

## Structure and Electrical Properties of Poly(vinyl Benzoate) Monolayers

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### Synopsis

The structure and electrical properties of mono- and multilayer poly(vinyl benzoate) (PVB) films have been studied by using the films as ultrathin insulating spacers between evaporated electrodes of Cu and Sn. PVB-stearic acid mixtures were also used. From capacity measurements, autoradiographs, and the layering conditions it is concluded that the compacted PVB film on the aqueous subphase has an average area per monomer unit of  $\sim 8 \text{ \AA}^2$  and is composed of several superimposed layers of molecules rather than a single layer. Usually each transfer operation yielded a PVB insulating film whose average thickness was estimated to be  $\sim 37 \text{ \AA}$ . Under certain and still unknown conditions, the PVB layer appeared to separate on transfer to give an average film thickness of approximately half of this value. The dielectric constant of the PVB films at room temperature and 1 kcycle/sec. was estimated to be  $\sim 3.3$ , and was found to be frequency-dependent within the measured range of 100 cycles/sec. to 20 kcycles/sec. Conduction through the metal-PVB-metal sandwiches was highly nonlinear and was believed to take place by tunneling in the thinner films ( $\sim 20 \text{ \AA}$ .) and by field-assisted thermionic emission in the thicker films ( $\sim 75 \text{ \AA}$ .) Interpretation of the conduction measurements in terms of a molecular model was not possible because of the wide variations in electrical properties and lack of reproducibility.

### INTRODUCTION

Ries, Beredjick, and Gabor<sup>1</sup> have reported that monolayers of poly(vinyl benzoate) (PVB) show strong film-forming properties similar to those of the vertically oriented fatty acids. The pressure-area isotherms of PVB in fact follow the classic pattern of stearic acid, that is, a region in which the compressibility is relatively high, followed by a region where a slight decrease in area gives a very great increase in pressure, and terminating abruptly at a well defined collapse pressure. The collapse pressure reported for PVB films is very high (53 dyne/cm.), indicating that a very rigid stable film is obtained. This behavior is in marked contrast to that of other horizontally oriented polar polymers such as poly(vinyl acetate) (PVA), for example, which shows high compressibility and a gradual transition to a collapsed state (Fig. 1). The difference in behavior between PVB and PVA monolayers is difficult to explain; hence the origin of the rigid film behavior of the PVB and the structure of the layers are of considerable fundamental interest. In addition, the remarkable tenacity and cohesion

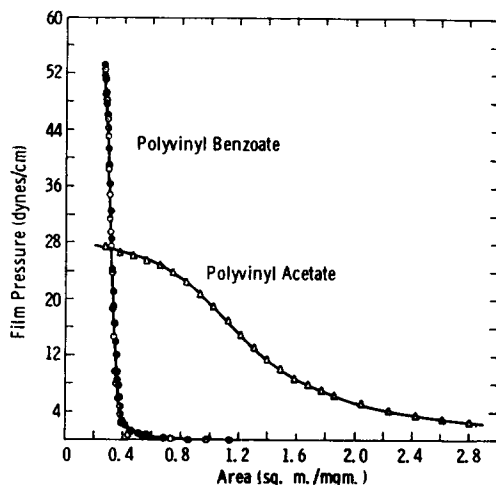


Fig. 1.  $P/A$  Isotherms of poly(vinyl benzoate) and poly(vinyl acetate). Data of Ries et al.<sup>1</sup>

of the PVB films make them an interesting subject for study as ultrathin insulators.

### EXPERIMENTAL

The experimental structure consisted of  $1 \times 3$  in. glass slides on which electrodes of copper and tin had been deposited by vacuum evaporation. The organic monolayers were transferred onto the slides as described below, and then a second electrode deposited over the top, again by vacuum evaporation. Each slide yielded 6 to 9 metal-organic-metal sandwiches, 1 mm.<sup>2</sup> in area.

Transfer of the organic films was carried out in a closed thermostatted cabinet containing the Teflon-coated trough, film balance, compression bars, dipping mechanisms, and so forth, the operation of which was carried out by remote control so as not to disturb the shock-mounted support table or set up waves in the bath. A detailed description of the apparatus has been given earlier.<sup>2</sup> The general procedure of film formation is given in a separate paper<sup>3</sup> dealing with the results obtained on vertically oriented film formers such as the metal stearates. The poly(vinyl benzoate) was prepared in this laboratory as follows. The inhibitor from vinyl benzoate obtained from the K and K Laboratories was removed by shaking the monomer repeatedly with 2% NaOH, washing with water until neutral, and then drying over calcium sulfate. Azobisisobutyronitrile was used as the initiator (0.5% by weight of monomer); the monomer-initiator mixture was frozen and evacuated several times, then sealed in a reaction tube and heated for 66 hr. at 80°C. The very viscous reaction product was dissolved in spectro grade benzene and reprecipitated with methanol. The precipitate was white PVB. Solutions of PVB in spectro grade benzene were made

in such a proportion that 1 ml. of solution contained 1 mg. of polymer which is reported to spread to 0.38 m<sup>2</sup>.<sup>1</sup> The spreading was carried out on deionized water at a pH of 6.2.

Four methods of transferring the PVB monolayers onto solid substrates were used with varying degrees of success: (1) dipping and retrieving the slides as in the classic Langmuir method, (2) placing the slide parallel to and just beneath the surface of the bath, spreading and compressing the monolayer, and then raising the slide up through the monolayer, (3) placing the slide parallel to and just above the floating monolayer and then pushing the surface to be coated into the PVB films, and (4) covering the slide with a monolayer of barium stearate, followed by several PVB transfer operations according to the usual Langmuir procedure. It was found with the last method that usually the only measurable coating was the stearate layer.

In addition to the PVB films, a number of samples were made using equiweight mixtures of PVB and stearic acid, with good results. The mixture had a collapse pressure close to that of the stearic acid (40–42 dyne/cm.), and behaved in most respects as though the stearic acid was controlling the transfer. The mixture was considerably more flexible than the pure PVB and so could be transferred at higher pressures with the Langmuir dip method, e.g., 25–31 dyne/cm. for the mixture versus ~ 20 dyne/cm. for the pure PVB. In one case the stearic acid used in the mixture was tagged with C<sup>14</sup>, and the autoradiographs taken of this slide<sup>3</sup> showed good layer continuity within the resolution of the emulsion (~25 μ). No gross defects were apparent, and the radioactive emission intensity increased in direct proportion to the number of transfer strokes.

## RESULTS

### Film Structure

The molecules of the linear polymers are not vertically oriented, hence the monolayer thickness is not given by the molecular length as it is for the stearates, nor is the mode of attachment of the molecules to the substrate so well defined. The capacity of the metal–organic–metal sandwiches, however, provides a measure of the thickness of the organic layers, since

$$\frac{1}{C} = \frac{t}{88.5\epsilon} \quad (1)$$

where  $\epsilon$  is the relative dielectric constant,  $t$  is the thickness in angstrom units, and  $C$  is the capacity in nanofarads/mm.<sup>2</sup>. The value of  $\epsilon$  is not known precisely, but can be presumed to be between 2 and 10 without serious risk of error. Based upon data available for PVA<sup>4</sup>, a narrower range of  $2 < \epsilon < 5$  appears reasonable for PVB at the measuring frequency of 1 kcycle/sec. and room temperature. If we assume that the dielectric constant is approximately independent of thickness over the range of interest, then according to eq. (1) the reciprocal capacity ( $1/C$ ) is directly

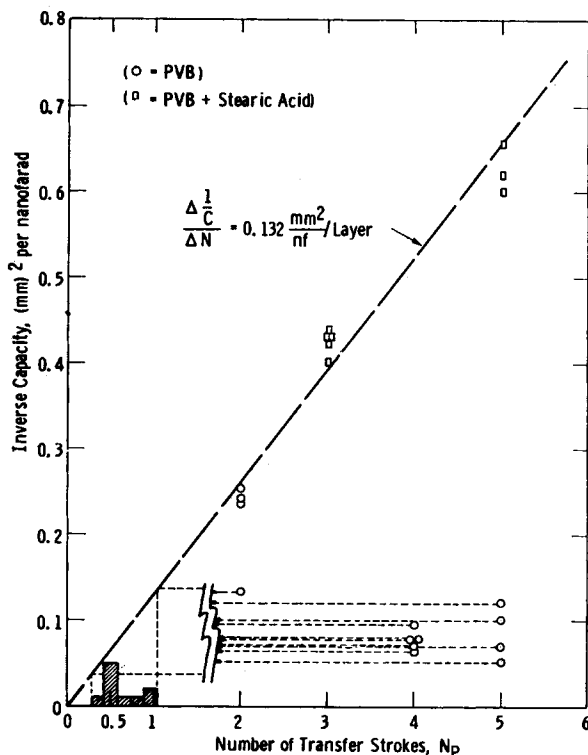


Fig. 2. Reciprocal capacitance vs. number of transfer strokes for PVB and PVB-stearic acid films.

proportional to thickness. A plot of  $(1/C)$  versus the predicted number of layers ( $N_p$ ) should yield a straight line passing close to zero, whose slope corresponds to the incremental thickness per layer. Figure 2 shows such a plot assuming that each transfer stroke yielded a layer. It should be noted that some of the layers are pure PVB and some are a PVB-stearic acid mixture. Of the 21 available data points, eleven fall approximately on a straight line passing through zero, and having a slope  $S = \Delta(1/C)/\Delta(N_p) = 0.132 \text{ mm.}^2/\text{nF./layer}$ . The remaining points lie well away from this line, and it is obvious that the number of layers actually transferred or retained in these cases was less than the predicted number. The number actually obtained can be determined by horizontally translating these points until they intersect the dashed line and then reading off the corresponding value of  $N_p$  (denoted  $N_p'$ ). Ideally, this process should yield only integer values for  $N_p'$ . It is seen that the  $N_p'$  points correspond to the range of values  $0.4 \leq N_p' \leq 1$ . However, if the distribution of points over this interval is determined, as shown by the shaded bars on the abscissa of Figure 2, it is seen that 50% of these points correspond approximately to  $N_p' = 1/2$ . The heavy concentration of the extrapolated points near  $N_p = 1/2$  suggests the possibility that the incremental or "single" monolayer thickness  $\Delta t/\Delta N_p$

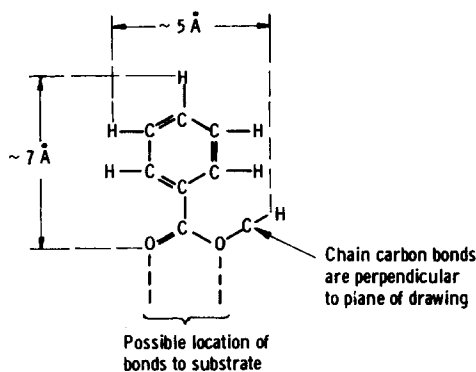


Fig. 3. Schematic drawing of PVB monomer unit.

measured by the slope  $S$ , may in fact be made up of more than one sheet of molecules, which customarily are picked up as a unit, but which can sometimes be separated; the implication being that failure to achieve the predicted number of layers is associated with this separation phenomenon. In other words, to account for the entire range of data in Figure 2, and particularly for the very thin layers obtained (small  $1/C$  values), we are led to the hypothesis that a compressed film of PVB may be made up of several stacked and probably interlocking sheets of molecules. Ries and co-workers<sup>1</sup> have proposed a similar hypothesis, i.e., coiling or folding of the chains, in order to account for the mechanical properties of the compressed PVB films.

The copper and tin electrodes used in these tests must inevitably have oxidized prior to transfer of the organic layers. The oxide thickness may be comparable with the monolayer thickness and cannot be neglected *a priori* in evaluating the electrical measurements. There is ample evidence to show that the organic films are frequently porous or inhomogeneous, and Handy and Scala<sup>3</sup> give an extensive discussion of the influence of the surface oxide on the electrical properties of the sandwiches. It is possible to show (from measurements on uncoated but oxidized electrodes) that if the leakage resistance of the metal-organic-metal sandwiches is sufficiently high to permit a capacity measurement, then the capacity values obtained will not be seriously in error due to the presence of the oxide. Hence, the capacity data of Figure 2 reflect principally the behavior of the organic films.

It is possible to test the stacking hypothesis in several ways. From the transfer conditions, i.e., area of the compressed film, molecular weight, and number of molecules spread, we obtain a value of  $7.65 \text{ \AA}^2$  for the average area per monomer unit in the compressed film (as compared to the value of  $9 \text{ \AA}^2$  obtained by Ries et al.). If we now consider the detailed structure of a single monomer unit as shown in Figure 3 (as if viewing the polymer chain end-on), then, by combining known bond lengths and bond angles,<sup>5</sup> it is possible to estimate the dimensions of the monomer unit, as shown. These dimensions yield a required area per monomer unit of approximately 15–20

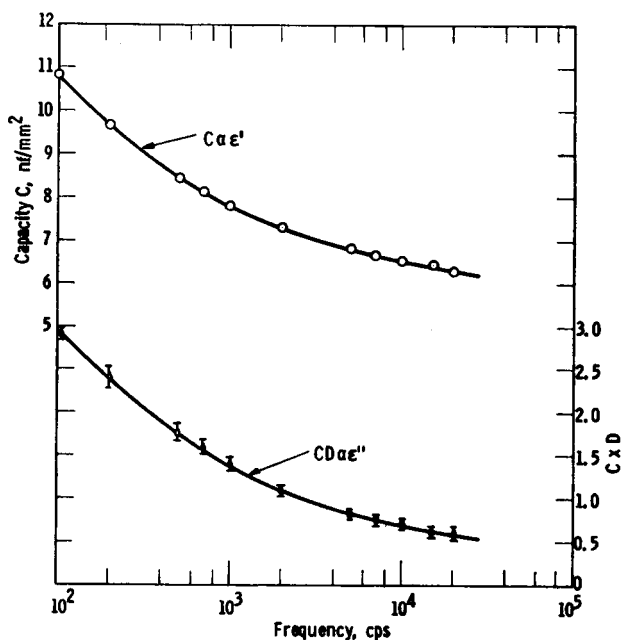


Fig. 4. Capacity  $C$  and capacity  $\times$  dissipation factor  $CD$  vs. frequency for a PVB film.

$\text{Å}^2$ , assuming no interleaving of the chains. This is between 2 and 3 times the average observed value of  $\sim 8 \text{ Å}^2$ , from which we conclude, in support of our electrical observations, that on the average there are several monomer units interleaved and stacked above each other in the compressed PVB monolayer.

There is another point of comparison which should be considered. Assuming each polymer chain to be lying approximately parallel to the plane of the electrode surface, then from Figure 3 the predicted thickness of a single sheet of molecules is approximately 7–10  $\text{Å}$ . For a relative dielectric constant of 3, approximately four such sheets would be required per incremental or "single monolayer" thickness to give the observed value of  $S = 0.132$ . This is roughly one more layer than is required to reconcile the observed and calculated area per monomer unit. Considering the estimates required for the various dimensions, this order of agreement is all that could be expected.

The dimensions of the PVB layers can be investigated further by examining the variation in complex dielectric constant

$$\epsilon^* = \epsilon^0(\epsilon' - j\epsilon'')$$

as a function of frequency. The variation with frequency of  $\epsilon'$  and  $\epsilon''$  may be obtained by plotting  $C$  versus  $f$  and the product  $CD$  versus  $f$ , respectively, where  $C$  is the capacity and  $D$  is the dissipation factor. Figure 4 shows such a plot for a PVB sample at room temperature over the range from 100 cycles/sec. to 20 kcycles/sec. Both  $\epsilon'$  and  $\epsilon''$  decrease with increasing frequency. This type of behavior is typical of polymeric materials with

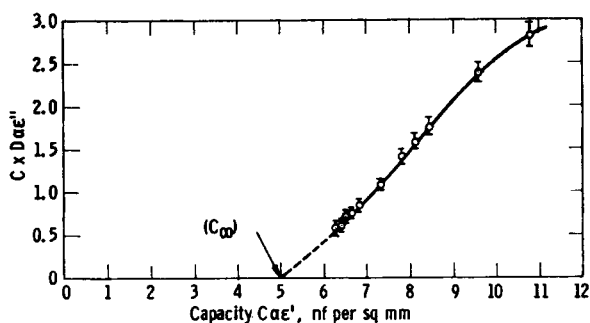


Fig. 5. Extrapolation of  $CD$  vs.  $C$  to obtain  $C_\infty$ .

dipoles undergoing hindered rotations in the field,<sup>6</sup> and for this set of data, it corresponds to the region where the effective dipole relaxation time is longer than the period of the test frequency. As the frequency is increased to infinity, the  $C$  value should tend to a value determined by the optical dielectric constant  $\epsilon_\infty$ , and the  $CD$  value should tend to zero, since  $CD \propto \epsilon'' \propto 1/f$ . The limiting value of  $C_\infty$  can be estimated by extrapolation of a plot of  $CD$  versus  $C$  as is shown in Figure 5. The optical dielectric constant of PVB can be reasonably estimated to be  $\epsilon_\infty = 2.1$ . Substituting  $C_\infty$  and  $\epsilon_\infty$  into eq. (1), we obtain a value of  $\sim 37$  Å. for the incremental thickness of the PVB layers. Again using  $\epsilon_\infty = 2.1$ , and the data of Figures 4 and 5, a value of  $\epsilon = 3.3$  at 1 kcycle/sec. is obtained, which falls within the range of the preliminary estimates based on published data for PVA. As a final test for consistency, one can use the incremental thickness value of  $\sim 37$  Å. and the 1 kcycle/sec. dielectric constant value of 3.3 obtained from the variable frequency measurements to predict the slope of the line drawn on Figure 2, obtaining  $0.128 \text{ mm.}^2/\text{nF./layer}$ , which compares closely to the measured value of 0.132.

### Electrical Properties

In addition to the capacity measurements and autoradiograph studies, current-voltage ( $I$ - $V$ ) measurements were made on a number of PVB samples at several temperatures. It is in this realm of the electrical properties that any oxide on the electrodes, or pores and inhomogeneities in the organic layers, have their most profound effects. The capacity measurements give a film thickness ( $t \propto 1/C$ ) in which nonuniformities in thickness  $t$  are weighted according to the factor  $(1/t)$ . The low voltage resistivity values ( $R_0$ ), taken from the linear region of the  $I$ - $V$  curves, however, are weighted according to the much more powerful factor  $(1/\exp t)$ , for conduction by electron tunneling. Small variations in thickness can, therefore, produce large variations in  $R_0$  for small variations in  $1/C$ . In addition, any exposed oxide regions due to incomplete coverage can be expected to contribute powerfully to the low voltage resistivity, even though they represent such a small fraction of the area as to have an in-

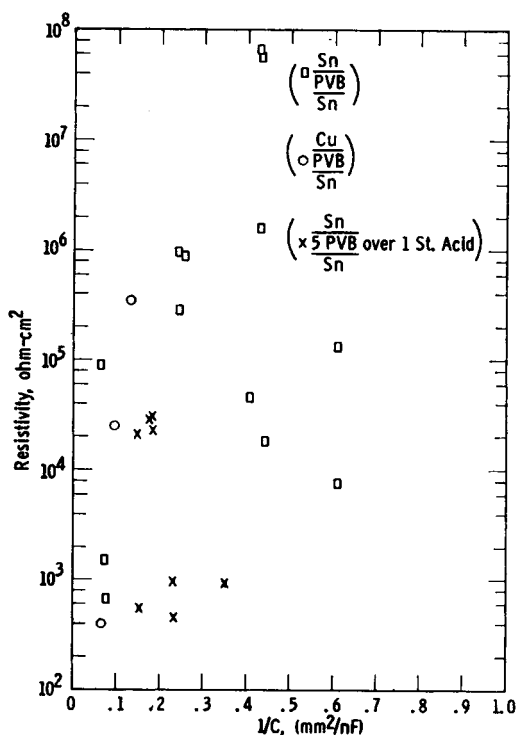


Fig. 6. Low voltage resistivity vs. reciprocal capacity ( $1/C$ ) for PVB and PVB-stearic acid samples.

consequential effect on the capacity measurements. This type of behavior is shown in Figure 6, in which  $R_0$  is plotted as a function of  $1/C$  for a number of PVB and PVB-stearic acid mixtures. It is obvious that  $R_0$  values differing by several orders of magnitude can be observed on samples having virtually the same average thickness. The wide scatter of  $R_0$  values is typical of all the PVB samples tested, and at best it is only possible to indicate a general trend of increasing low voltage resistivity with observed average thickness, and presumably greater effective coverage of the surface.

Interesting memory effects have been observed in the electrical properties of some samples. For example, a number of Sn-PVB-Sn junctions at room temperature could be made to exhibit, at will, either a symmetric (but non-linear) or a rectifying  $I-V$  characteristic for a.c. by initially applying a d.c. "forming" potential in the appropriate direction. The process was reversible upon reversal of the forming voltage and could be repeated many times. A similar reversal was observed under constant excitation but variable temperature, as follows: If a potential was applied to maintain the sample in the asymmetric state and the sample was then cooled to liquid nitrogen temperature, a gradual transition back to the symmetric form of the  $I-V$  curve was observed, despite the continued presence of the biasing signal. Upon warming the sample, the trend was reversed and the initial asym-



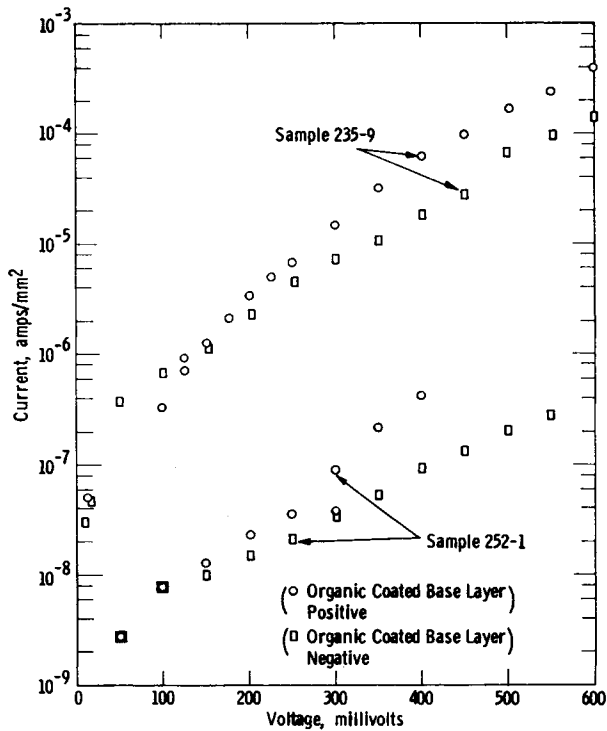


Fig. 7.  $I$ - $V$  characteristics for PVB films ( $T = 300^\circ\text{K}$ ).

metric curve was obtained. By contrast, a number of Sn-PVB-Cu junctions on the same sample undergoing the same temperature cycle exhibited the inverse of this process, being initially symmetric, becoming asymmetric at low temperature, and again symmetric upon return to room temperature. Attempts to produce additional samples exhibiting this type of behavior were largely unsuccessful, new and different characteristics being obtained despite the apparent similarity in formation procedures. These samples were among the thinnest PVB samples obtained, i.e., having  $N_p' \leq 1$ , and were subsequently found to exhibit changes in dielectric constant with frequency of the sort shown in Figure 4. We note that changes in asymmetry have also been observed<sup>7,8</sup> with sandwich structures of  $\text{Al}_2\text{O}_3$  insulating films of comparable thickness, and it seems plausible that the mechanism of field-driven ion motion suggested in that case may also apply here.

Current-voltage characteristics for two PVB samples of different thickness are shown in Figure 7. The upper set of datum points, corresponding to the thinner film ( $1/C = 0.076 \text{ mm.}^2/\text{nF.}$ ), exhibits qualitatively the characteristic features of tunnel conduction through an asymmetric potential barrier,<sup>8,9</sup> that is, a symmetric and linear low voltage region ( $V \leq 10 \text{ mv.}$ ), followed by a region of increasing asymmetry and nonlinearity ( $V \geq 10 \text{ mv.}$ ), and then a reversal of asymmetry (at  $V \approx 150 \text{ mv.}$ ). The lower

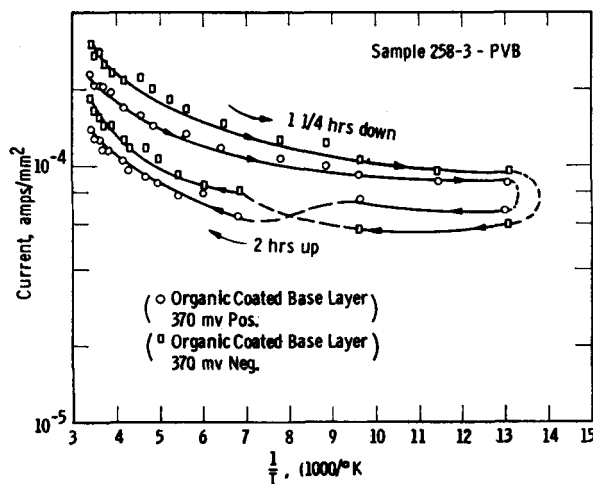


Fig. 8.  $I$  vs.  $1/T$  for PVB sample.

set of datum points, corresponding to the thicker film ( $1/C = 0.25 \text{ mm.}^2/\text{nF.}$ ), does not show the crossover in the  $I-V$  characteristics, which suggests that field-assisted thermionic emission may be predominant.<sup>9</sup> Converting the reciprocal capacity measurements to thickness values, using the results of the previous sections, we obtain  $\sim 21$  and  $\sim 75$  Å. for the average thickness of the two films. The values are of the correct size for the predominance of the respective conduction mechanism suggested by the  $I-V$  characteristics.<sup>9</sup>

The temperature dependence of another, and also very thin, PVB sample ( $1/C = 0.052 \text{ mm.}^2/\text{nF.}$ ) is shown in Figure 8. These data were obtained at very low frequency a.c. (0.1 cycle/sec.). A reversal of the asymmetry in going from room temperature to liquid nitrogen temperature to room temperature was observed. The temperature cycle also produced a change in the over-all current level, which shifted the curves vertically without a significant change in the endpoint ratio. Between room temperature and liquid nitrogen temperature the current (at constant voltage) drops by about a factor of three, again indicating the predominance of tunnel conduction in these thin PVB samples.<sup>10</sup>

## CONCLUSIONS

The electrical measurements on the PVB films can be briefly summarized by stating that the PVB films are arranged as complex multilayers on the substrate surface, that they yield unusual  $I-V$  characteristics of theoretical and possibly practical interest, but that wide variations of properties and lack of reproducibility have so far handicapped attempts to interpret these conduction characteristics in terms of a molecular model of the film. Capacity measurements, autoradiographs, and studies of the layering conditions have been more fruitful in that they lead to the following conclusions

about the PVB layers. (1) The compacted PVB film on the aqueous sub-phase has an average area per monomer unit of the order of  $8 \text{ \AA}^2$ , hence is composed of several superimposed layers of molecules rather than a single layer. (2) The high and well-defined collapse pressure observed suggests that the PVB molecules not only are superposed but are interlocked in a regular way over large areas of the surface. It is probable that the large "flat" benzoate groups prevent free motion of the chains and lead to the observed rigid properties of the compressed films. (3) The average thickness of this compacted "superimposed" PVB film after transfer is approximately  $37 \text{ \AA}$ ., and the film has a room temperature dielectric constant at 1 kcycle/sec. of approximately 3.3. Under certain and as yet unknown conditions, the compacted superposed layers separate during transfer, to give an average transferred film thickness of approximately half of this value. Since the dielectric constant value has been obtained by an extrapolation procedure, the calculated film thicknesses suffer from the same uncertainty and should be regarded as approximate. (4) The dielectric behavior of the transferred PVB films is typical of a material with polar groups undergoing hindered rotations in the field, and with a room temperature relaxation time  $[1/(2\pi f_m)]$  greater than  $1.6 \times 10^{-3} \text{ sec.}$ , where  $f_m$  is the frequency at maximum absorption.

The authors wish to thank W. R. Miller and W. O. Bartlett for their invaluable assistance in the preparation and testing of the samples, and Drs. T. P. Brody and J. E. Johnson of the Westinghouse Research Laboratories for many helpful suggestions.

The research reported in this paper was sponsored by the United States Army Electronics Research and Development Laboratory, Fort Monmouth, New Jersey, under contract No. DA36-039-AMC-00072.

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### Résumé

On a étudié la structure et les propriétés électriques de films de polybenzoate de vinyle (PVB) en couche simple et multiple en employant les films comme isolant ultra-mince entre électrodes de Cu et de Sn obtenues par évaporation. On a également employé des mélanges PVB-acide stéarique. A partir des mesures de capacité, des autoradiographies

et des conditions de formation des couches on peut conclure que le film de PVB aggloméré sur la phase aqueuse possède une surface moyenne de  $\sim 8 \text{ \AA}^2$  par unité monomérique et se compose de plusieurs couches de molécules superposées plutôt que d'une couche simple. Habituellement chaque opération de transfert fournit un film isolant de PVB dont l'épaisseur moyenne est estimée à  $\sim 37 \text{ \AA}$ . Dans certaines conditions encore inconnues, la couche de PVB semble se séparer par transfert pour donner une épaisseur moyenne de film d'environ la moitié de cette valeur. À température de chambre et pour 1 kc/sec, la constante diélectrique des films de PVB est évaluée à  $\sim 3.3$  et on a trouvé qu'elle dépendait de la fréquence dans le domaine de mesure situé entre 100 cycles/sec. et 20 kcycles/sec. La conduction à travers l'empilement de couches métal-PVB-métal n'est pas du tout linéaire et est considérée comme ayant lieu par effet tunnel dans les films plus minces ( $\sim 20 \text{ \AA}$ ) et par émission thermoionique assistée du champ dans les films plus épais ( $\sim 75 \text{ \AA}$ ). On ne peut pas interpréter les mesures de conduction sur la base d'un modèle moléculaire à cause des larges variations des propriétés électriques et du manque de reproductibilité.

### Zusammenfassung

Die Struktur und die elektrischen Eigenschaften von Polyvinylbenzoat-(PVB) ein- und mehrschichtfilmen wurden durch Verwendung dieser Filme als ultradünne isolierende Abstandhalter zwischen aufgedampften Cu- und Sn-Elektroden untersucht. Weiters wurden PVB-Stearinsäuremischungen verwendet. Aus Kapazitätsmessungen, Autoradiogrammen und den Schichtbildungsbedingungen wird geschlossen, dass der kompakte PVB-Film auf der wässrigen Subphase einen mittleren Flächenbedarf von  $\sim 8 \text{ \AA}^2$  besitzt und nicht aus einer einzelnen Schicht, sondern aus mehreren übereinandergelagerten Molekülschichten besteht. Gewöhnlich liefert jede Übertragungsoperation einen isolierenden PVB-Film mit einer geschätzten mittleren Dichte von  $\sim 37 \text{ \AA}$ . Unter gewissen, noch unbekanntenen Bedingungen schien sich die PVB-Schicht bei der Übertragung unter Bildung einer Filmdicke von angenähert der Hälfte dieses Werts zu trennen. Die Dielektrizitätskonstante der PVB-Filme wurde bei Raumtemperatur und 1 kHz zu etwa 3.3 bestimmt und erwies sich im gemessenen Bereich von 100 Hz bis 20 kHz als frequenzabhängig. Die elektrische Leitung durch die Metall-PVB-Metall-Sandwiches war in homöner Masse nichtlinear und scheint in den dünneren Filmen ( $\sim 20 \text{ \AA}$ ) durch einen Tunneleffekt und in den dickeren Filmen ( $\sim 75 \text{ \AA}$ ) durch eine feldunterstützte thermoionische Emission stattzufinden. Eine Interpretation der Leitfähigkeitsmessungen an einem Molekülmodell war wegen der grossen Variation der elektrischen Eigenschaften und des Mangels an Reproduzierbarkeit nicht möglich.

Received April 26, 1965