

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Ionic Conduction in Polymers

B. W. Cherry^a; Z. H. Stachurski^a; P. H. Wright^a

^a Department of Materials Engineering, Monash University Clayton, Victoria, Australia

To cite this Article Cherry, B. W. , Stachurski, Z. H. and Wright, P. H.(1972) 'Ionic Conduction in Polymers', Journal of Macromolecular Science, Part A, 6: 4, 797 – 809

To link to this Article: DOI: 10.1080/10601327208056876

URL: <http://dx.doi.org/10.1080/10601327208056876>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ionic Conduction in Polymers

B. W. CHERRY, Z. H. STACHURSKI, and P. H. WRIGHT

Department of Materials Engineering
Monash University
Clayton, Victoria 3168
Australia

ABSTRACT

The mechanism of ionic current flow through three polymer films immersed in electrolyte was investigated using current-voltage measurements. Results suggest that conductivity changes result from changes in the dissociation energy of ionogenic groups on ingress of water.

INTRODUCTION

The work which forms the subject of this paper is concerned with a study of the mechanism by which an electric current can flow through solid cross-linked polymer systems which contain some ionizable groups when such systems are immersed in water. The ultimate objective of this work is a determination of the way in which the structure of a polymeric insulant controls its ability to oppose current flow when exposed to moisture.

The conductivity of all polymers appears to be dependent on the applied electric field, increasing with increasing field strength [1], and over recent years there has been a great deal of work carried out to try and relate this non-ohmic behavior to the conduction mechanism [2-5].

Three mechanisms of steady-state conduction may be postulated to explain the conductivity of organic polymer membranes.

- 1) Electronic conduction as in a semiconductor with a large energy gap.
- 2) Ionic conduction as an activated diffusion process.
- 3) Aqueous conduction of ions through "virtual pores" when the polymer is in an aqueous environment.

Some polymers, notably polyethylene terephthalate and polytetrafluoroethylene [2, 3], under conditions of low humidity, do behave as semiconductors with large energy gaps. The voltage-current curves for these polymers suggest that the main current carriers are electrons injected from the contacting electrodes. The extremely high volume resistivity of these polymers (greater than 10^{17} ohm-cm) puts them in a class by themselves, and it is not surprising that the conduction mechanism may be different from that in the polymers studied here with resistivities of the order of 10^{13} to 10^{14} ohm-cm.

For nylon [5] and cellulose [6] under conditions of low humidity and high temperature, evidence has been put forward to show that the main current carriers are ions from the thermal breakdown of the polymers. This evidence is based on analysis of the gas given off at the contacting electrodes from the discharged current-carrying ions.

Thermosetting resins of the type used as the vehicles for corrosion-resistant paints have been examined by a number of authors [7-10] using aqueous electrodes. Although these resins are permeable to both ions and water molecules, it has been shown [7, 8] that it is possible to differentiate between an activated diffusion process and a process involving aqueous conduction through virtual pores on the basis of the temperature coefficient of resistance of the polymer. Thus, whereas the temperature coefficient of resistance of a membrane in which the conduction process was substantially aqueous conduction and was through virtual pores would be expected to be of the order of that for electrolyte solutions, e.g., about $1.6 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$, the temperature coefficient of resistance of the membranes examined by Cherry and Mayne [7] was often found to be of the order of $9 \times 10^{-2} \text{ }^\circ\text{C}^{-1}$.

This higher value for the temperature coefficient of resistance would correspond to an activation energy of the order of 1.3 eV/ion (30 kcal/mole) and so it was suggested that activated diffusion was the conduction mechanism in these systems. Sato [8] confirmed these findings by measurement of diffusion coefficients using a radioactive tracer technique, and Mayne and Scantlebury [10] showed that under many conditions both types of conduction mechanism could coexist. It is, however, assumed, on the basis of the results presented

by Cherry and Mayne [7], that in the more highly resistant films the predominant mechanism of ionic current flow is activated diffusion.

The process of activated diffusion may most easily be visualized in terms of "counterions" becoming dissociated from the ionic groups which are attached to the polymer network; each counterion then diffuses through the polymer network until it is attracted to a second fixed ion. This counterion "hopping" can be described by the following model. It is assumed that the polymer consists of material of low dielectric constant, D_0 , and throughout this material, there are uniformly distributed N_0 ionogenic groups, each of which can give rise to a mobile counterion and a fixed ion. Associated with each fixed ion is a region of higher dielectric constant due to molecules of water attracted to the ion.

If two ionogenic sites, P and Q, separated by distance d are considered, then for an ion moving from P to Q there is a potential barrier which must be surmounted (Fig. 1). If it is assumed that the activation energy ΔG for an ion moving from P to Q is constant over all ionogenic sites (this may not be the case, but for certain distributions of ΔG over the N_0 available sites will not affect the following argument), the number of counterions capable of moving from one site to the next at any moment will be given by Eq. (1), where f is a

$$n = \frac{N_0}{f} \exp\left(-\frac{\Delta G}{kT}\right) \tag{1}$$

partition function for translational motion, and k is Boltzmann's constant.

When a uniform electric field E in the direction PQ is applied,

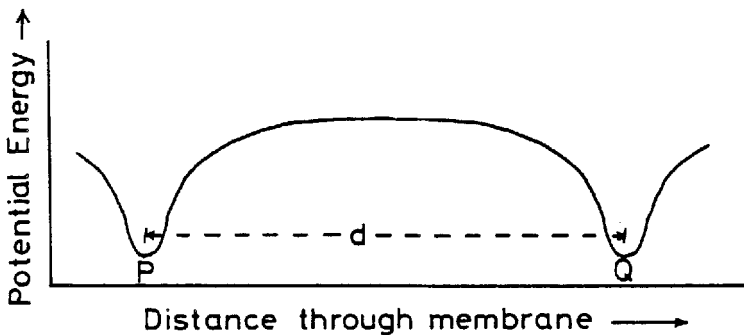


FIG. 1. Potential energy of counterion (no applied field).

the potential energy barrier to the right of P will be lowered by an amount $Eed/2D_0$ and the barrier to the left of P will be raised by a similar amount. Therefore the net current flowing through a specimen of thickness x with a voltage V applied will be given by

$$i = K \frac{2N_0}{f} \exp \left(-\frac{\Delta G}{kT} \right) \sinh \left(\frac{Ved}{2D_0 x kT} \right) \quad (2)$$

where K is a constant.

For a given polymer system examined at a fixed temperature, Eq. (2) may be written as

$$i = A \sinh B V \quad (3)$$

and the fit of the observed current-voltage relationship to this relationship will indicate the extent to which the proposed mechanism represents an adequate picture of the process of ionic conduction. From changes in the values of A and B measured under a series of known conditions, it should be possible to determine the way in which the structure of the system controls its electrical resistance.

EXPERIMENTAL

In the present work, three polymer systems were studied:

1) A pentaerythritol alkyd varnish formed by the condensation of phthalic anhydride and pentaerythritol and modified by the addition of linseed oil.

2) A phenol formaldehyde varnish formed by the polymerization of the condensation product of *p*-tert-butyl phenol and formaldehyde and modified by the addition of tung oil.

3) A polyamide-cured epoxy resin formed by the condensation of epichlorhydrin with dihydric phenol and cross-linked with the addition of polyamides formed from the reaction of dibasic unsaturated acids with ethylene diamine.

Films $2-3 \times 10^{-3}$ cm thick were prepared from these resins and mounted as described previously [7, 9] in cells in which the film formed the boundary between two half-cells, each of which could be filled with electrolyte. Any soluble low molecular weight products were leached out and the films were brought to a standard state by filling the cells with 0.001 N hydrochloric acid and

maintaining the system at 65° C for 50 hr. The cells were then filled with new electrolyte, and electrical contact with the membranes was made through this electrolyte using silver/silver chloride electrodes dipping into the solutions.

The sign of the fixed-ion attached to the polymer network was determined by measuring the diffusion potentials set up when a polymer membrane separated solutions of 3 and 0.001 N potassium chloride. By using Planck's equation [11] the transport numbers of the cations and anions in the membrane could be calculated. The results are shown in Table 1.

TABLE 1. Diffusion Potentials

Membrane	Diffusion potential (mV)	Transport Nos.		Fixed ion charge
		t ₊	t ₋	
Linseed oil Pentaerythritol alkyd	+128	0.833	0.167	-
Tung oil Phenol formaldehyde	+188	0.980	0.020	-
Polyamide Epoxide	-168	0.063	0.937	+

It is assumed that, whereas the pentaerythritol alkyd system and the tung oil-phenol formaldehyde system contained carboxyl groups which were capable of ionizing on ingress of water to yield hydrated protons capable of diffusing through the membrane and carboxyl groups attached to the polymer framework, the polyamide cured-epoxide system contains substituted amines which can yield quaternary ammonium salts, which in turn can ionize to give anions capable of diffusing through the polymer system and cations attached to the polymer framework.

These membranes demonstrated an effect noted previously that the resistance of the membranes increased as the concentration of electrolyte in the cell increased. This has been explained [7, 9] as resulting from the fact that the lower water activity of the more concentrated solution means that the membrane cannot absorb as much water from the solution and ionization of the ionogenic groups was suppressed. In polymers with a lower degree of cross-linking this effect has been found to be absent and the conductivity of the

membrane has followed that of the solution [10]. However, polymers in this state generally have a lower resistance than those for which the resistance of the membrane runs counter to that of the solution, and so systems of this type were neglected in the present study. In order to avoid any effects due either to changes in water activity of the surrounding electrolyte or to changes in the nature of the counterion species due to ion exchange effects [7], all initial measurements were carried out with the membrane immersed in 0.001 N hydrochloric acid.

Determinations of the current-voltage relationship for these membranes were made using a Vibron 33B electrometer in conjunction with an A33B resistance and current measuring unit. The voltage supply to the cell consisted of a series of dry cells and, because the resistance of the electrolyte solutions in the conductance cell were many orders of magnitude less than that of the membrane, the electric field was essentially uniform over the whole of the membrane. This field could be varied in steps of 0.2 MV/m up to 10 MV/m. The variation of current with applied potential for the three systems is shown in Figs. 2, 3, and 4 for 0.001 N hydrochloric acid as the surrounding electrolyte.

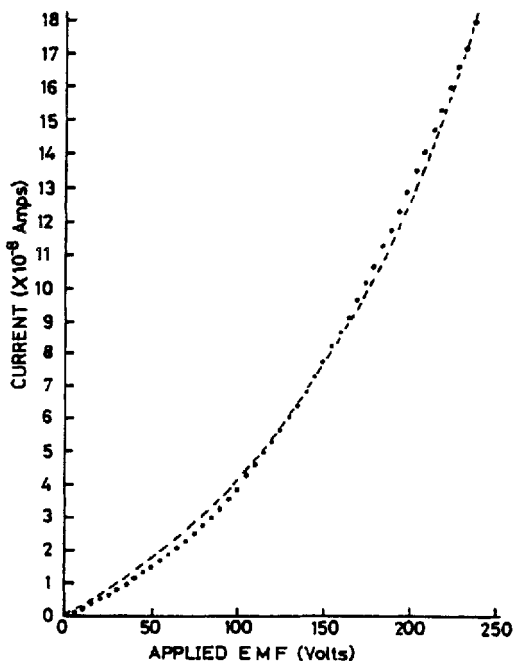


FIG. 2. Linseed oil-pentaerythritol alkyd varnish.

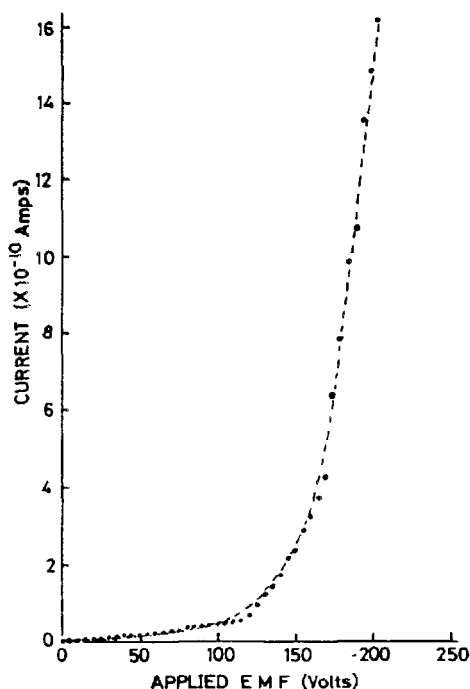


FIG. 3. Tung oil-phenol formaldehyde varnish.

In order to examine further the nature of the change in the conductivity brought about by changing the water activity of the external solution, current-voltage curves were plotted for the pentaerythritol alkyd membrane with solutions in the cell of calcium chloride of known water activity.

RESULTS

The results for the variation of current with applied potential for the three membranes are shown in Figs. 2, 3, and 4. These were fitted to the theoretical curve of Eq. (3) by setting up the function

$$i' = A_1 \sinh B_1 V \quad (4)$$

using the experimental values for V and arbitrary values of the constants A_1 and B_1 . The values for A and B which give the curve which lies closest to the experimental points may then be found by determining the minimum value of the function ϕ , where ϕ is

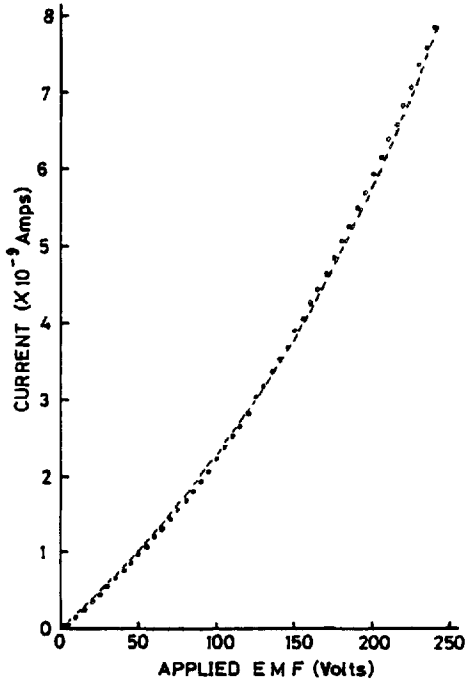


FIG. 4. Polyamide-epoxide varnish.

given by

$$\phi = \sum (i - i')^2 = \sum (i - A_1 \sinh B_1 V)^2 \quad (5)$$

and i is the experimentally determined value of the current. For a minimum value of ϕ ,

$$d\phi/dA_1 = \sum \sinh B_1 V (i - A_1 \sinh B V) = 0 \quad (6a)$$

$$d\phi/dB_1 = \Sigma V \cosh B_1 V (i - A_1 \sinh B_1 V) = 0 \tag{6b}$$

are used. Hence, Eq. (7) is obtained by eliminating A_1 .

$$\frac{\Sigma Vi \cosh B_1 V}{\Sigma V \cosh B V \sinh B V} - \frac{\Sigma i \sinh B_1 V}{\Sigma \sinh^2 B_1 V} = 0 \tag{7}$$

Equation (7) was solved for B_1 using a digital computer and then this value of B_1 was used to calculate a best value for A_1 from the relationship of Eq. (6b) (Eq. 8).

$$A = \frac{\Sigma Vi \cosh B V}{\Sigma V \cosh B V \sinh B V} \tag{8}$$

The results for the three systems are shown in Table 2 and the theoretical curves are plotted as dotted lines in Figs. 2, 3, and 4.

TABLE 2. Counterion Jump Distance

Membrane	Limiting resistivity (ohm-cm)	A (A)	B (V^{-1})	Jump distance d (Å)
Linseed oil				
Pentaerythritol alkyd	1.64×10^{13}	3.69×10^{-8}	9.71×10^{-3}	400
Tung oil				
Phenol formaldehyde	4.70×10^{14}	2.50×10^{-12}	3.54×10^{-2}	1700
Polyamide				
Epoxide	1.65×10^{13}	2.82×10^{-9}	7.40×10^{-3}	440

Also included in Table 2 is an estimate of the value of d in Eq. (1) assuming a value for D_0 , the average dielectric constant of the intervening area of low dielectric constant, of 4. This value of D_0 is almost certainly in error, but assuming this value enables the trend between systems to be observed.

For the pentaerythritol alkyd resin a number of current-voltage

TABLE 3. Linseed Oil Pentaerythritol Alkyd [13]

Molality of CaCl ₂ solution	Water activity	Specimen resistance (at 20 V) (ohm)	A ($\times 10^{-8}$) (A)	B ($\times 10^{-3}$) (V ⁻¹)
Distilled water	1.000	4.6×10^9	2.26	9.56
0.5	0.974	4.8×10^9	2.24	9.31
1.0	0.942	5.2×10^9	2.06	9.27
1.3	0.922	5.8×10^9	1.61	10.81
1.7	0.887	6.7×10^9	1.62	9.26
2.0	0.860	8.3×10^9	1.51	8.01

curves were obtained at different levels of absorbed water in order to determine whether the activation energy term or the ionic jump distance dependent term changes with changes in absorbed water. The amount of water absorbed by the polymer was controlled by having solutions of differing water activities in the conductance cell. The results are shown in Table 3 and Figs. 5 and 6.

DISCUSSION

The very close fit of the experimental points to a theoretical sinh relationship appears to afford considerable evidence in favor of the activated diffusion mechanism proposed earlier in the paper. It seems unlikely, however, that the mechanism proposed can be completely described by Eq. (2) as the distances obtained for the interionic jump distances seem too large (in the case of the tung oil-phenol formaldehyde system—far too large) to be realistic. No explanation can currently be offered for this result, although it might imply that the ionogenic sites occur in clusters.

From Table 2 there appears to be a correlation between the limiting resistivity and the ionic jump distance of the polymers, although the exact nature of this relationship has not been determined.

The results shown in Figs. 5 and 6 and Table 3 suggest that the effect of increased uptake of water is to lower the activation energy for ionization for those groups which are already active in the conduction process rather than to increase the number of such groups by facilitating the ionization of groups which previously had played no part in the conduction process.

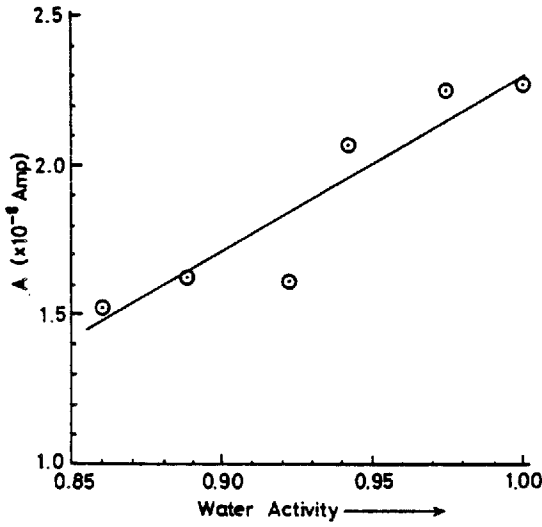


FIG. 5. Values of A for linseed oil-pentaerythritol alkyd.

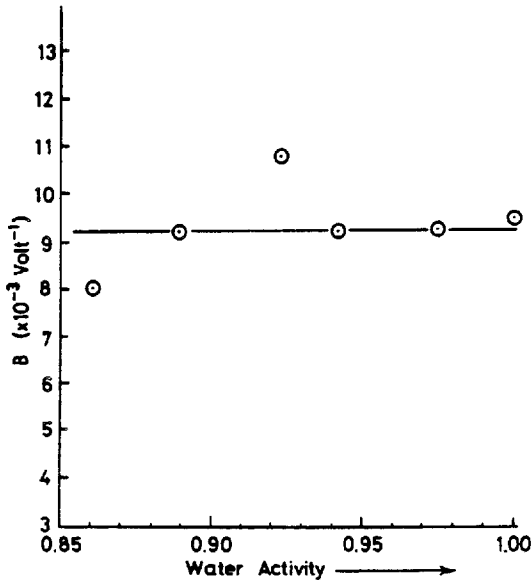


FIG. 6. Values of B for linseed oil-pentaerythritol alkyd.

The pentaerythritol alkyd resin at 25°C and 100% r.h. will absorb 2.50% of its own weight of water [12]. The vapor pressures of the salt solutions are directly proportional to the water activities of the solutions, and thus it may be assumed that the amount of water absorbed by the polymer is approximately proportional to the water activity of the external solution. Thus water activities in the range 1.000 to 0.860 imply water absorption by the polymer in the range 2.50 to 2.15%. This small change in the moisture content brings about a large change in the electrical resistance of the polymer, the resistance (at 20 V) changed from 4.6×10^9 to 8.3×10^9 ohms. Using the values of A from Table 3, the change in the activation energy, ΔG , can be calculated, and it is found to change by 1.0×10^{-2} eV. If the activation energy calculated from the temperature coefficients of resistance [9] is correct (i.e., 1.3 eV), this implies a change in activation energy of the order of 0.8%.

Thus it may be seen that decreasing the moisture content of the film by 14% increases the activation energy only 0.8%, but this increases the electrical resistance of the polymer by 80%.

These initial calculations imply that the electrical resistance of the polymers may be improved greatly just by improving their resistance to moisture absorption. (This is consistent with the observation that polyethylene terephthalate and polytetrafluoroethylene are both hydrophobic.)

These results must be confirmed by measuring the temperature coefficient of resistance of membranes immersed in solutions of varying water activity, and such measurements are currently in progress and will be reported at a later date.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support which they have received from the Radio Research Board during the later stages of this project, and one of us (B.W.C.) acknowledges many valuable discussions with Dr. J. E. O. Mayne of Cambridge University. The three varnishes were supplied by Beck, Koller and Co. Ltd.

REFERENCES

- [1] Y. Inuishi and D. A. Powers, *J. Appl. Phys.*, **28**, 1017 (1957).
- [2] A. C. Lilly, Jr. and J. R. McDowell, *J. Appl. Phys.*, **39**, 141 (1968).
- [3] G. Lengyel, *J. Appl. Phys.*, **37**, 807 (1966).
- [4] M. Ieda, M. Kosaki, and K. Sugiyama, *Proceedings of 39th*

- [5] Annual Conference on Electrical Insulation and Dielectric Phenomena, National Academy of Sciences, Washington D. C., 1971, p. 17.
- [5] D. A. Seanor, J. Polym. Sci., Part A-2, **6**, 463 (1968).
- [6] E. J. Murphy, Can. J. Phys., **41**, 1022 (1963).
- [7] B. W. Cherry and J. E. O. Mayne, Proceedings of the First International Congress on Metallic Corrosion, Butterworths, London, 1962, p. 539.
- [8] Y. Sato, J. Electrochem. Soc. Japan, **28**, E224 (1960).
- [9] C. C. Maitland and J. E. O. Mayne, Offic. Dig. Fed. Soc. Paint Technol., **34**, 972 (1962).
- [10] J. E. O. Mayne and J. D. Scantlebury, Brit. Polym. J., **2**, 240 (1970).
- [11] G. Kortüm, Treatise on Electrochemistry, Elsevier, New York, 1965, p. 292.
- [12] E. M. Kinsella, J. E. O. Mayne, and J. D. Scantlebury, Brit. Polym. J., **3**, 41 (1971).
- [13] R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworths, London, 1955, Appendix 8.10.

Received for publication February 7, 1972