

## Electrical Conductivity of Polypropylene

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### INTRODUCTION

Historically, one of the first applications of synthetic organic polymers was as electrical insulators. This remains a major use today. However, relatively little appears to be known about the steady-state (d.c.) conduction process in such systems.<sup>1</sup> Besides their intrinsic electrochemical interest and their importance to electrical designs with plastics, conductance measurements of polymers should be a valuable tool in the study of polymer structure, especially when analyzed in conjunction with other transport experiments such as of diffusion and viscous flow.

We present here the results of a study of the electrical conductivity of polypropylene (PP) as a function of temperature and field strength. The response of this polymer to alternating current stress has been studied<sup>2</sup> and is typical of a polymeric paraffinic compound.

### EXPERIMENTAL

A commercial sample of PP sheet was kindly donated by the Seiberling Rubber Company (Hercules Pro-fax polymer) and an experimental lower-density film sample was provided by the Film Department of E. I. du Pont de Nemours. The density of the Pro-fax (after annealing) was 0.913 g./ml., corresponding to about 70% crystallinity;<sup>3</sup> that of the Du Pont sample was 0.889 g./ml., corresponding to about 45%. The density was determined by floating films in an acetylacetone-toluene mixture of known density. No attempt was made to characterize further the polymers or possible impurities except to note that the ash content of the Pro-fax was less than 0.1%.

Thin films were made by pressing polymer between ferrotype plates in a heated press. The samples were then annealed in a dry nitrogen atmosphere at 150°C. for 8 hrs. A guarded electrode system was applied to the sample by evaporating aluminum. The sample thickness was measured with a micrometer and the "cell constant" ranged from 30 to 2000 cm.

We measured the conductivity by determining the leakage current flowing through the sample upon application of a constant voltage. The apparatus is sketched in Figure 1. All the components and connecting cables

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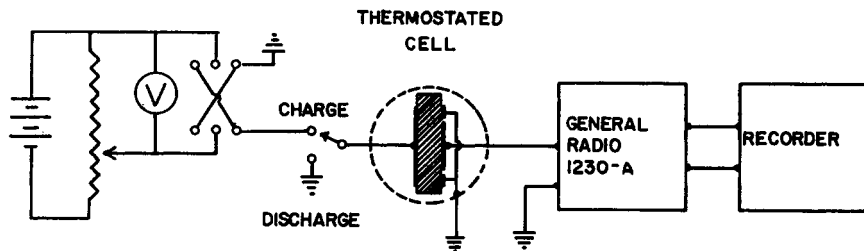


Fig. 1. Low-level conductivity apparatus.

are shielded and the electrometer and recorder are shock mounted. The cell is thermostated in an oil bath and the sample temperature is measured with a thermocouple in good thermal contact with the high-voltage electrode. This electrode is supported in a ball bushing mount to allow for thermal expansion of the sample. The sample thickness was measured before and after each run to ensure that there had been no sag, but no correction for thermal expansion was applied. Dry nitrogen was flushed through the cell when test temperatures exceeded 100°C.

Since the existence of long-lived transient currents is well known in polymers,<sup>4</sup> we monitored the charge current as a function of time until it was constant. The asymptotic value was taken as the true irreversible conduction current from which the conductance was calculated. After the sample had reached this steady state, it was short-circuited through the electrometer and the monitoring was repeated until the discharge current became immeasurably small or negligible compared with the steady-state current. The polarity of the voltage was reversed after each run. At high fields, particularly, we found that electrets<sup>5</sup> were often formed and that these were difficult or impossible to erase by the usual technique of raising the temperature. Heating almost to the crystalline melting point (155°C.) was ineffective in most cases.

While the precision of any one run is estimated to be  $\pm 5\%$ , the overall precision is much poorer because of irreproducibility of runs. Most of the data reported here are the average of several runs; nevertheless, we feel that attention should be focussed on orders of magnitude and trends rather than on specific values.

### EXPERIMENTAL RESULTS

The conductivity of PP has been determined at 25 to 150°C. At lower temperatures the current was too small for the electrometer; at higher temperatures, sample degradation and deformation became limiting. The variation of specific conductance of PP with temperature is shown in Figure 2. The temperature coefficient appears to be field dependent; the "zero field" curve is given by the equation

$$\log \kappa = -(7.54 \times 10^3 / T^\circ\text{K.}) + 6.45 \quad (1)$$

where  $\kappa$  is measured in mhos per centimeter.

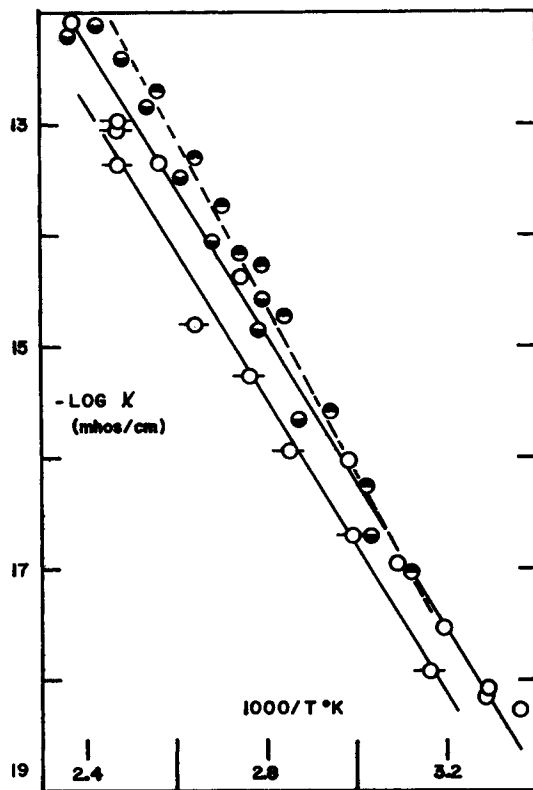


Fig. 2. Logarithm of (apparent) specific conductance plotted against reciprocal absolute temperature: (●) Pro-fax sample T-1, 0.63 kv./cm.; (○) Pro-fax sample T-3, 0.62 kv./cm.; (○) Pro-fax sample T-2, 10.4 kv./cm.; (-○-) Du Pont sample PP-11, 10.5 kv./cm.

This equation yields a temperature coefficient, expressed as a molar activation energy for conduction, of 34.6 kcal.

That the conductivity of PP is nonohmic is shown by the data plotted in Figure 3. Specific conductance is thus insignificant except in the limit of zero field strength.

Transient currents in polymers are manifestations of polarization phenomena which, in some cases,<sup>6</sup> have been related to the molecular mechanism responsible for the glass transition ( $T_g$ ). We worked with temperatures considerably above  $T_g$  and, indeed, found that transients could be traced essentially to geometric rather than molecular origins.

## DISCUSSION

The fundamental equation for electrical conduction is

$$\kappa = J/E = \sum_j n_j e_j u_j \quad (2)$$

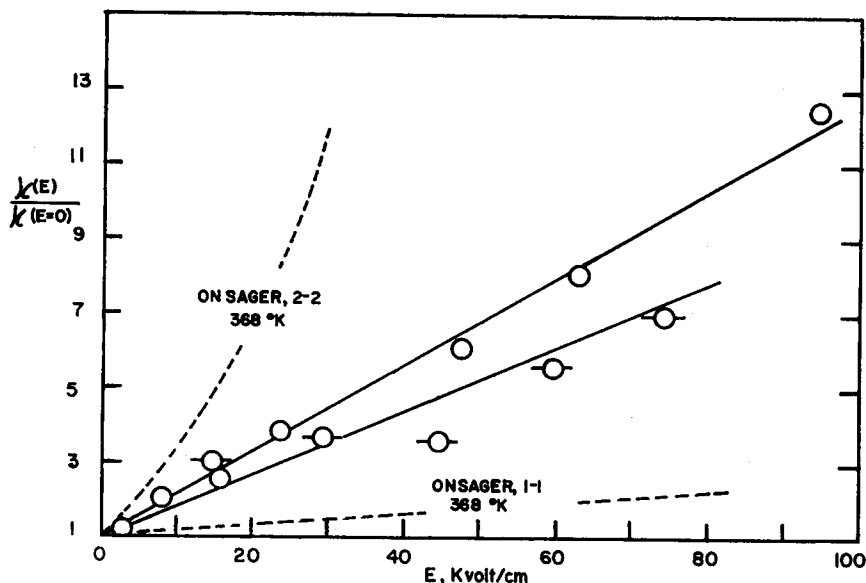


Fig. 3. Conductance quotient plotted against field strength: (—) calculated from Onsager's theory for a 1-1 or 2-2 electrolyte in a medium of dielectric constant 2.2; (O) 368°K; (-O-) 405°K.

where  $J$  is the current density,  $E$  the field strength,  $n_j$  the number of charge carriers of type  $j$  in unit volume,  $e_j$  their charge, and  $u_j$  their mobility. Ideally, to define completely the conduction process one needs to determine the identity of the charge carriers and the influence of electrical and polymer variables on their number and mobility. Our data are neither precise nor extensive enough to permit such an analysis and we must content ourselves with a more qualitative discussion.

The consensus of opinion is that conduction in most polymers is electrolytic, but this question has been investigated actually in only a few cases.<sup>7</sup> We have used this model as a working hypothesis, but it should be noted that many of the results reported here and elsewhere fit equally well with a generalized band theory of electronic conduction. Consider the positive temperature coefficient of conduction which has been taken as prime evidence of semiconduction. A similar positive coefficient obtains, of course, in electrolytic conduction where two molecular processes may be involved. The temperature dependence of the mobility may be the dominant factor, so that the increased conductivity at higher temperatures is essentially a measure of the decreased solvent "viscosity." This is the basis of Walden's Rule. If the temperature coefficient for conduction in PP is characteristic of a diffusion mechanism, we anticipate some correlation between the energetics of conduction and small-molecule diffusion in PP. The permeation and diffusion experiments of Brandt<sup>8</sup> and Szwarc et al.<sup>9</sup> yield molar activation energies for diffusion of much less than 35 kcal. This lack of agreement with conduction data suggests that tem-

perature dependence of carrier concentration, rather than of mobility, is the limiting factor. The observation that the conductivity and the activation energy for conduction are seemingly insensitive to crystallinity lends some indirect support to this. The experimental activation energy is then to be considered in terms of an ionization process, the details of which cannot be determined if the identity of the charge carriers is unknown.

The field dependence of the conductivity provides another test of any conduction mechanism, since high fields may influence both the concentration and mobility of the charge carriers. The concentration of ions is augmented by high fields, according to Onsager's<sup>10</sup> dissociation field theory for weak electrolytes. Onsager's expression for the conductance quotient is

$$\kappa(E)/\kappa(E = 0) = 1 + b/2 + b^2/24 + \dots \quad (3)$$

where  $b = 9.695E/DT^2$  for a 1-1 electrolyte,  $D$  being the dielectric constant of the solution. For the maximum fields attained in this study,  $b \approx 2.7$ , so that only the term linear in  $b$  is important. The straight-line plot of Figure 3 is thus verified, although the relative increase that we measure is greater than predicted by the theory. Higher-valence ions enhance the dissociation effect, the exact amount depending on the valence and the mobility of the ions. In lieu of any knowledge of those parameters, we have plotted in Figure 3 the curve expected for a 2-2 electrolyte whose ions have equal mobility; this is obviously an overcorrection.

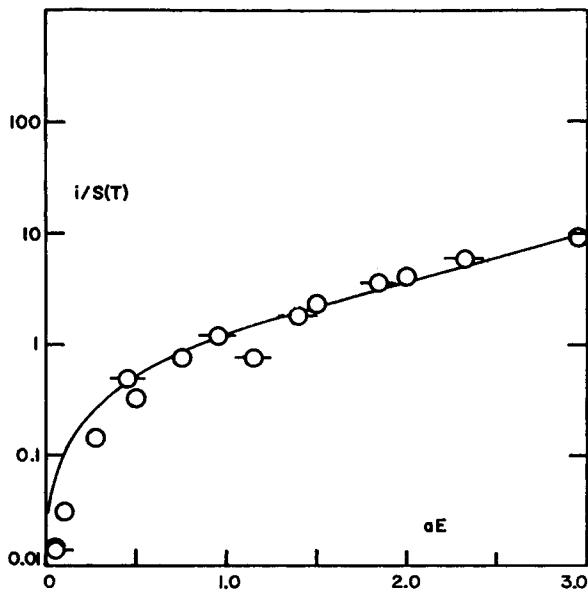


Fig. 4. Plot of  $i/S(T)$  versus  $aE$ : (—) the curve  $i/S(T) = \sinh(0.0314aE)$  with  $E$  in kv./cm.; (O) 368°K.,  $S(T) = 4.5 \times 10^{-9}$  amp.; (—O) 405°K.,  $S(T) = 9.0 \times 10^{-9}$  amp.

According to Onsager, the conductance quotient should vary as  $1/T^2$  (assuming the dielectric constant to remain essentially constant). Again, experimental results are in qualitative agreement with the theory, but the observed variation is larger than predicted.

The influence of high fields on the mobility is given by the equation

$$J = S(T) \sinh(\lambda eE/2kT) = S(T) \sinh(aE) \quad (4)$$

which results from an analysis of the net jump rate of an ion across a barrier under the influence of the field.<sup>11</sup> Here  $\lambda$  is the distance an ion "jumps" from one equilibrium position to the next. The local field acting on the ion,  $E$ , has been approximated in our simple analysis by the external field. The exact functional form of  $S(T)$ , the rate of passage across the barrier in the absence of the external field, is not known but it is assumed to have the form  $S(T) = K \exp\{-\Delta F^\ddagger/RT\}$  where  $K$  is essentially independent of temperature and  $\Delta F^\ddagger$  is the molar activation free energy, a measure of the height of the barrier. We find  $a = 0.0314 \text{ kv.}^{-1}$  adequate to fit our data at 368 and 405°K.; see Figure 4. Unfortunately, these runs were made with different samples of the Du Pont polymer, and a comparison of the  $S(T)$  values, which fix the scale of the temperature dependence curves, do not agree well with the data in Figure 2. It has been shown by Amborski<sup>12</sup> that eq. (4) is valid for polyethylene terephthalate with consistent values of  $S(T)$ . From an analysis of the isothermal field dependence of the conductivity we calculate  $\lambda \approx 200 \text{ \AA}$ . The significance of such a large distance is not clear and the crudity of the model doesn't warrant much further speculation. We do note, however, that the "mean free path" deduced by similar analysis from diffusion of small molecules in polymers<sup>13</sup> is of a similar order of magnitude.

Since  $\sinh(z) = \frac{1}{2} \exp\{z\}$  when  $z$  is large compared with unity, we note that eq. (4) becomes

$$J = K' \exp\{(-\Delta H^\ddagger/RT) + (\lambda eE/2kT)\} \quad (5)$$

A plot of  $\log i$  versus  $1/T$  should thus have a slope which increases with the field, as we have observed; see Figure 2. In principle, one should be able to evaluate  $\lambda$  from the change of temperature coefficient with field strength. Such a calculation depends sensitively on the experimentally determined temperature coefficient, and our data scatter too much for a significant analysis.

This work was initiated with the help of a grant from Research Corporation and has been supported by the National Science Foundation under Grant NSF-G9921. We wish to thank both sponsors for their assistance.

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### Synopsis

The steady-state (d.c.) electrical conductivity of polypropylene has been measured as a function of temperature (25–150°C.) and field strength (0–94 kv./cm.). The temperature coefficient of the conductivity is 34.6 kcal./mole expressed as an activation energy. This is much larger than the activation energy for diffusion of small molecules in the same polymer. Thus, ionization rather than diffusion appears to be the primary activation process. The conductivity is nonohmic; the conductance quotient is a linear function of field strength but is larger than predicted by Onsager's theory. The ion "jump distance," as evaluated from the isothermal field dependence, is the same order of magnitude as the diffusional mean free path estimated from diffusion studies in other polymers. The conductivity, conduction activation energy, and field dependence appear to be relatively insensitive to polymer crystallinity.

### Résumé

On a mesuré la conductivité électrique (DC) à l'état stationnaire du polypropylène en fonction de la température (25–150°C.) et de la force du champ (0–94 kv./cm.). Le coefficient de température de la conductivité, exprimé sous la forme d'une énergie d'activation, vaut 34.6 kcal./mole. Ceci est beaucoup plus élevé que l'énergie d'activation pour la diffusion de petites molécules dans le même polymère. Ainsi, donc, l'ionisation plutôt que la diffusion apparaît être le processus primaire d'activation. La conductivité est non-ohmique; le quotient de conductance est une fonction linéaire de la force du champ mais est plus élevé que prévu par la théorie d'Onsager. La distance de déplacement ionique, ainsi évaluée à partir de la dépendance du champ isothermique, est du même ordre de grandeur que le libre parcours moyen de diffusion estimé à partir d'études de diffusion dans le cas d'autres polymères. La conductivité, l'énergie d'activation de conduction et la dépendance du champ semblent être relativement indépendantes de la cristallinité du polymère.

### Zusammenfassung

Die stationäre Gleichstromleitfähigkeit von Polypropylen wurde als Funktion der Temperatur (25 bis 150°C) und Feldstärke (0–94 kv./cm.) gemessen. Der Temperaturkoeffizient der Leitfähigkeit liefert eine Aktivierungsenergie von 34.6 kcal./mole. Das

ist viel höher als die Aktivierungsenergie für die Diffusion kleiner Molekel im gleichen Polymeren. Es scheint daher die Ionisierung und nicht die Diffusion der Aktivierungsvorgang zu sein. Die Leitfähigkeit gehorcht nicht dem Ohmschen Gesetz; der Leitfähigkeitsquotient ist eine lineare Funktion der Feldstärke, ist aber grösser als nach der Theorie von Onsager zu erwarten wäre. Die "Sprungweite" der Ionen, wie sie sich aus der isothermen Feldabhängigkeit ergibt, besitzt die gleiche Grössenordnung wie die bei Diffusionsmessungen an anderen Polymeren bestimmte mittlere freie Diffusionsweglänge. Leitfähigkeit, ihre Aktivierungsenergie und Feldabhängigkeit scheinen verhältnismässig unempfindlich gegen die Kristallinität des Polymeren zu sein.

Received February 2, 1962