CONDUCTIVITY IN POLYMERIC SOLIDS

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INTRODUCTION

The number of studies of the electronic properties of organic solids continues to increase¹. A recent literature search² lists over 1600 references appearing in the period July 1961 through September 1963. Our understanding of charge-transport in simple organic solids such as anthracene has improved considerably in the last few years. Experimentally, employing the pulse excitation techniques first used by Kepler³ and LeBlanc⁴, measurements of mobility of charge carriers in hydrocarbon crystals have been employed to obtain information about the nature of the carrier generation process and the role of impurities in carrier generation and transport⁵. Theoretical models have been advanced; most recently in a series of papers by Rice and co-workers⁶ the band structures of a number of aromatic solids have been determined in detail.

Less clear is our understanding of charge-transport in the charge-transfer complexes. Here, despite some work with single crystals of reasonable purity⁷, a knowledge of the mechanism of conduction and an understanding of the correlation of structure with conductivity still remains a field of active investigation and speculation. When we turn our attention to polymeric solids, very few studies on materials of known structures have been performed, and studies generally must rely on measurements on compressed powders rather than on single crystals.

The difficulties in interpreting conductivity measurements in materials of high impurity and defect concentrations are well known in the inorganic semiconductor field. These difficulties are equally serious in studies of polymeric solids. For polymer systems, very little experimental work has been done on each material, and for many other systems the experimental techniques employed in performing the measurements have not been sufficiently elucidated to allow a critical evaluation of the validity of the experiment. Because of the particularly confusing state of this field, it is important that we call for future investigations to specifically state details regarding measurement techniques, manipulation of samples, and structure of the polymers.

The polymer systems thus far studied are, in general, highly impure and highly disordered. Each polymer chain in addition may contain chemical and structural imperfections within itself. There is little doubt that many of the cases in the literature which report conductivity in polymeric solids are actually observations of conductivity within an impurity—for example, along a surface layer on a compacted disc. Furthermore, in many cases the character of the conductivity process observed may tell us more about the electrode-sample interface than about the sample itself.

It is not hard to understand that simultaneously with the growth and interest in simple organic solids and their electronic properties has come an interest in the properties of polymeric solids. Once one begins to conceive of applications for simple organic crystals, the appeal of the polymer and its properties is obvious. But let us not forget that those experiments which are uninterpretable in a simple molecular solid, which one can obtain in a single crystal form, will usually be similarly uninterpretable in a polymer matrix. Thus, performing the type of measurement on a polymer which has failed to give us useful information on a simple molecular solid does not seem to be a profitable mode of operation. I will attempt to identify that type of experiment which has little meaning and show that this lack of meaning has been established by studies in simpler organic solids.

On the more optimistic side, polymers of known structure have been prepared which have conductivities ranging from that of a poor metal to an insulator. Secondly, the photoconductive properties of polymer systems have led to a number of interesting applications, and remain an area in which basic information about energy transfer processes can be accumulated. Thirdly, from the theoretical point of view, it has been suggested that polymeric systems can be found which display not only semiconductivity but perhaps superconductivity⁸.

Specifically excluded from this discussion are polymers formed under drastic synthetic conditions and polymer carbons. We will discuss only synthetic polymers and restrict ourselves to polymers whose structures can be specified.

PITFALLS IN PERFORMING MEASUREMENTS

The procedure of compacting a powder into a tablet, painting on two electrodes, and measuring the conductivity is fraught with difficulties. For example, the conductivities of polyvinylenes have been reported to vary from 10^{-6} to 10^{-15} ohm⁻¹ cm⁻¹, as shown in Table 1. It is tempting to attribute the four decade increase in conductivity when one goes from amorphous to crystalline polyvinylene to an effect of crystallinity. Yet how can

Table 1. Conductivity of polyvinylenes

Investigators	Starting compound	Condition	σ , ohm ⁻¹ cm ⁻¹	E_a
Hatano, Kambara ^a and Okamoto	Acetylene	Ziegler—Amorphous	10^{-10}	0.41
Hatano, Kambara ^a and Okamoto	Acetylene	Ziegler—Crystalline	10^{-6}	0.23
Geiderich <i>et al.</i> ^b	Polyvinylchloride	ZnCl ₂ —250°	10^{-7}	0.2
Bohrer ^c	Polyvinylchloride	Morpholine or alc. base	10^{-15}	—
Mainthia, Kronick and Labes ^d	Polyvinylchloride	H ₂ SO ₄ , “drying”	10^{-7}	0.53
Mainthia, Kronick and Labes ^d	Polyvinylchloride	H ₂ SO ₄ , “superdrying”	10^{-11}	—

^a *J. Polymer Sci.* **51**, S26 (1961).

^b *J. Polymer Sci.* **54**, 621 (1961).

^c *Trans. N.Y. Acad. Sci.* **20**, 2, 367 (1958).

^d *J. Chem. Phys.* **37**, 2509 (1962).

one do this with confidence when a variation in the drying procedure can cause the same magnitude change in the conductivity? It was our experience that polyvinylene's conductivity decreased from 10^{-7} to 10^{-11} ohm $^{-1}$ cm $^{-1}$ when one used the precaution of drying at 1μ at 110° and performing all transfer operations in a glove box filled and flushed with argon. It is not too surprising that a polymer such as this would tenaciously hold small amounts of ionic impurities and water.

Some workers have felt that the reproducibility of a measurement of the temperature dependence of resistivity is a criterion for purity. We found that the measurement of the temperature dependence of resistivity on a polyvinylene sample that was *not* thoroughly dried gave the usual linear dependence of $1/T$ °K *vs.* $\log \rho$, reversible in the temperature range 25° to 90° . Thus, reversibility and reproducibility are not an indication of the absence of effect of vaporizable impurities.

This difficulty is, of course, not unique to polymer systems. Most measurements of dark conductivity on molecular crystals such as anthracene must be regarded as involving carrier injection from electrode material, ambient gas, impurities or surface imperfections. Simple d.c. measurements by two-probe techniques which neglect polarization or space-charge effects are relatively meaningless.

1,6-Diaminopyrene forms highly conducting complexes with a wide variety of substituted quinones⁹. All our attempts to purify the parent amine by multiple crystallizations, sublimations, *etc.*, lead to a material with a resistivity of 10^8 ohm-cm (single crystal and powder measurements by two and four probe techniques). We interpret this, however, not as an intrinsic property of pure diaminopyrene, but as a reflection of its easy oxidation. It is probable that a highly reactive diamine of this type is almost impossible to obtain in a form which does not contain acceptor impurities in the crystal. If one measures an "activation energy" ($\rho = \rho_0 \exp E_a/kT$) for conduction, a value of 0.3 eV is obtained, reproducible with temperature cycling.

Another example of a molecular solid with purported high conductivity is cyamelurine (I), in which one would have considerable difficulty in evolving an explanation of charge transport through an essentially non-aromatic lattice.

A sample of this material was sent to us for evaluation because of an apparent resistivity of 10^6 ohm-cm. This material undergoes a continual change in resistivity with passage of current; in 45 min with a current of 10^{-10} amp, the resistivity had changed to 10^9 ohm-cm.

Although no further study was made, we assume this sample, considered "pure" by conventional chemical standards, is grossly impure from an electrical point of view.

Thus the common practice of performing a simple two-probe measurement leaves much to be desired. Huggins and Sharbaugh¹⁰ have pointed out that even four-probe techniques can lead to errors for powdered samples, and that a.c. techniques to eliminate interparticle contact resistances have been misapplied. They show that a more elaborate a.c. analysis allows one to measure what appears to be a specific conductivity, independent of packing pressure or filling factor.

Measurements on powders mask one of the more interesting features of conduction in organic systems—the structural anisotropy. A comparison of single crystal and compacted disc measurements clearly indicates the difficulties in assessing the meaning of powder measurements^{7a}. Table 2 shows such a comparison for charge transfer complex single crystals and compacted

Table 2. Comparison of single crystal and compacted disc measurements^a

Compound	Single crystal				Compacted disc	
	Resistivity (ohm cm) at 25° Crystal direction ^b			E_a (eV) in X direction	Resistivity (ohm cm) at 25°	E_a (eV)
	X	Y	Z			
Diaminodurene-chloranil	7×10^4	6.9×10^4	8.4×10^4	0.26	3×10^4	0.29
1,6-diaminopyrene-chloranil	10^5	10^6	10^9	0.19	10^3	0.15
1,6-diaminopyrene-bromanil	7×10^3				10^3	0.15
1,5-diaminonaphthalene-chloranil	1.3×10^9	6.3×10^{11}	2.0×10^{11}	0.60	7.2×10^{11}	0.65

^a See ref. 7a for details.

^b X, Y, and Z denote three directions corresponding to the developed faces of the crystals, X being the long direction.

discs. For 1,5-diaminonaphthalene-chloranil, one would not be aware of the higher conductivity occurring in one crystal direction in the absence of single crystal measurements. For 1,6-diaminopyrene-chloranil, we have now shown that chemical changes occur upon compaction so that the compacted disc has a much higher conductivity and radical ion content.

These observations make it clear that care must be exercised in performing electrical measurements, and that the nature of this care should be specified by the investigators.

STUDIES OF DARK CONDUCTIVITY

Of the many reports in the literature of dark conductivity in polymers, I have chosen a few examples of interesting materials. The first of these is the inorganic polymer, polysulphur nitride. The formation of this polymer was first observed in 1910^{11a}, but elucidation of the chemistry was conducted only recently by Becke-Goehring and co-workers^{11b}. It must be prepared with great care since one of the intermediates is explosive^{11c}. We measured

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the resistivity as a function of temperature *in vacuo* on a Kelvin double bridge using platinum probes and a thermocouple embedded in a sample compressed in a special die at 5000 atm. The results are presented in *Figure 1*. The absolute resistivity varied considerably with the history of the sample, but each individual sample was reproducible after temperature cycling

Figure 1. Relative resistivity referred to 0°C, of polysulphur nitride as a function of temperature. Resistivity (ohm-cm) at 0°: ○, 0.29; ⊗, 0.59; ⊕, 0.61; △, 0.04; □, 0.04

except when cooled in liquid nitrogen. In this latter case the resistivity was always 10 per cent higher upon returning to room temperature, presumably because of mechanical relaxation. Relative changes in resistivity with temperature were the same for all samples (*Figure 1*). Plots of $\log \rho$ vs. $1/T$ give experimental activation energies < 0.02 eV, but show great curvature. It is possible that we are observing the effect of a temperature-dependent mobility on an essentially metallic conductor. Chapman *et al.*^{11d} studied the electronic and vibrational spectra of poly(sulphur nitride) and also discussed its conducting properties.

For organic conjugated polymers it is calculated that chain-chain interaction and the extent of delocalization of π electrons within the individual chains is small. For $(\text{SN})_x$ the individual chains represent a conjugated system with resonance forms involving the alternation of positive and negative sulphur atoms, which is believed to lead to a high intrachain conductivity. In addition, the expansion of the sulphur valence shell gives more opportunity for interaction involving the $d\pi$ orbitals. The extra electrons on the negatively charged sulphur, situated in such an expanded orbital, might be expected then to facilitate charge transport between chains. The thermal conductance, $k = 6.4 \times 10^{-2} w \text{ cm}^{-1} \text{ deg}^{-1}$, of an order of magnitude between those of ordinary semicrystalline polymers (*e.g.*, nylon, $k = 2.5 \times 10^{-3} w \text{ cm}^{-1} \text{ deg}^{-1}$; polyethylene, $k = 3.4 \times 10^{-3} w \text{ cm}^{-1} \text{ deg}^{-1}$) and of

graphite ($k = 1.4w \text{ cm}^{-1} \text{ deg}^{-1}$), indicates enhanced intermolecular coupling over that in insulating molecular crystals. Thus it may be possible that the incorporation of heteroatoms such as sulphur into a polymer can so increase chain-chain interaction as to lead to an increase in conductivity. Further work along these lines is necessary.

Reports of high conductivity in coordination polymers are also quite intriguing. Table 3 shows a few examples of the polymers reported to have the highest conductivities. Two groups have studied copper rubeanates and report resistivities which differ by three decades. These are difficult systems to purify and it is therefore not clear that the high conductivity is intrinsic.

Table 3. Reported coordination polymers of high conductivity

Investigators	Metal	Ligand	$R \text{ ohm-cm}$
Vozzhennikov <i>et al.</i> ^a	Cu^{2+}		2×10^7
Kanda and Kawaguchi ^b	Cu^{2+}		5×10^4
Terentiev <i>et al.</i> ^c	Cu^+		6×10^3
Terentiev <i>et al.</i> ^c	Cu^+		3×10^4

^a Dokl. Akad. SSSR **143**, 1131 (1962).

^b J. Chem. Phys. **34**, 1070 (1961).

^c Dokl. Akad. Nauk. SSSR **140**, 1093 (1961).

Dewar and Talati¹² recently suggested that coordination polymers probably have quite high mobilities based on the values of the pre-exponential factor of the equation $\rho = \rho_0 (\exp E/kT)$. That any significance may be attached to the pre-exponential factor observed in measurements on organic crystals is doubtful. For example, Mette and Pick¹³ report ρ_0 in the *ab* plane of anthracene as 10^2 ohm-cm , whereas Inokuchi¹⁴ reports 10^{-2} ohm-cm . This unfortunately appears not to be an atypical situation. Values of ρ_0 as low as those reported by Dewar and Talati¹² are not uncommon; some have in fact been observed which would suggest impossible mobilities. Brown and Aftergut¹⁵ report a ρ_0 of 10^{-38} ohm-cm for 2-methoxynaphthalene among a host of other very small ρ_0 values. The hydrocarbon-halogen complexes¹⁶ have ρ_0 values of 1-10, while the polymer complexes poly-

(phenylene)-iodine, and poly(4-vinylpyridine)-iodine have ρ_0 of 10^{-7} and 10^{-6} ohm-cm, respectively. In the absence of direct mobility data, the conclusion that coordination polymers have high mobilities must therefore be regarded as tenuous.

Only one study of a polymer single crystal has been performed—on polyethylene by van Roggen¹⁷, working with crystals ~ 100 Å thick. He describes the system as a crystal having an inner region of a perfect lattice with large energy gap, with outer layers of thin imperfect crystals consisting of the chain folds. The current through the single crystal consists of two parts: *a*) tunneling through the whole crystal, (*b*) charge injection into the outer layers followed by tunneling through the perfect part of the crystal. The current through two crystals is smaller than that through a single crystal of the same thickness because the contact of the crystallites represents an area of strong carrier scattering. van Roggen examined several electrode systems and current-voltage characteristics of the systems carefully.

PHOTOCONDUCTIVITY IN POLYMERS

A great deal of work has been performed on electrostatic imaging processes involving organic polymers. It is beyond the scope of this paper to review this field¹⁸. It should be pointed out, however, that these systems involve both polymer structures themselves which are purportedly photoconductive, and polymers doped with simpler photoconductors. Sensitization of photoconductivity is possible by the use of electron acceptors and/or donors in suitable matrices.

Further, thermoplastic recording media have been designed in which a transparent photoconductive and thermoplastic coating can be charged and exposed to light to create a latent image by changing the charge distribution. By heating this film, deformation of the plastic occurs differentially at these charged regions to create an image which can be displayed using schlieren optics. In spite of the number of photoconducting systems designed, there remains a paucity of fundamental understanding of photoconduction in polymers.

One such organic photoconductive system consists of a triphenylmethane or benzophenone derivative and a low concentration of a dye in an insulating polymer that does not itself show photoconductivity¹⁹. It displays photoconductivity although the solute molecules are supposed to be separated from each other by large distances. The peak photocurrents occur in the absorption maxima of the dye spectrum; no photoconductivity is observed in the polymer doped with dye alone. A single crystal of bis (4,4'-dimethylaminophenyl)phenyl methane shows photoconductivity but dye sensitization has not been obtained. Mylnikov and Terenin²⁰ attribute such polymer sensitization to aggregated dye particles in the polymer films which exhibit their own photo-response, but this does not explain the role of the triphenylmethane or benzophenone in the polymer film or the absence of photoconductivity in a dye doped polymer. Terenin and co-workers²⁰ have reported on the photoconducting properties of acetylenic polymers and copper phenyl acetylide and claim true spectral sensitization. Determination of sensitization as a function of dye concentration shows an optimum (about

10^{-3} M for methylene blue in copper phenyl acetylide, for example). Evidence is presented for dimer and higher aggregates forming at high dye concentrations and also causing photosensitization.

The fundamental mechanism of dye sensitization of photoconductivity is far from clear. Further attention must be paid to the use of photoexcitation techniques in the exploration of charge transport in polymers. It is precisely these techniques which have made advances in our understanding of the simpler organic solids.

POLYMER CHARGE-TRANSFER COMPLEXES

A major problem in achieving high conductivity in polymeric solids is to increase chain-chain interaction. Charge-transfer complexing has been an effective mode of increasing molecule-molecule interaction, and should be effective in polymer situations as well. Conceptually, a donor polymer-acceptor polymer system can be envisioned. In practice, only donor polymers-monomeric acceptors have been prepared and dramatic changes in conductivity have occurred. This type of system offers the advantage that well-defined polymers can be employed and involved in mild interactions.

Figure 2. Resistivity of polyphenylene-iodine. $\circ$: solid-vapour preparation in room air $\bullet$: solid vapour preparation in dry nitrogen, $\times$: solution preparation in room air

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For example, we have studied the conductivity of poly(phenylene)²¹ and poly(vinylpyridines)²² with electron acceptors. *Figure 2* shows the dramatic change in the resistivity of polyphenylene as it interacts with iodine. The resistivity of the complex is 10^4 times lower than that of iodine alone and much lower than a simple admixture of polymer and iodine. *Table 4* gives the resistivity of poly-2 and 4-(vinylpyridine)-iodine complexes. These complexes retain their iodine tenaciously, do not change their bulk properties upon exposure to moisture and are stable to 147°C whereupon they melt and dissociate.

Table 4. Resistivities of poly(vinylpyridine)-iodine complexes

<i>Donor polymer</i>	<i>Method of preparation</i>	<i>Mole ratio I₂/polymer unit</i>	<i>Resistivity (25°C) ohm-cm</i>
poly(4-vinylpyridine)	Solution	2.0	10^4
poly(4-vinylpyridine)	Vapour	0.3	10^7
poly(2-vinylpyridine)	Solution	0.6	10^4

Lupinski and Kopple²³ report preparing complexes of poly(vinylpyridines with tetracyanoquinodimethane (TCNQ), which are polymeric analogue, of the radical ion salts studied by DuPont investigators²⁴. One such complex) poly(methyl-2-vinylpyridinium TCNQ) + 15 per cent neutral TCNQ has a conductivity of 10^{-4} ohm⁻¹ cm⁻¹. These polymer complexes can be deposited from solution as homogeneous films. Hatano *et al.*²⁵ have also reported similar compounds recently.

The possibility of preparing polymer-polymer systems seems promising. For example, attempts should be made using such electron acceptor polymers as poly(dicyanoacetylene)²⁶ or perhaps a polyquinone.

That such studies may have interesting synthetic as well as electrical consequences is indicated by two recent developments. Yang and Gaoni²⁷ report the formation of a copolymer having the structure —D—A—D—A—D—A— where D is 4-vinylpyridine and A is trinitrostyrene. Since trinitrostyrene usually will not polymerize, the donor-acceptor interaction is in fact responsible for the polymerization which occurs exothermically at room temperature.

In an attempt to prepare a polymer charge transfer complex Scott, Miller and Labes²⁸ observed charge-transfer (radical-ion) initiation of vinylcarbazole polymerization which has several novel mechanistic features. Several other examples of initiation by charge-transfer have now appeared²⁹.

CONCLUSIONS

I have indicated areas where further work is necessary and where promise of obtaining fundamental information seems the greatest. It cannot be stressed too strongly that caution must be exercised in performing electrical

measurements on complex systems, and that the nature of this caution should be made clear in published information. I am sure I have omitted many important pieces of work from this discussion, but have instead given a personal view of the problems and progress in this field.

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