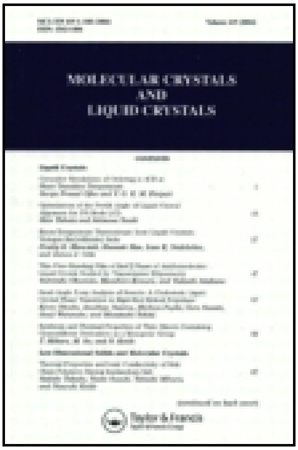

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Studies of Organic Semiconductors for 40 Years—VI

M. Pope [a]
[a] Chemistry Department and Radiation and Solid State Laboratory, New York University, New York, U.S.A.

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Studies of Organic Semiconductors for 40 Years—VI

M. POPE

Chemistry Department and Radiation and Solid State Laboratory, New York University, New York, U.S.A.

INTRODUCTION

Although isolated studies of organic semiconductors and photoconductors were made starting from the beginning of this century, there was no comprehensive theory to rationalize the results. The publication of the book by Mott and Gurney[1] explaining the electronic properties of ionic crystals in quantum mechanical terms played a significant role in establishing the latter part of 1940 as the beginning of modern studies of organic semiconductors.

The renaissance of organic conductivity did not originate in the United States. The countries most often associated with this aspect are the U.S.S.R. and England. However, it is interesting to note that the first practical use made of organic conductivity was in electro-photography. This became known as the Xerox process and it was patented in the U.S. in 1938 by Chester F. Carlson. This revolutionary invention made use of anthracene as the photoconductor. This organic compound was displaced by selenium, and the rest is history. It is remarkable in retrospect to note that at the same time that the groundwork had barely been laid for understanding the properties of the poorly conducting organic compounds, the first discoveries were made by Akamatu and Inokuchi of the more highly conductive donor-acceptor complexes. The current explosion of research in the area of high-conductivity materials can trace its origin to this early work of Akamatu and Inokuchi in Japan. It is a matter of extreme sadness that Professor Akamatu did not live to celebrate this noteworthy occasion. In a major sense, this paper is dedicated to his memory.

The task of recording the most significant events in the history of conductive studies in solid organic systems in the U.S. from 1948 to 1988 is formidable. It is inevitable that there will be errors of commission and of omission. I apologize in advance for these errors, and trust that future reviewers will correct them. In order to fit this review into this allotted space, the following restrictions have been adhered to: discoveries and innovations made outside the U.S. will be mentioned only in passing. Conductivity in organic liquids will not be discussed, with few exceptions. In addition, only work that relates directly to conductivity will be discussed; thus, spectroscopy in all its forms is not included, and the field of excitons will not be included except insofar as excitons participate in the production and/or excitation of free or trapped carriers. Finally, the emphasis herein will be on work that produced a qualitative change in a particular field. A more comprehensive review of the important work in organic conductivity has been reported on by Pope and Swenberg.[2,3]

Rather than presenting an overall chronology of events, I will discuss a few areas of research and include the chronology within these areas. Thus I will discuss photogeneration of carriers, current-voltage behavior, trapping, carrier recombination, carrier transport, highly conductive polymers, radical-ion complexes, superconductors, and some miscellaneous subjects.

PHOTOGENERATION OF CARRIERS

The first studies of organic semiconductivity in the U.S in which the concepts of solid-state physics were used were carried out by Nelson,[4] who worked with thin films of triphenylmethane dyes. The early studies with dyes and phthalocyanines, which started in the USSR and England were probably based on the structural similarity between these compounds (particularly the phthalocyanines) and chlorophyll. The underlying expectation was that photosynthesis could be better understood by using the concepts and methods of solid-state physics. However, the utilization of such concepts depended upon the existence of such basic information as the magnitude of the band gap, and the roles of excitons, carrier mobility, recombination and electrodes; this information was not available and thus it was not possible to develop and test suitable theories to explain and to guide further studies. Furthermore, despite the attractiveness of the dyes and phthalocyanines, there were difficulties with reproducibility, a dependence on the nature of the ambient gas, and the question of material purity; this apparently shifted the attention of physicists and chemists to single crystal organic materials, chiefly anthracene. The studies with anthracene began in the late 1950's.

A major uncertainty was the magnitude of the band gap, or the minimum energy required to produce completely separated and mobile carriers in the bulk of the crystal. The association of the onset of photoconductivity with the absorption spectrum led some investigators to the conclusion that the band gap energy was identical with, or even less than that of the first excited singlet state. With the discovery of electroluminescence[5] in anthracene crystal, it became possible to resolve this question. This was done independently at the same time by Sano et al[6] and Helfrich and Schneider[7] who showed that the recombination of holes and electrons resulted in the emission of the same fluorescence as that produced by optical excitation of the first excited singlet state; the band gap in anthracene thus had to be greater than 3.1 eV.

It was known that singlet excitons could induce photoconductivity in anthracene.

Since excitons were mobile and energetic, it was possible for them to participate in a wide variety of processes, the end result of which would be the production of either one or two free carriers (a hole and an electron) inside the solid depending upon whether the excitons reacted with a surface structure or in the bulk of the crystal with each other, or with a photon. Choi and Rice[8] made the first theoretical study of the exciton-exciton annihilation process and estimated the bimolecular rate constant for the singlet exciton-exciton carrier generation process. The first experimental demonstration of an intrinsic carrier generation process in anthracene was made by Silver *et al.*[9] In this experiment, a singlet exciton was ionized by an absorbed photon.[10] The first example of intrinsic ionization produced by a singlet-singlet exciton annihilation mechanism was made by Pope *et al.*,[11] and Bergmann *et al.*[12] The first demonstration of a direct photogeneration process in which an absorbed photon created a separated hole-electron pair was made by Castro and Hornig.[13] This clearly established the band gap of anthracene as being equal to or greater than 4 eV. Important corroborative work was done by Chaiken and Kearns.[14] In the meantime, the one-electron band theory seemed to be successful in rationalizing some of the mobility data, so it was natural to expect the intrinsic carrier generation step to be a single step valence band to conduction band (BB) transition as is the case in the inorganic crystalline system. However, this view was challenged by Pope[15] and his colleagues, who proposed a two-step process involving the autoionization of an intermediate molecular state. A quantum mechanical theory of autoionization was provided by Jortner.[16] A two-step process is the accepted mechanism at present; in the energy range below the band-gap, Bounds and Siebrand[17] in Canada showed that the first transition is to a bound charge transfer (CT) exciton state which then dissociates thermally to produce carriers that must overcome geminate recombination. The search for the important CT exciton, which is an intermediate state in the generation and recombination process was carried out theoretically and experimentally. Important ideas were contributed by Merrifield,[18] Choi *et al.*,[19] Ewing and Kearns,[20] and Hernandez and Choi.[21] The first use of electroreflectance spectroscopy to detect a CT transition in a homomolecular crystal was made by Abbi and Hanson.[22] The first calculation showing that the CT state lay above the first singlet exciton state in anthracene was made by Berry *et al.*[23] The first experimental evidence for the existence of the CT exciton, in which its energy and estimated lifetime were given, was provided by Pope *et al.*[24a] Firm theoretical limits to the combined values of the CT exciton lifetime and energy were given by Morris and Silver.[24b]

Charge injection, space charge limited currents (SCLC), and trapping

The passage of current through an insulator is almost always accompanied by the accumulation of space charge consisting of excess free and trapped carriers. In addition, the contacts introduce unknown voltage drops. The contact problem and the space charge complicate the interpretation of the current-voltage (J-V) response. The task of analyzing the J-V response was greatly simplified by the discovery of ohmic contacts to organic crystals; this eliminated the contact problem. This was done by Pope and Kallmann[25] who developed the use of oxidizing electrolytic contacts such as $Ce(SO_4)_2$(aqueous) and I_3^-(aqueous) for this purpose. In addition to making possible the passage of SCLC through the organic crystals, the use of electrolytic contacts started a new field of organic electrochemistry in which the organic material acted as the electrode. The photovoltaic effect in organic crystals was discovered by Kallmann and Pope,[26] and the theory of the energetics of charge injection into organic materials was also laid out by Kallmann and Pope.[26]

The discovery of charge injection into organic insulators made possible the systematic study of the J-V relationship in both dark conductivity and photoconductivity. This was first done for organic crystals by Mark and Helfrich,[27] using the theories of Rose[28] and Lampert.[29] Mark and Helfrich[27] provided a solid basis for understanding the effect of light intensity on SCLC, the energetic distribution of trapping states, and the spatial distribution of carriers within the crystal. Using the carrier mobility, Mark and Helfrich were able to calculate the density of free and trapped carriers.

Although it was possible to deduce the trap depths using SCLC technique, it was even more desirable to know the identity of these traps. The first work in this direction was that of Hoesterey and Letson[30] who took anthracene of extreme purity and added known amounts of impurities such as tetracene, anthrone, and anthraquinone, which are the most probable contaminants of anthracene. They showed that impurity levels as low as 10 ppm had a drastic effect on the carrier lifetimes. They were able to calculate the cross-section of capture of electrons and holes for each impurity trap, and in addition showed that the hole band width was indeed of the order of kT by calculating the density of states in that band; it was equal to the molecular density. This was consistent with the band theory of anthracene conductivity.

A major advance in the understanding of detrapping of carrier by excitons, particularly triplet excitons was brought about by Merrifield and his colleagues in their development of the theory of magnetic field effects on the interaction of triplet excitons with triplet excitons, and other paramagnetic species, such as free radicals and charge carriers.[31,32] This theory was first applied by Geacintov *et al.*[33] to reveal the unequivocal triplet exciton signature in a carrier detrapping process.

The first studies of transient SCLC in anthracene were made by Silver *et al.*[34] in the U.S. and Helfrich and Mark in Germany.[35] The role of crystal defects as traps was demonstrated by the transient SCLC studies of Weisz *et al.*[36] who demonstrated that these defects appeared as fast trapping site which could be annealed out of the crystal, thus identifying them as crystal defects.

CHARGE TRANSPORT

The earliest measurements of conductivity were often difficult to duplicate not only in different laboratories, but in the same laboratory. This was in most part due to the presence of impurities whose identity and concentration were unknown. A development of first-rate importance, marking the beginning of unusually reproducible experimental studies, was the introduction of zone-refining as a technique for the purification of organic compounds; this was done by Sloan[37] in 1960. The impurity level was reduced thereby to the range of one or two parts per million, and in addition since this process also concentrates impurities in one small section of the crystal sample, it was possible to identify the impurities that were present.[38] With the appearance of highly purified anthracene came the first dependable measurement of the drift mobility of electrons and holes. This was done by Kepler[39] and LeBlanc.[40] Kepler carried out a more complete study[41] in which he measured the temperature dependence of the mobility in the chief crystallographic directions.

The existence of reliable measurements of drift mobility and its temperature and crystal direction dependence led to the first significant one-electron band theory calculation of the mobility; this was made by LeBlanc[42] who simplified matters by assuming one molecule per unit cell in anthracene, instead of two. One puzzling result was that despite the success of the theory in calculating the mobility and its anisotropy, the bandwidth was so narrow (~0.6 kT) that the scattering length was of the order of the intermolecular distance, which normally should have ruled out the applicability of band theory. A more exact band theory was developed by Katz *et al.*[43] They were able to calculate the ratios of the mobilities to each other. They found good agreement between theory and experiment for holes in all crystallographic direction, and for electrons in the *a* and *b* directions. Agreement was poor in the *c′* direction. The central question posed by Glarum[44] was whether the carrier transport could best be described within the context of the standard band theory that was so successful with inorganic semiconductors, or whether the transport represented a random hopping motion from one site to a neighboring site. This question has not yet been completely resolved.

An important advance was made by Silbey *et al.*[45] who extended the polaron theory introduced by Holstein[46] to include quadratic electron-phonon coupling. This introduced the notions of polaron mobility. The first attempt at a calculation of the mobility, with no adjustable parameters, was made by Friedman,[46] who used only elastic longitudinal acoustic mode phonon scattering. The magnitudes and anisotropy of holes and electrons in the *ab* plane were in reasonable agreement with experiment. There was however, no resolution of the conflict between theory and experiment in all crystallographic directions. Friedman also used band theory to predict unusual magnetic and thermoelectric responses; thus, since the allowed energy bands were so narrow (<kT), a carrier could be moving at the top of the band where its effective mass would be negative. This would lead to anomalies in which the Hall potential for electrons would have the hole sign and vice versa. The first Hall effect measurements in organic crystals were made by Heilmeier *et al.*[48] and by Dresner.[49] They reported anomalies, but these experiments were too difficult to continue.

One of the few methods for measuring the absolute magnitude of the effective mass is that of cyclotron resonance absorption. This extremely difficult experiment was carried out by Burland[50] who found that the effective mass of the hole was eleven times the free electron mass. From this value of the effective mass, a hole mobility was estimated at 2K to be $\sim 10^4$ $cm^2V^{-1}s^{-1}$. This is a high mobility, but recent experimental results obtained by Warta and Karl[51] in Germany, who prepared ultrapure crystals, has yielded mobilities that approach 10^3 $cm^2V^{-1}s^{-1}$.

Although the mobility of the hole in anthracene was shown to be bandlike in all directions,[41,43] the calculated mobility of the electron in the c' direction, $\mu_{c'c'} = 0$ did not agree at all with the measured value of 0.4 $cm^2V^{-1}s^{-1}$. An important contribution to the solution of the electron mobility problem was made by Schein *et al.*[52] who observed the first transition from band motion to hopping motion for the electron in the c' direction in naphthalene for $T = 100$ K. Below 100 K, $\mu_{c'c'}$ increased with decreasing temperature. Above 100 K, $\mu_{c'c'}$ was constant as the temperature increased. In addition, in anthracene[53] for $T > 78$ K, there was essentially no temperature dependence for the observed electron mobility in the c' direction. Schein *et al.* also carried out a series of experiments involving the field dependence[54a] and deuteration dependence[54b] of the mobility that posed severe challenges to any theory purporting to explain the electron mobility in naphthalene and anthracene. Andersen *et al.*,[55] showed that by assuming dominant longitudinal acoustic phonon-electron scattering, it was possible to obtain the observed $\mu \propto T^{-3/2}$ dependence for electrons in all crystallographic directions in naphthalene for $T < 100$ K. However, the lack of a temperature dependence in anthracene and naphthalene for $T > 100$ K was still unexplained. A basis for understanding this lack of temperature dependence was provided by Sumi[56] with his idea of a temperature-dependent overlap integral arising from the rotation of the molecules around the moving carrier. More recently Silinsh[57] has used a nearly-small polaron approach to explain the $T > 100$ K results.

CARRIER RECOMBINATION

It had been noticed by several investigators that the quantum efficiency of intrinsic carrier generation was quite small, due mainly to the low probability of separation of the newly created hole-electron pair (geminate pair). A major breakthrough in arriving at a quantitative understanding of this was reported in a series of papers by Braun and coworkers,[58,59] who used the treatment of geminate recombination of electrons and ions given by Onsager[60] in 1938. Chance and Braun[59] (1973) showed conclusively that the Onsager theory (1938) of geminate recombination was the most suitable continuum theory to use to explain the field dependence of the photocarrier yield certainly in anthracene, and undoubtedly in most organic crystals. Similar results had already been found in liquids.[61] In passing, it must be said that the pioneering work of Mozumder[62] on geminate recombination in liquids, and now in solids, in which the thermalization process itself was included, was of great assistance to theorists working in solids. Again, in organic liquids, Braun and Scott[63] made the first real-time study of the recombination of geminate cation-electron pairs, using a ps laser.

More recently, the Onsager 1934 theory[64] has been used to explain the field dependence of the carrier yield when the final state of recombination was a small radius charge-transfer exciton or exciplex with a lifetime long enough to be considered as a source of electrons in the presence of an applied field. The importance of using the Onsager 1934 theory instead of the 1938 theory was pointed out by Geacintov and Pope,[65] Pope and Swenberg[2] (p. 739); however, the definitive application of the Onsager 1934 theory to this problem was made by Braun.[66] When the 1938 theory was used to explain the ionization efficiency in donor-acceptor (D-A) crystals, an electron-hole thermalization distance of 2 to 3 nm was obtained. However, optical excitation of such a crystal was known to produce a CT state with a nearest neighbor separation of 0.5 nm. Braun showed that reasonable values for the ionization efficiency in (D-A) crystals could be obtained without the need for invoking large thermalization distances.

The Onsager theory of geminate recombination is a continuum theory that assumes a point sink at the origin (which contains the hole) and an initial distribution of free carriers at a characteristic distance r_o from the origin. However, the real situation corresponds to a crystal with a lattice; this implies discrete jumps usually in preferred directions. The first quantum mechanical solution of the problem of geminate recombination on a face centered cubic lattice (f.c.c.) and more recently on a simple cubic lattice (s.c.) was given by Rackovsky and Scher.[67] Geminate recombination was treated as a random walk on lattice sites in the presence of both an external and Coulomb field. Molecular parameters were introduced, such as wave function overlap, energetic differences between sites, and electron-vibrational interactions which determine the relative transition rates to neighbors. One important conclusion emerging from this treatment is that ϕ_o and r_o as calculated using the Onsager theory do not give physically meaningful values of the primary photoionization yield and thermalization distance respectively. These important papers by Rackovsky and Scher[67] also point out sources of error in simulation studies of recombination.

HIGHLY CONDUCTIVE POLYMERS

The study of electronic conductivity in organic polymers was revolutionized in 1977 by the discovery by MacDiarmid *et al.*[68] that the conductivity of polyacetylene could be varied from 10^{-13} to 10^3 S cm^{-1} by suitable doping with donors and acceptors. A typical acceptor would be AsF_5[69] and a typical donor would be sodium. These dopants introduce mobile charge carriers into the π-electron system of the host. More recently, chiefly because of the ability to prepare high-purity polymers with very few sp^3 defects (which occur at the ends of the chains, or at crosslinks) first accomplished by Naarmann[70] in Germany and by Basescu *et al.*[71] in the U.S., it has become possible to prepare doped polyacetylene with a room temperature conductivity that is equal to or greater than that of copper. Conductivities of 1.5×10^5 S cm^{-1} have already been reached,[71] and since the temperature dependence of the heavily doped polyacetylene is still not characteristic of a metal,[71] the implication here is that with more assiduous purification, the conductivity could exceed that of copper, which is 5×10^5 S cm^{-1} at room temperature. A calculation by Kivelson and Heeger[72] of the intrinsic limit that would be placed in doped polyacetylene by virtue of phonon scattering yielded a value 2×10^6 S cm^{-1}.

As for the mechanism of carrier transport, there seem to be several depending on the degree of doping. For undoped or lightly doped $(CH)_x$, transport is via solitons.[73,74] The soliton is a new concept in organic conductivity. This state results from the fact that in trans-polyacetylene, the ground state is doubly degenerate.

When both states exist on the same polymeric strand a defect appears in the form of a kink, where two single bonds are formed adjacent to each other. This kink is mobile, and constitutes the soliton. The injection of a hole or electron into polyacetylene creates a charged soliton and this is the entity that carries the current. The theory describing the movement of the charged soliton from one polymer chain to an adjoining one, referred to as intersoliton hopping, was worked out initially by Kivelson.[75]

At higher dopant levels (0.01–0.04 dopant molecules per C atom), transport appears to be one of variable range hopping among states near the Fermi energy.[76] At still higher dopant levels (> 0.05 dopant molecules per C atom), the polymer was first described as a dirty metal, in which disorder is introduced by doping,[77] and more recently as an anisotropic metal[78] in which the dopant has been shown to contribute very little to the electron scattering process that would disrupt the metallic conductivity.

In many polymers, such as poly(*p*-phenylene), a degenerate ground state does not exist, eliminating the possibility of soliton formation. Nevertheless, a spinless conductivity is observed, similar to that of soliton conductivity. For these compounds, a polaron-bipolaron model theory was proposed by Bredas *et al.*,[79] which accommodates the experimental results observed with these compounds.

RADICAL—ION COMPLEXES

The original highly conductive organic compounds were the charge-transfer complexes of Akamatu and Inokuchi.[80] These were donor-acceptor complexes in which the donors (D) and acceptors (A) are arranged as sandwich compounds with the sequence . . . .DADADA. . . . . The development of what have been referred to as organic metals began with the discovery of the properties of tetracyanoquinodimethane (TCNQ) and its salts by Acker *et al.*[81] This compound crystallizes in the form of a stack of molecules with their planes parallel to each other, and with intermolecular distances smaller than the van der Waals separation of ~3.4A. The most characteristic feature of this high conductivity is that the carrier transport is restricted in its dimensionality. The molecules that are arranged parallel to each other in stacks permit easy transport along the stack, but not in the direct perpendicular to the stacks. This type of conductivity is referred to as one-dimensional or 1-D.

The next important development was the discovery of tetrathiafulvalene (TTF) by Wudl *et al.*[82] This compound crystallizes in stacks like those of TCNQ, and the combination of TTF as a donor and TCNQ as an acceptor to create the first organic "metal" was accomplished by Ferraris *et al.*,[83] and Coleman *et al.*[84] This was the first organic metal in the sense that the conductivity of this compound increases as the temperature decreases although at a certain temperature, a metal-insulator transition occurs, and the conductivity drops radically. At its maximum, in these early compounds, the conductivity was 9000 S cm^{-1}. These compounds represented a new class of compounds referred to as radical-cation salts, and they introduced the concept of one-dimensional conductivity. Compared with a typical conductivity of ~20 S cm^{-1} for a perylene-I_2 CT complex, the radical-ion salt TTF-TCNQ exhibits a conductivity of 900 S cm^{-1}. From the theoretical side, the contributions of Soos[85] and of Bloch[86] should be mentioned. They pointed out the necessity for incomplete charge transfer on the DA stacks for high conductivity.

A major advance was made in the understanding of charge generation and transport in quasi one-dimensional (1-D) materials by a series of studies first undertaken by Miller and Epstein[87] who prepared a model 1-D system with the composition $[NMP]_{1-x}$ $[Phen]_x$ [TCNQ], where NMP = *N*-methylphenazinium, Phen = phenazine, and TCNQ is tetracyanoquinodimethane. This system of compounds is isomorphous with the well-characterized [NMP] [TCNQ] system, but the phenazine is inert as an electron donor or acceptor. The substitution of phenazine permitted the variation of the degree of band filling continuously from the half-filled to the quarter-filled case. With this fine control of band-filling, it was possible to provide a direct demonstration of the existence of solitons in charge-transfer salts. Disorder in the donor stacks was shown to be of no significance to conduction in the acceptor stacks. A new[88] single transport model of conductivity based on a mobility that increases with decreasing temperature and a carrier concentration that increases with increasing temperature was developed; this explained a temperature dependent conductivity maximum formerly attributed to a metal-insulator transition often observed in 1-D systems.

ORGANIC SUPERCONDUCTORS

The idea that high temperature (T_c) superconductivity could be attained in organic materials was first proposed by Little.[89] He suggested that an attractive potential between conduction electrons could be produced by an intramolecular polarization, producing an effect similar to that of lattice phonons in the creation of Cooper pairs. In view of the fact that this would involve excitons instead of phonons, Little calculated that the binding energy of the pair would be greater, which would lead to a higher T_c. Although no molecule has as yet been synthesized that successfully incorporates Little's ideas, he generated considerable interest in this field. Superconductivity has been attained in quasi-1D organic materials, but the mechanism is different.

The first superconductive organic materials[90] $(TMTSF)_2PF_6$ were not discovered in the U.S., although the first proof that superconductivity was attained at elevated pressure in this material was obtained in the U.S.[91] The $(TMTSF)_2$ cation contains selenium; for some time, only the selenium-containing compounds showed superconductivity. The first non-Se containing organic superconductor[92] was the salt $(BEDT\text{-}TTF)_4(ReO_4)_2$, where the cation contains sulfur instead of selenium. This increases the possibility of deducing the requirements for the attainment of superconductivity in organic materials.

The first polymeric superconductor was poly-sulfur nitride $(SN)_x$. Although it is not an organic system, it is an infinite π-bonded, non-metallic system. Following the initial discovery of its metal-like temperature dependence,[93] it was found to be superconductive at ~0.3K.[94]

ELECTROPHOTOGRAPHY

The first practical single layer organic system to be used in electrophotography was a CT complex of poly-*N*-vinyl carbazole(PVK) and 2,4,7 trinitro-9-fluorenone (TNF).[95] Another important single-layer system was the molecularly doped two-phase aggregate photoconductor consisting of a thiopyrilium dye and a polycarbonate polymer[96] in an amorphous phase of triphenylmethane in the polycarbonate polymer. It is clear that in the face of the almost infinite variety of polymers and dopants that can be synthesized for application to electrophotography, it is essential that there be a consistent, reliable and easily applicable theory for making the proper choices of materials to synthesize. Seminal work in this area was carried out by Duke and Meyer.[97]

The first detailed study of mobility in an organic polymer was made by Regensburger[98] on PVK. A seminal contribution was made by Scher and Montroll[99] who rationalized the interpretation of transit time measurement in polymeric systems, in which dispersive transport is a dominant feature. Their theory is of universal relevance to all amorphous systems. A remarkable recent finding that dispersive transport is not an inescapable property of systems such as molecularly doped polymers was made by Stolka *et al.*,[100] and Schein *et al.*;[101] by careful purification of all materials, they obtained non-dispersive transients.

MISCELLANEOUS

Although not strictly a conduction phenomenon, Chittipeddi *et al.* synthesized the first linear chain organic molecular compound with a ferromagnetic ground state,[102] namely the charge-transfer complex decamethyl ferrocenium tetracyanoethenide (DMeFcTCNE). This compound exhibits a spontaneous magnetization for $T <$ 4.8K; the saturation magnetic moment in the presence of an applied field was 1.64×10^4 emu G/mole, indicating the formation of ferromagnetic domains. The theory that best explains this phenomenon was given first by McConnell.[103]

Unfortunately, space limitations prevent discussion of the emerging field of molecular electronics in which micro-assemblies of organic molecules are synthesized to achieve a desired function. Novel applications of this approach are being made by Wrighton,[104] Heller,[105] and others[105] to create analogs of solid state devices that show selective response to chemical stimuli. In addition, the application of fractal theory to carrier recombination in restricted geometries has been pioneered by Kopelman.[106]

The future for organic conductivity seems assured. There are still fundamental questions unanswered, and superconductivity in organics is a sleeping giant. Metallic conductivity is in hand, and there is promise of surprises in theory and variety in practical applications, particularly those involving polymers.

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References

1. N. F. Mott and G. W. Gurney, *Electronic Processes in Ionic Crystals*, Oxford University Press, 1940.
2. M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals*, Oxford University Press, 1982.
3. M. Pope and C. E. Swenberg, *Ann. Rev. Phys. Chem.*, **35**, 613 (1984).
4. R. C. Nelson, *J. Chem. Phys.*, **19**, 798 (1951).
5. M. Pope, H. Kallmann, and P. Magnante, *J. Chem. Phys.*, **38**, 2042 (1963).
6. M. Sano, M. Pope, and H. Kallmann, *J. Chem. Phys.*, **43**, 2920 (1965).
7. W. Helfrich and W. G. Schneider, *Phys. Rev. Lett.*, **14**, 229 (1965).
8. S.-I. Choi and S. A. Rice, *J. Chem. Phys.*, **38**, 366 (1963).
9. M. Silver, D. Olness, M. Swicord, and R. C. Jarnagin, *Phys. Rev. Lett.*, **10**, 12 (1963).
10. See R. G. Kepler and R. E. Merrifield, *J. Chem. Phys.*, **40**, 1173 (1964) and R. G. Kepler, *Phys. Rev. Lett.*, **18**, 951 (1967).
11. M. Pope, H. Kallmann, and J. Giachino, *J. Chem. Phys.*, **42**, 2540 (1965).
12. A. Bergmann, M. Levine, and J. Jortner, *Phys. Rev. Lett.*, **18**, 593 (1967).
13. G. Castro and J. F. Hornig, *J. Chem. Phys.*, **42**, 1459 (1965).
14. R. F. Chaiken and D. R. Kearns, *J. Chem. Phys.*, **45**, 3966 (1966).
15. M. Pope, *J. Chem. Phys.*, **45**, 2197 (1967); N. E. Geacintov and M. Pope, *J. Chem. Phys.*, **47**, 1194 (1967); M. Pope and J. Burgos, *Mol. Cryst.*, **3**, 215 (1967).
16. J. Jortner, *Phys. Rev. Lett.*, **20**, 244 (1968).
17. P. J. Bounds and W. Siebrand, *Chem. Phys. Lett.*, **75**, 414 (1980).
18. R. E. Merrifield, *J. Chem. Phys.*, **34**, 1835 (1961).
19. S.-I. Choi, J. Jortner, S. A. Rice, and R. Silbey, *J. Chem. Phys.*, **41**, 3294 (1969).
20. J. J. Ewing and D. R. Kearns, *J. Chem. Phys.*, **44**, 3139 (1966).
21. J. P. Hernandez and S.-I. Choi, *J. Chem. Phys.*, **50**, 1524 (1969).
22. S. C. Abbi and D. M. Hanson, *J. Chem. Phys.*, **60**, 319 (1974).
23. R. S. Berry, J. Jortner, J. C. Mackie, E. S. Pysh and S. A. Rice, *J. Chem. Phys.*, **42**, 1535 (1965).
24. *a*. M. Pope and J. Burgos, *Mol. Cryst.*, **1**, 395 (1966); M. Pope, J. Burgos, and J. Giachino, *J. Chem. Phys.*, **43**, 3367 (1965). *b*. R. Morris and M. Silver, *J. Chem. Phys.*, **50**, 2969 (1969).
25. H. Kallmann and M. Pope, *J. Chem. Phys.*, **32**, 300 (1960); M. Pope and H. Kallmann in *Symposium on Electrical Conductivity in Organic Solids*, H. Kallmann and M. Silver, Eds., Interscience Publishers, New York, 1961, p. 83.
26. H. Kallmann and M. Pope, ibid., p. 18.
27. P. Mark and W. Helfrich, *J. Appl. Phys.*, **33**, 205 (1962).
28. A. Rose, *Phys. Rev.*, **97**, 1538 (1955).
29. M. A. Lampert, *Phys. Rev.*, **103**, 1648 (1956).
30. D. C. Hoesterey and G. M. Letson, *J. Phys. Chem. Solids.*, **24**, 1609 (1963).
31. R. E. Merrifield, *J. Chem. Phys.*, **48**, 4318 (1968); *Pure Appl. Chem.*, **27**, 481 (1971).
32. R. P. Groff, R. E. Merrifield, A. Suna and P. Avakian, *Phys. Rev. Lett.*, **29**, 429 (1972).
33. N. E. Geacintov, M. Pope, and S. Fox, *J. Phys. Chem. Solids*, **31**, 1375 (1970).
34. M. Silver, M. Swicord, R. C. Jarnagin, A. Many, S. Z. Weisz, and M. Simhony, *J. Phys. Chem. Solids*, **23**, 419 (1962).
35. W. Helfrich and P. Mark, *Z. Physik.*, **166**, 370 (1962).
36. S. Z. Weisz, R. C. Jarnagin, M. Silver, M. Simhony, and J. Balberg, *J. Chem. Phys.*, **40**, 3365 (1964).
37. G. J. Sloan, *Mol. Cryst.*, **1**, 161 (1966).
38. See also complete description in G. J. Sloan and A. R. McGhie, *Techniques of Melt Crystallization*, Wiley-Interscience, New York, 1988.
39. R. G. Kepler, *Phys. Rev.*, **119**, 1226 (1960).
40. O. H. LeBlanc, *J. Chem. Phys.*, **33**, 626 (1960).
41. R. G. Kepler in *Organic Semiconductors*, J. J. Brophy and J. W. Buttrey Eds., Macmillan, New York, 1962.

42. S. H. Glarum, *J. Phys. Chem. Solids*, **24**, 1577 (1963).
43. O. H. LeBlanc, *J. Chem. Phys.*, **35**, 1275 (1961).
44. J. L. Katz, S. A. Rice, S.-I. Choi, and J. Jortner, *J. Chem. Phys.*, **39**, 1683 (1963).
45. R. Silbey, J. Jortner, S. A. Rice and M. J. Vala, *J. Chem. Phys.*, **43**, 2959 (1965).
46. L. Friedman, *Phys. Rev.*, **A140**, 1649 (1965).
47. G. H. Heilmeier, *Org. Cryst. Symp.*, 1965.
48. G. H. Heilmeier, G. Warfield and S. E. Harrison, *Phys. Rev. Lett.*, **18**, 309 (1962).
49. J. Dresner, *Phys. Rev.*, **143**, 558 (1966).
50. D. M. Burland, *Phys. Rev. Lett.*, **33**, 833 (1974); D. M. Burland and V. Konzelmann, *J. Chem. Phys.*, **67**, 319 (1977).
51. W. Warta and N. Karl, *Phys. Rev.*, **32**, 1171 (1985).
52. L. B. Schein, C. B. Duke, and A. R. McGhie, *Phys. Rev. Lett.*, **40**, 197 (1978).
53. L. B. Schein, *Chem. Phys. Lett.*, **48**, 571 (1977).
54. *a*. L. B. Schein, R. S. Narang, R. W. Anderson, and K. E. Meyer, *Chem. Phys. Lett.*, **100**, 37 (1983). *b*. L. B. Schein, W. Warta, A. R. McGhie, and N. Karl, *Chem. Phys. Lett.*, **100**, 34 (1983).
55. J. D. Andersen, C. B. Duke and V. M. Kenkre, *Phys. Rev. Lett.*, **51**, 2202 (1983).
56. H. Sumi, *Solid State Comm.*, **28**, 309 (1978); *J. Chem. Phys.*, **71**, 3403 (1979); ibid., **75**, 2987 (1981).
57. E. A. Silinsh, A. J. Jurgis and G. A. Shlihta, *Material Science*, **13**, 247 (1987).
58. R. H. Batt, C. L. Braun, and J. F. Hornig, *J. Chem. Phys.*, **49**, 1967 (1968); *J. Appl. Opt., Supplement*, **3**, 20 (1969).
59. R. R. Chance and C. L. Braun, *J. Chem. Phys.*, **59**, 2269 (1973); **64**, 3573 (1976).
60. L. Onsager, *Phys. Rev.*, **54**, 554 (1938).
61. A. Hummel, A. I. Allen, and F. H. Watson, Jr., *J. Phys. Chem.*, **44**, 3431 (1966).
62. H. Sano and A. Mozumder, *J. Chem. Phys.*, **66**, 689 (1977); A. Mozumder, S. M. Pimblott, P. Clifford, and N. J. B. Green, *Chem. Phys. Lett.*, **142**, 385 (1987).
63. C. L. Braun and T. W. Scott, *J. Phys. Chem.*, **87**, 4776 (1983).
64. L. Onsager, *J. Chem. Phys.*, **2**, 599 (1934).
65. N. Geacintov and M. Pope in *Proc. 3rd Photocond. Conf., 1969*, E. M. Pell, Ed., Pergamon Press, Oxford, 1971; M. Pope and C. E. Swenberg, op. cit., p. 739.
66. C. L. Braun, *J. Chem. Phys.*, **80**, 4157 (1987).
67. S. Rackovsky and H. Scher, *Phys. Rev. Lett.*, **52**, 453 (1984); *J. Chem. Phys.*, (to be published).
68. A. G. MacDiarmid, C. K. Chiang, C. F. Fincher, Jr., Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis and S. C. Gau, *Phys. Rev. Lett.*, **39**, 1098 (1977).
69. Y. Tomkiewicz, N. S. Shiren, T. D. Schultz, H. Thomaan, L. R. Dalton, A. Zettl, G. Grunar, and T. C. Clarke, *Mol. Cryst. Liq. Cryst.*, **83**, 1049 (1982).
70. H. Naarmann, *Synth. Met.*, **17**, 223 (1987).
71. N. Basescu, Z.-X. Lui, D. Moses, A. J. Heeger, H. Naarmann, and N. Theophilou, *Nature*, **327**, 403-(1987).
72. S. Kivelson and A. J. Heeger, *Synth. Met.*, **22**, 371 (1988).
73. M. J. Rice, *Phys. Lett.*, **71A**, 152 (1979).
74. W. P. Su, J. R. Schrieffer, and A. J. Heeger, *Phys. Rev. Lett.*, **42**, 1698 (1979); *Phys. Rev. B.*, **22**, 2099 (1980).
75. S. Kivelson, *Mol. Cryst. Liq. Cryst.*, **77**, 65 (1981); *Phys. Rev. Lett.*, **46**, 1344 (1981).
76. A. J. Epstein, H. W. Gibson, P. M. Chaikin, W. G. Clark, and G. Gruner, *Phys. Rev. Lett.*, **45**, 1730 (1980).
77. E. J. Mele and M. J. Rice, *Phys. Rev.*, **B23**, 5397 (1981).
78. A. J. Epstein, H. Rommelman, R. Bigelon, H. W. Gibson, D. M. Hoffman and D. B. Tanner, *Phys. Rev. Lett.*, **50**, 1866 (1983).
79. J. L. Bredas, R. R. Chance, and R. Silbey, *Phys. Rev.*, **26**, 5843 (1982).
80. H. Akamatu and H. Inokuchi, *J. Chem. Phys.*, **18**, 810 (1950).
81. D. S. Acker, R. J. Harder, W. R. Hertler, W. Mehler, L. R. Melby, R. E. Benson, and W. E. Mochel, *J. Am. Chem. Soc.*, **82**, 6408 (1960).
82. J. Wudl, G. M. Smith and E. J. Hufnagel, *J. Chem. Soc. Chem. Commun.*, 1453 (1970).
83. J. Ferraris, D. O. Cowan, V. V. Walatka Jr., and J. H. Perlstein, *J. Am. Chem. Soc.*, **95**, 948 (1973).
84. L. B. Coleman, M. J. Cohen, P. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, *Solid State Comm.*, **12**, 1225 (1973).
85. Z. G. Soos, *Ann. Rev. Phys. Chem.*, **25**, 121 (1974).

86. A. N. Bloch in *Energy and Charge Transfer in Organic Semiconductors*, K. Masuda and M. Silver, Eds., Plenum Press NY pp. 159–166 (1974); A. N. Bloch, D. O. Cowan, and T. O. Pochler, ibid., pp. 167–176.
87. J. S. Miller and A. J. Epstein, *J. Am. Chem. Soc.*, **100**, 1639 (1978).
88. A. J. Epstein, J. W. Kaufer, H. Rommelman, I. A. Howard, E. M. Conwell, J. S. Miller, J. P. Pouget, and R. Comes, *Phys. Rev. Lett.*, **49**, 1037 (1982); see also J. S. Miller and A. J. Epstein, *Angew. Chem. Int. Ed., Engl.*, **26**, 287 (1987).
89. W. A. Little, *Phys. Rev.*, **A134**, 1416 (1964).
90. D. Jerome, A. Mazaud, M. R. Ribault, and K. Bechgaard, *J. Phys. Lett.*, **41**, L-95 (1980).
91. K. Andres, F. Wudl, D. B. McWhan, G. A. Thomas, D. Nalewajek, and A. L. Stevens, *Phys. Rev. Lett.*, **45**, 1449 (1980).
92. S. S. P. Parkin, E. M. Engler, R. R. Schumaker, R. Lagier, V. Y. Lee, J. C. Scott, and R. L. Greene, *Phys. Rev. Lett.*, **50**, 270 (1983).
93. V. V. Walatka, Jr., M. M. Labes, and J. H. Perlstein, *Phys. Rev. Lett.*, **31**, 1139 (1973).
94. R. L. Greene, G. B. Street, and L. J. Suter, *Phys. Rev. Lett.*, **34**, 577 (1975).
95. W. D. Gill, *J. Appl. Phys.*, **43**, 5052 (1972).
96. W. J. Dullmage, W. A. Light, S. J. Marino, C. D. Saltzberg, D. L. Smith, and W. J. Staudenmayer, *J. Appl. Phys.*, **49**, 5543 (1978); P. M. Borsenberger, A. Chowdry, D. C. Hoesterey, and W. Mey, *J. Appl. Phys.*, **49**, 5555 (1978).
97. C. B. Duke and R. J. Meyer, *Phys. Rev.* **B23**, 2111 (1981).
98. P. J. Regensburger, *Photochem. and Photobiol.*, **8**, 429 (1968).
99. H. Scher and E. W. Montroll, *Phys. Rev.*, **B12**, 2455 (1975).
100. M. Stolka, J. F. Yanus, and D. M. Pai, *J. Phys. Chem.*, **88**, 4707 (1984).
101. L. B. Schein, A. Rosenberg, and S. L. Rice, *J. Appl. Phys.*, **60**, 4287 (1986).
102. S. Chittipeddi, K. R. Cromack, J. S. Miller and A. J. Epstein, *Phys. Rev. Lett.*, **58**, 2695 (1987).
103. H. M. McConnell, *Proc. Robert A. Welch Found. Conf. Chem. Res.*, **11**, 144 (1967).
104. M. S. Wrighton, *Comments Inorg. Chem.*, **4**, 269 (1985).
105. A. Heller, *Science*, **223**, 1141 (1984).
106. L. Li and R. Kopelman, *J. Lum.*, **40/41**, 688 (1988); P. Argyrakis and R. Kopelman, ibid., **40/41**, 690 (1988).