) was inconsistent for the different fractions; changes in this region decreased for some fractions and increased for others. Two dispersion regions (B) and (C) were observed for all of the fractions measured.

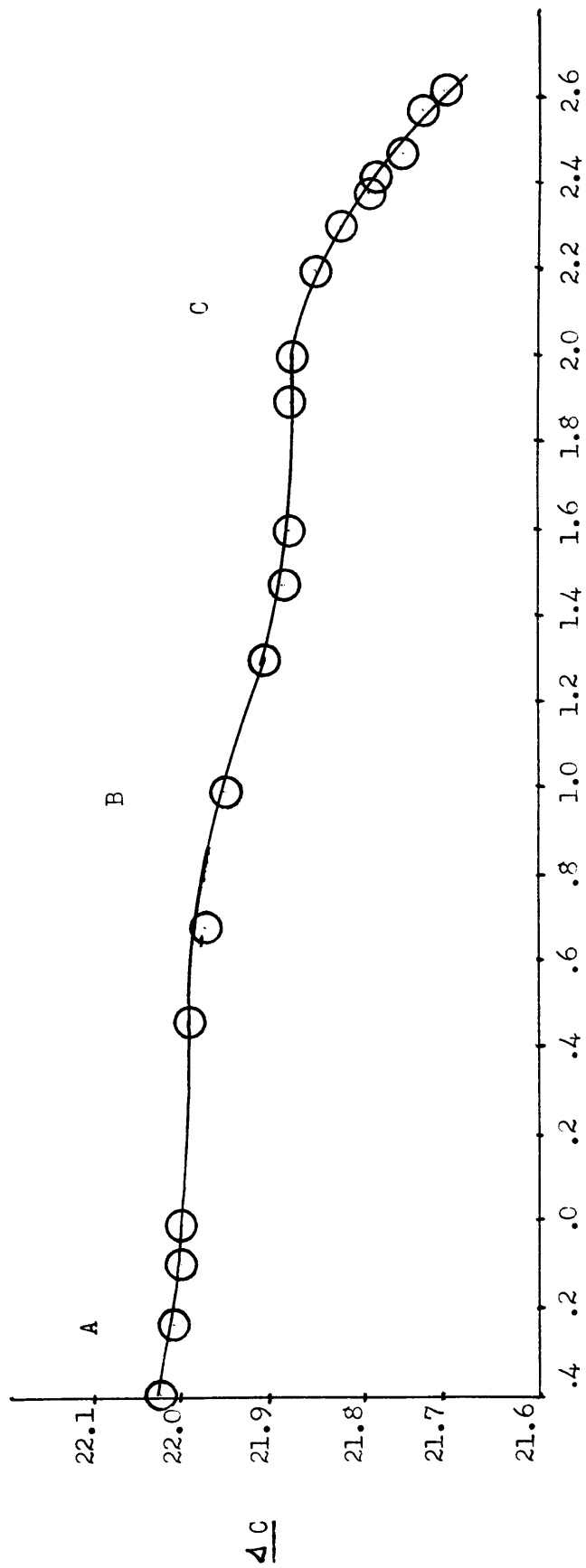
Region (B) was investigated more extensively in an attempt to establish a correlation between the molecular weight and dielectric dispersion. Table 1 indicates the resulting critical frequencies (V_c) obtained from four fractions for which measurements were made in the region of interest. The dispersion observed in this region was of the order of magnitude of 0.1 to 0.3 uuf. The average molecular weight values and the intrinsic viscosity measurements were made by Chinai, Scherer, and Levi. (3). They established a relationship between intrinsic viscosity and weight-average molecular weight for poly(vinyl acetate). The relation was given by:

$$[\eta] = 8.6 \times 10^{-5} M_w^{0.74}$$

The molecular weight was determined by light scattering measurements, and the viscosity was measured in acetone at 30° C.

Poly(vinyl Acetate) in Dioxane

Original Material



Log Frequency

FIGURE 2

TABLE 1

Critical Frequency - Molecular Weight Relation
For
Poly(vinyl Acetate) in Dioxane

<u>Fraction</u>	<u>[η]</u>	<u>$\bar{M}_w \times 10^{-5}$ Light Scatt.</u>	<u>V_c (KC.)</u>
F-2	1.25	6.6	21
F-3	1.01	3.3	31
F-6	0.70	1.9	40
O-1	0.62	1.6	50

The increase in critical frequency with decreasing molecular weight, as indicated in the table, is what might be expected if the critical frequency is related to the DP.

Readings taken immediately after connecting the cell containing solution into the bridge changed slowly with time. One set of measurements was made by taking these readings quickly. Such measurements give a linear log V_c versus M_w plot as shown in Figure 3. The values for V_c correspond to those in Table 1. An attempt was made to eliminate the "creeping" effect (change of capacitance readings with time) by allowing the cell containing solution to set for a period of time, connected to the bridge, before measurements were made. This, apparently, did not prevent the change from occurring, but it did seem to decrease the rate of change. Finally, the problem was solved by changing the method of preparation of the sample (to eliminate excessive moisture) and by providing better control over temperature variations. The procedure was to dry the polymer in an oven for approximately one hour at 100° C. prior to weighing the sample. After the sample was weighed

Poly(vinyl Acetate) in Dioxane

Log V_c Versus Log \bar{M}_w

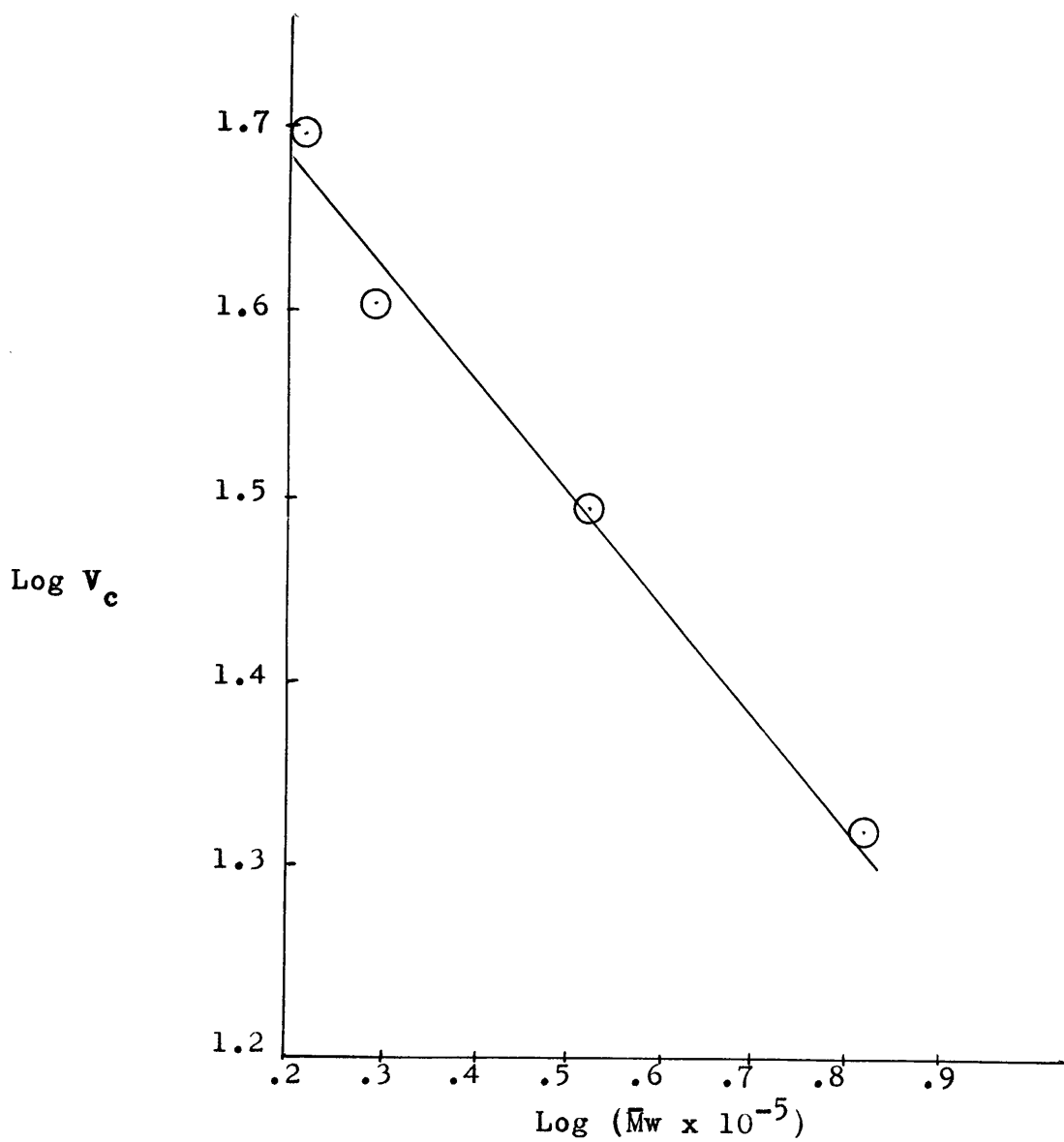


FIGURE 3

accurately (5 gms.) and the solvent (100 ml. dioxane) added, the mixture was mechanically agitated in an oven at constant temperature until dissolution was complete. The cell was filled to a mark well above the electrodes and sealed with paraffin wax. The cell was then placed in a Dewar flask, and the solution was allowed to stand until temperature equilibrium was attained.

Another set of measurements was then made on three fractions in the frequency range of .4 to 70 KC. The results are reported in Table 2.

TABLE 2

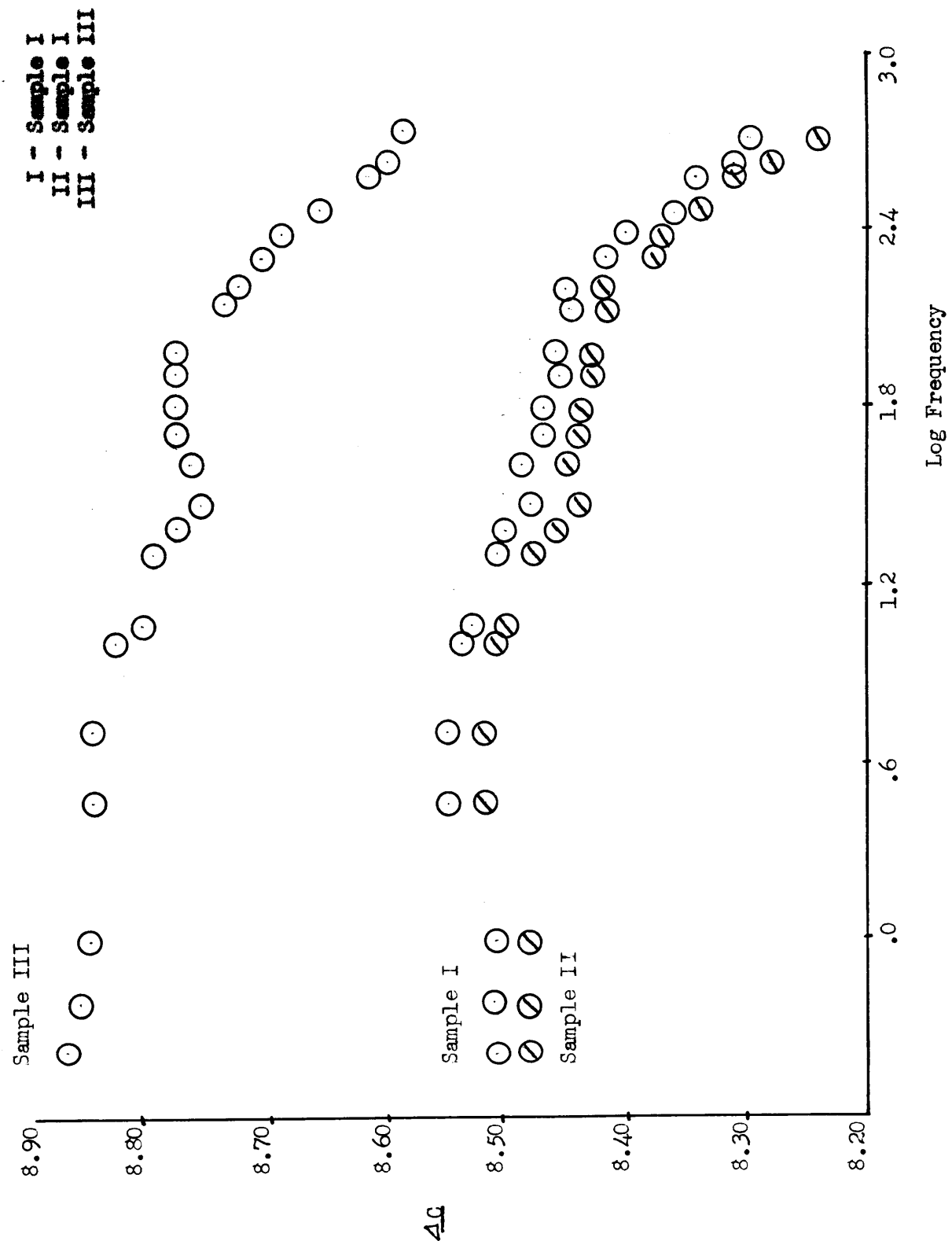
Critical Frequency - Molecular Weight Relation
For
Poly(vinyl Acetate) in Dioxane

<u>Fraction</u>	<u>[η]</u>	<u>$\bar{M}_w \times 10^{-5}$ Light Scatt.</u>	<u>V_c (KC.)</u>
F-2	1.25	6.6	17
F-3	1.01	3.3	22
F-5	0.70	1.9	27

Again, a straight line was obtained in a plot of $\log V_c$ versus $\log \bar{M}_w \times 10^{-5}$.

Two consecutive sets of capacitance readings were taken for each of the fractions in order to check the precision of the measurements. In addition to the two readings for a solution of F-2, another solution was prepared and measured to determine the reproducibility of the data. These results are presented in Figure 4. Prior to the time when this data was recorded, rather flexible copper wire had been used for leads in the cell-to-bridge connect-

FIGURE 4
Poly(vinyl Acetate) in Dioxane



ions. In an effort to remove a possible cause of inconsistency in measurements, rigid leads were cut from bicycle spokes and used throughout the remainder of this research.

The first attempt to increase the size of the capacitance drop involved trials of different methods that were listed in the "Operating Instructions for Type 716-C Capacitance Bridge" and, also, trials of combinations of these methods. None of these were satisfactory. It was also found that an increase in concentration from 5 gms. of polymer per 100 ml. dioxane to 10 gms. of polymer per 100 ml. of dioxane gave no appreciable increase in capacitance change. The next approach to the problem was based on the assumption that an increase in the polarity of the polymer molecule should have an effect on the dielectric dispersion and the effect should be that of increasing the capacitance drop. To increase the polarity of the molecule, partial hydrolysis of the acetate groups in the polymer chains was accomplished by an acid catalyzed reaction in methanol.

In order to determine the extent of hydrolysis, the sample was assayed for the percentage of acetic acid available from the sample and this was subtracted from the percentage obtained from pure poly(vinyl acetate). The percentage of acetic acid unavailable in the hydrolyzed material was found to be 4.2%. The sample was prepared in the usual manner and a run was made by the differential method. The results indicated no appreciable change in the magnitude of the capacitance drop. In this case, the $C_0 - C_{\infty}$ was 0.11 uuf. over the frequency range of .6 to 100 KC.

As a point of interest, the dispersion of a sample of polystyrene was measured in dioxane using the differential method. A 5 gm. sample in 100 ml. of dioxane showed a capacitance change of 0.09 uuf. in the first dispersion region. No further investigation was made on polystyrene

since the behavior seemed to be similar to that of poly(vinyl acetate).

Dielectric Dispersion of Poly(vinyl Acetate) in Ethylene Chloride

Concurrent with the work being done on poly(vinyl acetate) in dioxane, Dr. P. C. Scherer and Mr. W. C. Lawrence were carrying out investigations of polymer solutions in which solvents of high dielectric constant were employed. At this stage of their research, a method had been devised which allowed measurements of polymer in ethylene chloride (dielectric constant; 10.3). Their results indicated that use of a more polar solvent increased the magnitude of the total dispersion. Since the small change in dispersion had been a major problem with poly(vinyl acetate) in a solvent of low dielectric constant (dioxane; $\epsilon = 2.28$), the application of a high dielectric system to poly(vinyl acetate) seemed worthy of investigation.

When dioxane was used as a solvent, it was found that the cell containing solution exhibited high parallel resistance and low conductivity. Any changes in resistance over the frequency range were taken care of by a variable capacitor in one ratio arm of the bridge controlled by the dissipation dial. The dissipation was never large enough to necessitate the use of a correction factor for capacitance readings. However, when ethylene chloride was used as a solvent, the polymer solution showed a relatively low parallel resistance and high conductivity. This resulted in large dissipation readings which could not be accurately corrected. In order to surmount this difficulty, the resistance decade, previously described, was connected to one ratio arm of the bridge to balance the resistance in the cell. This arrangement eliminated the necessity for making dissipation

corrections.

The difficulties encountered immediately with this new system were numerous. The capacitance of the empty cell multiplied by the dielectric constant of the solvent gives approximately the capacitance reading of the bridge dial when the cell containing solution is measured. For example, when a 100 uuf. cell was filled with ethylene chloride, the expected reading on the bridge dial would be 1030 uuf. (100×10.3). The highest possible bridge reading was 1150 uuf. Also, the effect of concentration had to be considered; the higher concentration gave a higher capacitance reading. Therefore, the sample weights per 100 ml. of solvent were decreased to .5 gms. and this was found to be satisfactory for a 100 uuf. or 50 uuf. cell. As far as increasing the magnitude of the capacitance drop, the decrease of concentration was a step in the reverse direction.

One of the major problems encountered was that of creep. The instability of the capacitance readings was far more pronounced than that found in dioxane. It was more rapid at low frequencies than at high frequencies. Readings could be taken by connecting two 0.03 microfarad condensers in parallel with the two ratio arms of the bridge. These condensers had to be removed, usually at 3 KC., because of the insensitivity of the balancing capacitor at higher frequencies. Probably, the condensers simply decreased the sensitivity of the measurements and the accuracy of the results were obviously questionable under these circumstances.

One of the theories as to the cause of the creeping was that preferential adsorption of the polymer molecules on the reference electrodes occurred. This adsorption would create a depleted layer of solvent around the electrodes.

If the rate of the adsorption of polymer on the electrodes were more rapid than the rate of diffusion of polymer molecules into the depleted layer, then the solution would not be at equilibrium. The presence of a depleted layer would cause the parallel resistance to be greater than the normal resistance. Diffusion of polymer molecules into this depleted layer would then result in a gradual decrease in the parallel resistance. This was evidenced by the fact that the creeping stopped if the sample were allowed to stand for a period of time (three days or so). The parallel resistance method used at this stage of the experiment may be described as follows: The cell containing the solution was connected to the unknown substitution terminals of the bridge. The balancing precision capacitor was connected to the unknown direct terminals and the resistance decade was connected in parallel with this capacitor. The method switch was set on substitution. The filter settings were adjusted for the particular frequency in order to obtain a maximum reading on the null detector scale. The capacitance dial on the bridge (C_b) was set at 1000 uuf., and with the leads to the cell and resistor decade disconnected, a balance was obtained by alternately adjusting the capacitor dial (C_p) and the dissipation dial. The leads are then connected and the capacitance balance again obtained by changing C_b and the resistance on the resistance decade. The actual capacitance of the cell containing solution was found by subtracting the reading (C_b) obtained with the cell connected to the bridge from 1000 uuf., which was the original reading at C_b .

Table 3 shows a typical set of data obtained from this system. Obviously, there are no constant capacitance readings at low frequencies from which C_0 may be defined.

TABLE 3

Poly(vinyl Acetate) in Ethylene Chloride (F-2)

Parallel Resistance Method

0.5 gms. per 100 ml. Solvent 50 uuf. Cell

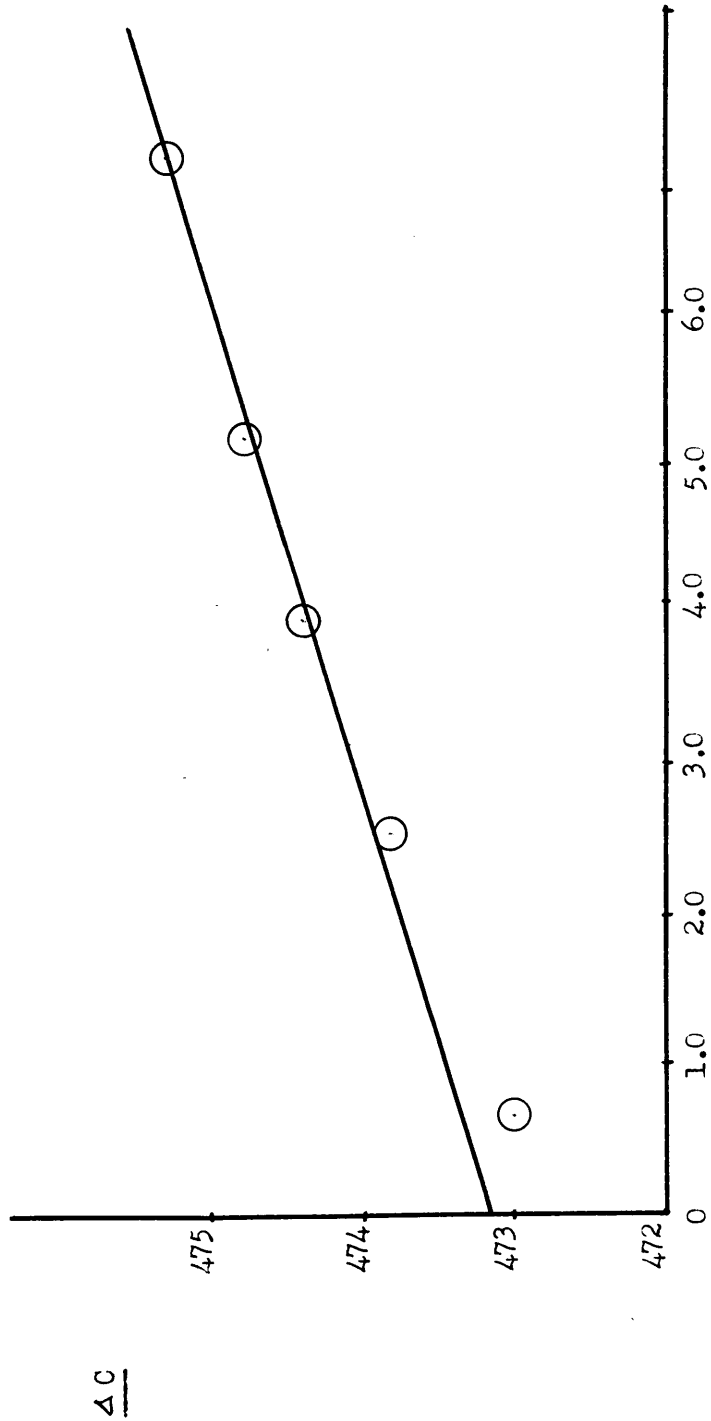
<u>Frequency</u>	<u>Capacitance</u>
0.5	475.6
0.6	475.3
0.7	474.8
0.8	474.4
0.9	474.1
1.0	473.8
2.0	473.0
3.0	472.2
5.0	471.1
10.0	470.5
15.0	470.3
20.0	470.3
30.0	470.1
40.0	470.0
50.0	470.0
60.0	469.9
70.0	469.9
80.0	469.9

A plot of ΔC versus $\frac{10^2}{\omega^2}$ with extrapolation of the line to zero was the means by which C_0 was obtained. The graph in Figure 5 to determine C_0 corresponds to the data from Table 3. These data were collected under the conditions previously described in which the 0.03 uuf. condensers were used to control the creeping effect.

Mr. W. C. Lawrence found that the creeping could be stopped in some cases by heating the solution in the cell at constant temperature and then tumbling the cell mechanically for about four hours before starting a run. This procedure was applied to a solution of poly(vinyl acetate) and additional measurements were made. The creeping was reduced to the extent that the .03 uuf. condensers could be eliminated, but the results were never reproducible. The use of acetone as a solvent presented the same problems as those encountered with ethylene chloride. The value of C_0 had to be determined by the same procedure and the creeping effect was present.

FIGURE 5

Poly(vinyl Acetate) in Ethylene Chloride
Determination of C_0



DISCUSSION

DISCUSSION

The determination of the dielectric dispersion of poly(vinyl acetate) in dioxane could be measured only with relatively concentrated solutions (5 gms. per 100 ml.). The capacitance changes were in the order of magnitude of 0.05 to 0.30 uuf. Experimental data indicated that two dispersion regions were present; however, with the apparatus available, only the first region could be investigated to any extent. The first dispersion region seemed to be related to the molecular weight in that the critical frequencies showed a linear correlation with the average molecular weight values obtained from light scattering measurements. Proof of this relationship was impossible because of the inability to reproduce the critical frequencies. Such small changes in capacitance measurements were sensitive to any slight variations in experimental conditions or to any small errors in measurement.

The attempts to enlarge the capacitance drop met with little success. The failure to obtain an increase in dispersion by use of partially hydrolyzed poly(vinyl acetate) may be explained by the small extent of hydrolysis in the sample that was prepared. Lack of time prevented further investigation in this area. When ethylene chloride was used as a solvent for poly(vinyl acetate) the concentration of the solutions had to be reduced, and this prevented a very large improvement in the magnitude of capacitance changes. In general, the capacitance changes were from 0.5 to 4 uuf. with this system. Apparently, the dispersion region was shifted to a lower frequency range, and the first level portion of the dispersion curve was obscured by the

polarization occurring there. The means of obtaining C_0 by a plot of ΔC versus $\frac{10^2}{\omega^2}$ and extrapolating to zero was unsatisfactory. This method of calculating C_0 was developed by Johnson and Cole (12) and is based on the following relation:

$$\epsilon_{true} = \epsilon_{app} - \frac{K}{\omega^2}$$

In this, ϵ_{app} is the dielectric constant as measured at a frequency $\omega = 2\pi f$. In this work, the dielectric constant is replaced by measured ΔC values.

In an attempt to obtain information as to the relationship of the collected data to theoretical considerations, some of the experimental distribution curves were compared with the Debye curve. The Debye curve is based on the assumption of only one relaxation time. Deviation from this curve implies a distribution of relaxation times. A typical comparison is shown by the curves in Figure 6. The corresponding data is presented in Table 4. The equation for the Debye curve is:

$$\epsilon' = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + \omega^2 \tau^2}$$

By use of the identities given below, simpler calculations can be made:

$$\frac{C - C_{\infty}}{C_0 - C_{\infty}} = \frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}} = \frac{1}{1 + (f/f_m)^2}$$

Figure 7 is made up of a collection of dispersion curves over the frequency range of 0.4 to 420 KC. The samples were measured in dioxane solution using the differential method and concentration of 5 gms. per 100 ml.

TABLE 4

Data for Comparison of Experimental and Debye Curve
Poly(vinyl Acetate in Dioxane F-6 (5 gms./100 ml.))

<u>Frequency</u> <u>(cps.)</u>	<u>Log</u> <u>Frequency</u>	$\frac{C-C_{\infty}}{C_0-C_{\infty}}$	ΔC	
400	2.602	1.11	19.53	$C_0 = 19.49$
600	2.778	1.00	19.49	
800	2.903	0.917	19.47	$\Delta C = 19.13$
1,000	3.000	0.888	19.46	
3,000	3.477	0.778	19.41	
5,000	3.699	0.667	19.37	
10,000	4.000	0.500	19.31	$C_0 - C_{\infty} = 0.36$
20,000	4.301	0.250	19.22	
30,000	4.477	0.084	19.16	
40,000	4.602	0.084	19.16	
50,000	4.699	0.056	19.15	
80,000	4.903	0	19.13	
100,000	5.000	0	19.13	

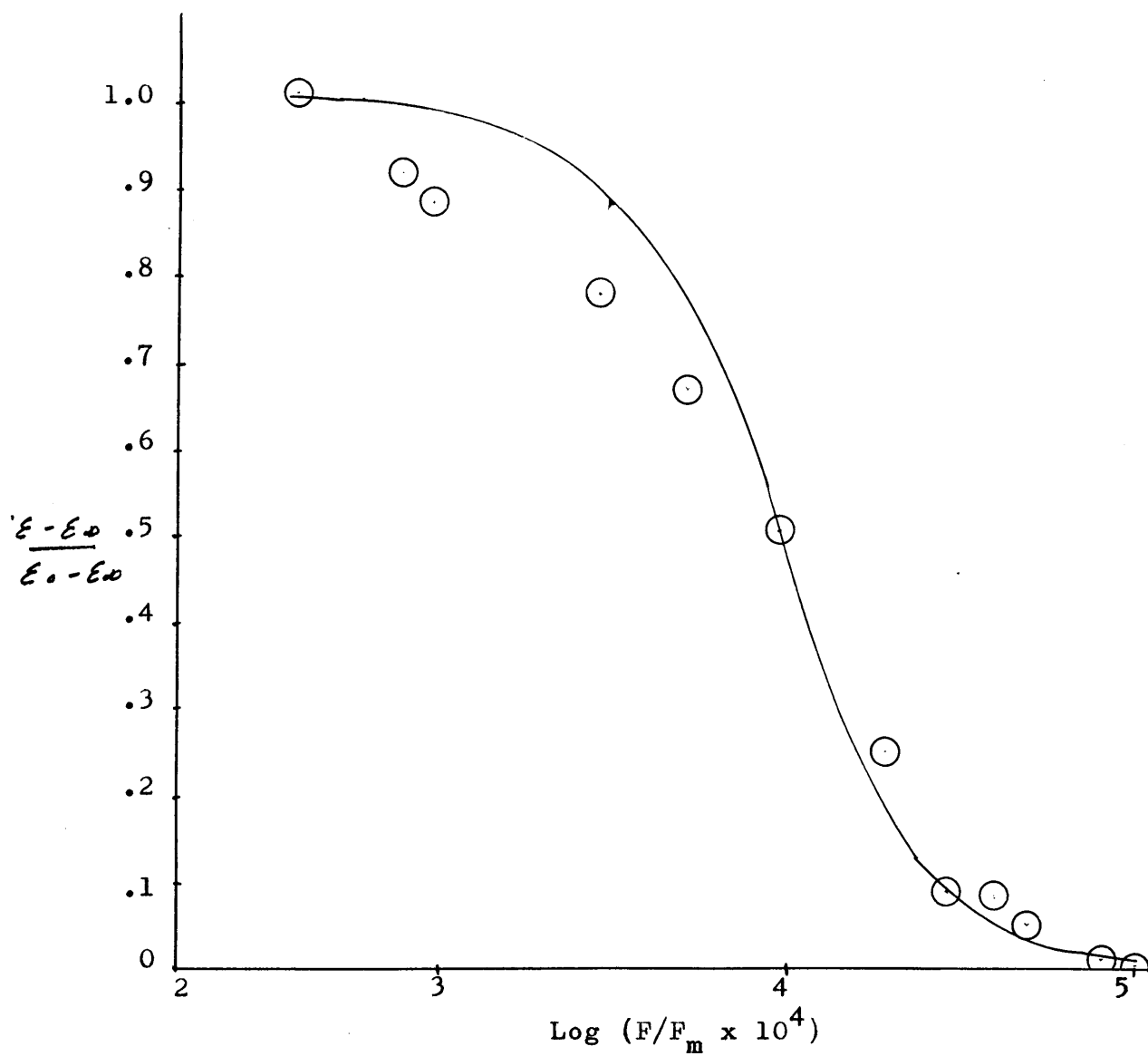
At Dispersion = 0.5 $F_m = 10,000$

$$\tau = \frac{1}{2(3.1416)(10,000)} = 1.59 \times 10^{-5}$$

<u>F</u>	$\frac{F}{F_m}$	$(\frac{F}{F_m})^2$	$\frac{1}{1+(\frac{F}{F_m})^2} = \frac{\epsilon - \epsilon_{\infty}}{\epsilon_0 - \epsilon_{\infty}}$	<u>Log</u> $(\frac{F}{F_m} \times 10^4)$
400	0.0400	0.00160	0.998	2.602
600	0.0600	0.00360	0.996	2.778
800	0.0800	0.00640	0.994	2.903
1,000	0.100	0.0100	0.990	3.000
3,000	0.300	0.0900	0.917	3.477
5,000	0.500	0.250	0.800	3.699
10,000	1.00	1.00	0.500	4.000
20,000	2.00	4.00	0.200	4.301
30,000	3.00	9.00	0.100	4.477
40,000	4.00	16.00	0.059	4.602
50,000	5.00	25.00	0.038	4.699
80,000	8.00	64.00	0.015	4.903
100,000	10.00	100.00	0.0099	5.000

FIGURE 6

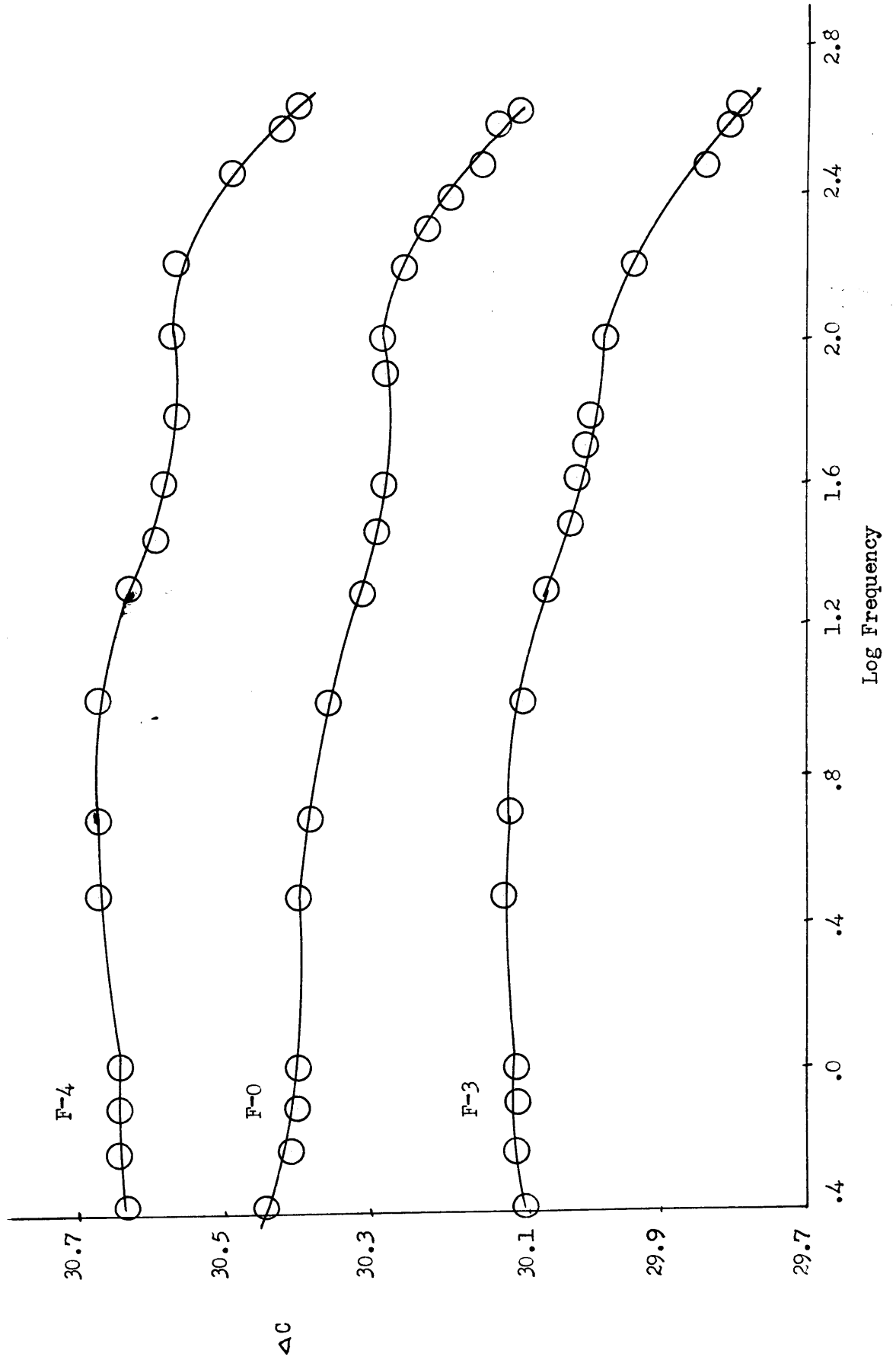
Poly(vinyl Acetate) in Dioxane F-6



Experimental Points
Line = Debye Curve

FIGURE 7

Poly(vinyl Acetate) in Dioxane



CONCLUSIONS

1. A dielectric cell filled with a solution of poly(vinyl acetate) in dioxane (5 gms. per 100 ml.) exhibits a decrease in capacitance with an increase in frequency in the range of 0.4 to 500 KC.
2. Dielectric measurements may be made on solutions of poly(vinyl acetate) in ethylene chloride by using a resistance decade to balance the resistance in the solution.
3. Measurements are also possible on acetone-poly(vinyl acetate) solutions using the resistance decade. The dispersion regions are apparently shifted to a lower frequency range when high dielectric solvents are employed.
4. Investigation of the effect of partial hydrolysis of poly(vinyl acetate) on the dielectric properties should be further studied.

BIBLIOGRAPHY

REFERENCES CITED

1. E. R. Blout, "Monomers", Interscience Publishers, Inc., New York (1949).
2. S. N. Chinai, Ph.D. Thesis, Virginia Polytechnic Institute.
3. S. N. Chinai, P. C. Scherer, and D. W. Levi, J. Polymer Sci., 27; 117-124 (1955).
4. P. Drude, Z. Physik. Chem., 23; 267 (1897).
5. C. Ellis, "The Chemistry of Synthetic Resins", 2; 1020 (1935).
6. P. J. Flory, J. Polymer Sci., 2; 36-40 (1947).
7. C. S. Fuller, Chem. Revs., 26; 163 (1940).
8. B. L. Funt and S. G. Mason, Can. J. Research, 28-B; (1950).
9. B. L. Funt and T. H. Sutherland, Can. J. Chem., 33; 1669-1676 (1955).
10. W. G. Hammerle and J. G. Kirkwood, J. Chem. Phys., 24; 1277 (1956).
11. W. G. Hammerle and J. G. Kirkwood, Ibid, 23; 1743-1749 (1955).
12. J. F. Johnson and R. H. Cole, J. Am. Chem. Soc., 73; 4536 (1951).
13. Klatta, Ind. Eng. Chem., 28; 1123 (1936).
14. C. S. Marvel, "The Chemistry of Large Molecules", Interscience Publishers, Inc., New York (1943).

15. C. S. Marvel and C. E. Denoon, *J. Am. Chem. Soc.*, 60; 1045 (1938).
16. J. C. Oncley, *Ibid*, 60; 1115 (1938).
17. P. C. Scherer, M. C. Hawkins, and D. W. Levi, *J. Polymer Sci.*, 27; 129-134 (1958).
18. P. C. Scherer, D. W. Levi, and M. C. Hawkins, *Ibid*, 24; 19-26 (1957).
19. C. P. Smyth, "Dielectric Behavior and Structure", *International Chemical Series*, McGraw-Hill Book Co., Inc., New York (1955).
20. H. Staudinger, *Ber.* 60; 1782 (1927).
21. H. Staudinger, K. Frey and W. Starck, *Ibid*, 60-B; 1782 (1927).
22. H. Staudinger and A. Schwalbach, *Ann.*, 488; 8 (1931)

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ABSTRACT

The dielectric dispersion of poly(vinyl acetate) solutions was studied in an attempt to relate this behavior to the chemical nature of the material. The bridge method was employed in which capacitance measurement of solutions were made over a frequency range of 400 cycles to 500 kilocycles.

The results of these experiments indicate that a vinyl type material possesses greater flexibility than cellulose derivatives in solution and, thus, the magnitude of capacitance changes over a frequency range is considerably reduced. Because of the very small changes in capacitance, reproducible results are difficult to obtain and definite conclusions as to the relation of dispersion to molecular weight are impossible.

Dielectric dispersion studies were made on solutions of poly(vinyl acetate) in dioxane, ethylene chloride and acetone.