

polymer reviews

Control of electrical properties of polymers by chemical modification

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This article reviews the use of chemical modification of preformed polymers as a means of tailoring their electrical properties. Specifically, triboelectric charging, photoconductivity and dark conductivity are considered.

Keywords Triboelectric charging; photoconductivity; photoconductive polymers; conductive polymers

INTRODUCTION

Purposeful chemical modification of preformed polymers to improve physical properties is an old technique. Chemical manipulation of natural polymers formed the basis of several industries. An excellent example of such a natural polymer is cellulose, which can by chemical modification be converted into polymers useful as plastic film for wrapping, and photography (cellulose acetate), for filters (cellulose acetate), for explosives (cellulose nitrate), and for fibres (cellulose acetate and triacetate), among others. Rubber is another natural polymer whose property manipulation by chemical modification forms the basis of an entire industry.

The advent of synthetic polymers and the age of 'plastics' has not caused an abatement of the efforts toward utilization of chemical modification of polymers. It is probably true that chemical modification has been investigated as a means of optimization of essentially every physical property of polymers. Bulk properties can be varied by chemical modification of polymers in solution or melt. Surface properties are often easily dealt with by reaction of the solid polymer surface, as well as bulk modification.

This review is limited to the control of electrical properties of polymers, specifically triboelectric charging, photoconductivity and (dark) conductivity. This discussion will provide the reader with a broad range of successful examples of the application of the chemical modification technique to physical property manipulation using both surface and bulk chemical modification processes.

TRIBOELECTRIC CHARGING

Triboelectrification is the process by which two bodies in contact with each other become equally and oppositely charged. The process has been known since at least 600 BC¹. The phenomenon plays a central role in a number of processes of practical importance: electrical storms², explosions in fuel pipelines and storage tanks³, the electrostatic separation of materials^{4,5}, electrostatic paint application⁶, self-clinging wrapping materials, and

adhesion⁷. Xerography⁸ is, in terms of sales dollars, perhaps the largest useful application of triboelectric charging.

Inasmuch as triboelectrification is central to xerography, a brief digression to describe the xerographic process will be taken. The basic steps and elements in the process are illustrated in *Figure 1*. A photoconductor (a material that conducts electricity several orders of magnitude faster under actinic light than in the dark) is first charged by spraying ions formed from molecules in the air under a high electric field (corotron). In the absence of light this leads to a uniform charge distribution on the surface of the photoconductor, with the appropriate number of countercharges on the back (grounded) surface (Step 1). Exposure of the photoconductor to actinic radiation in an imagewise pattern (e.g., by reflection and projection from an original document) results in the loss of charge in light-struck areas. Charge is retained in areas not illuminated, resulting in a pattern of charge that corresponds to the exposure pattern (Step 2). Following this imaging step, the electrostatic image is developed. The developer usually consists of two components: carrier and toner⁹. The carrier usually comprises of metal (coated or uncoated) beads, while the toner is a polymer containing a colourant (dye or pigment) to provide contrast. The carrier and toner are agitated; this results in triboelectric charging that leads to toner particles of sign opposite the imagewise pattern on the photoconductor. When the developer is exposed to the image, the toner particles are electrostatically attracted to the charged areas, forming a visual positive image (Step 3). This image is then transferred and fixed to paper (Step 4).

The control of both the sign and magnitude of triboelectric charging is therefore of some practical significance. Control of charging requires a knowledge of the relationship of molecular structure to the charge exchange process. As discussed below, the systematic variation of molecular structure, including polymer modification, has been used to provide such knowledge, as well as to produce practically useful materials. This discussion is restricted to insulating, i.e., non-conductive polymers.

BASIC STEPS IN XEROGRAPHY

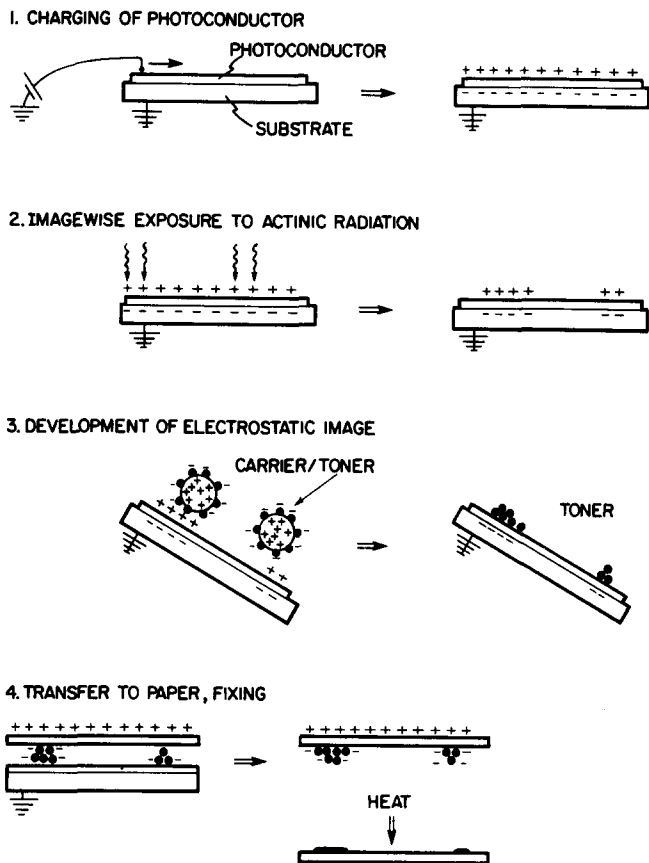


Figure 1 Scheme of the xerographic process

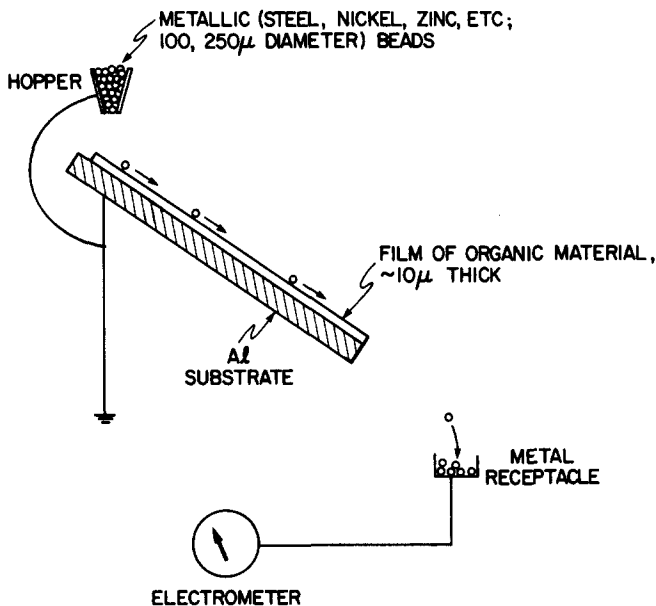


Figure 2 Device for measurement of triboelectric charging

Chemical modification of polymers in solution

The aminolysis of a styrene-*n*-butyl methacrylate copolymer (1) by a variety of amines (2)¹⁰ was studied to determine the relationship between (1) charging and extent of reaction for a given amine and (2) charging and the nature of the amine¹¹. In Figure 2 the apparatus

used to measure the charge is depicted. It consists of an inclined plane upon which the polymer film rests, a source of metal beads which cascade over the film and an electrometer, which measures the charge on the metal beads. A discussion of the apparatus and the measurement technique has been published¹².

Figure 3 is a plot of Q/M , the charge to mass ratio of the beads at the end of the measurement, versus the extent of aminolysis with 6-aminohexanol¹¹. As can be seen, the relationship is essentially linear. In contrast, when physical blending of the starting polymer 1 and product polymer are used, the S-shaped curve of Figure 4 is produced¹¹. Triboelectric charging is a surface phenomenon. Because of phase separation of the polymers in the mixture, the surface composition varies from the bulk composition¹³. Hence, the triboelectric

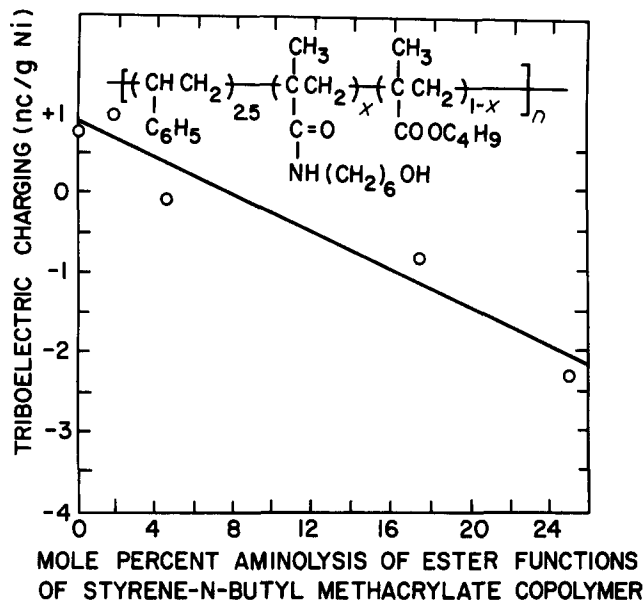


Figure 3 Triboelectric charge versus extent of aminolysis of styrene-*n*-butyl methacrylate copolymer

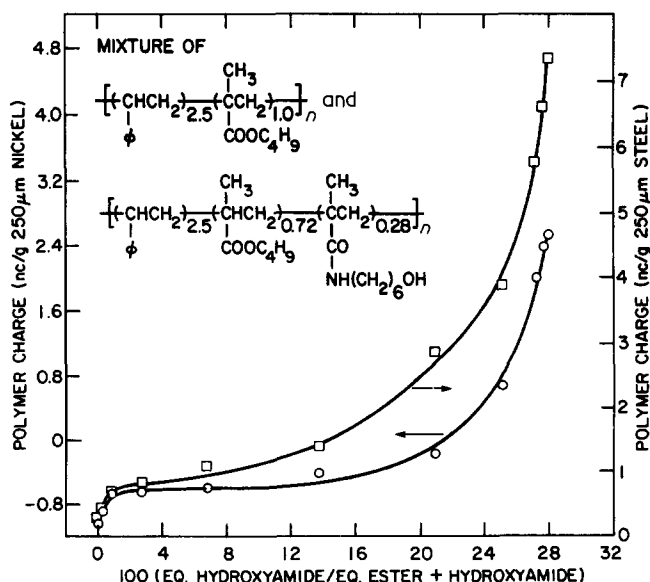


Figure 4 Triboelectric charge versus composition for blends of styrene-*n*-butyl methacrylate copolymer and its aminolysis product

charging curve (Figure 4) reflects the surface composition of the polymer mixture. Since the polymer modification is carried out in solution, the distribution of aminolysed ester groups is random and due to constraints of the chains, remains so in the cast films. Thus, a definite advantage of the chemical modification approach over the blending approach is direct linear control over the charging in most cases (see below, however). S-shaped curves have also been reported for plots of triboelectric charging *versus* bulk composition for certain copolymers, such as styrene-methyl methacrylate¹⁴. This may be the result of formation of extensive blocks of one monomer unit at extremes of composition during polymerization and these blocks may then phase separate to some extent at the surface depending upon the surface energies. A further complication of such systems arises in the preparation of developers by solvent removal by spray drying; that is the problem of the dependence of surface composition upon the solvent and its rate of removal¹⁵. Here again chemical modification with its random introduction of functionality offers a distinct advantage.

The reactivity of the pendant hydroxyl functionalities of 3 was utilized for covalent dyeing, yielding coloured polymers (4) of use as toners in xerography^{10,16}. Again, as shown in Figure 5, linear control of charging following the two chemical modification steps (aminolysis to 3 and dyeing of 3 to 4) and film casting is achieved.

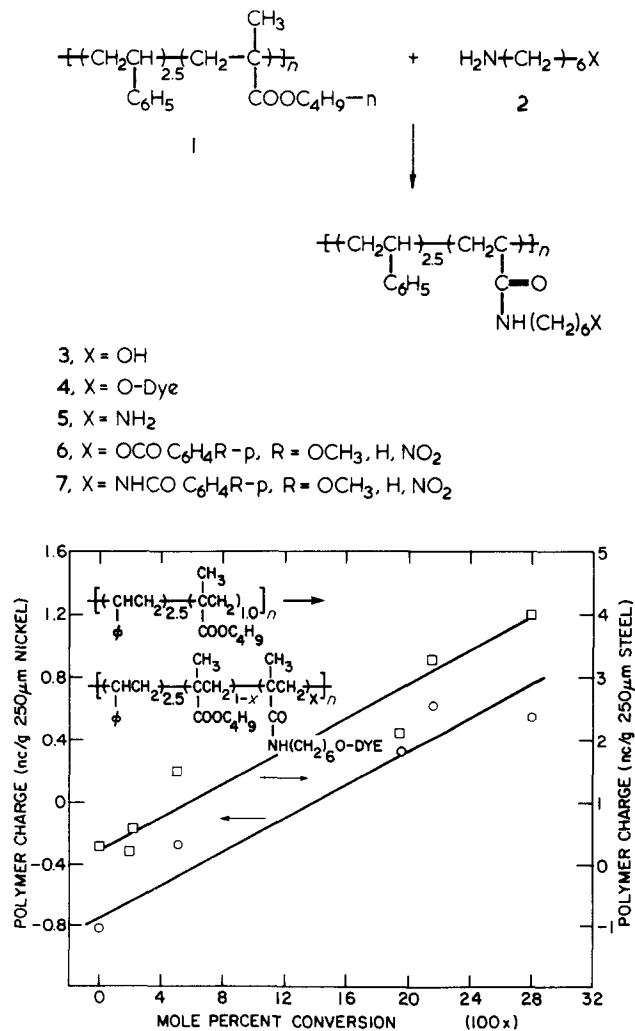
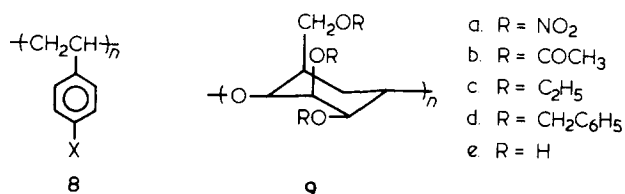


Figure 5 Triboelectric charge *versus* extent of reaction for dyed aminolysis product from styrene-n-butyl methacrylate copolymer

By acylation of polymers 3 and 5, the benzoate ester polymers 6 and the benzamide polymers 7 were synthesized¹⁰. Charging studies of these systems revealed relationships between both aliphatic and aromatic molecular structures and charging¹¹. The charging of the acylated polymers was found to be less positive (more negative) than the parent polymers, either the hydroxy or the amino functionalized polymer. Silylation causes similar changes in hydroxy or amino functionalized materials, as does acylation of alcohols such as poly(vinyl alcohol) and ethyl cellulose¹⁷. It appeared that the charging was related to the substituent constants in both series of acylated polymers. Such relationships were subsequently verified by studies of a series of aliphatic polymers¹⁸ and a series of substituted polystyrenes 8¹⁹, some of which were prepared by chemical modification of polystyrene. A semilog plot of the *Q/M* ratio *versus* Hammett substituent constant is given in Figure 6 for the substituted polystyrenes.



Japanese workers had independently reached similar qualitative conclusions based on limited series of oligomeric polystyrene derivatives²⁰. They utilized the related measurement technique of mercury contact charging as schematically illustrated in Figure 7, as well as a frictional method. Later work^{21,22} using a complex frictional charging apparatus *in vacuo* also confirmed the results of Figure 7, as shown in Figure 8, a plot of the contact potential difference between a metal reference electrode and the films *versus* Hammett constant.

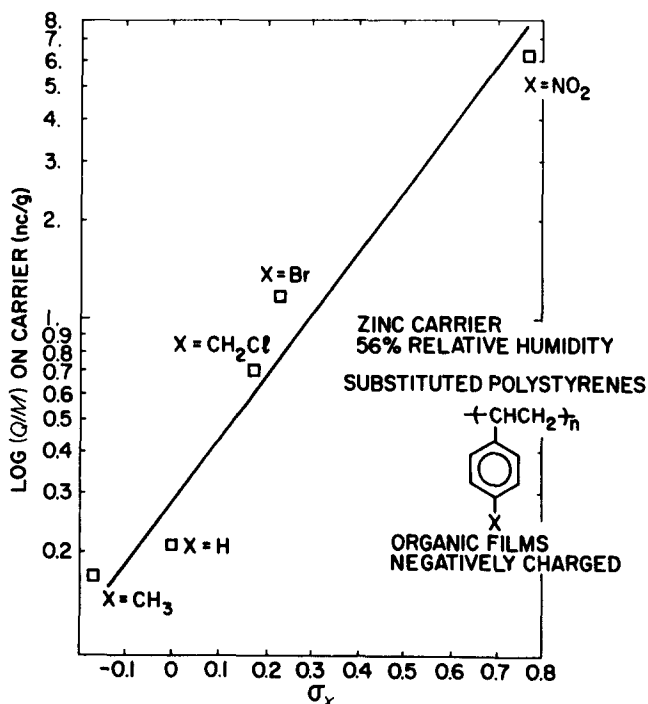


Figure 6 Triboelectric charge *versus* Hammett substituent constant for substituted polystyrenes

MERCURY CONTACT CHARGING APPARATUS

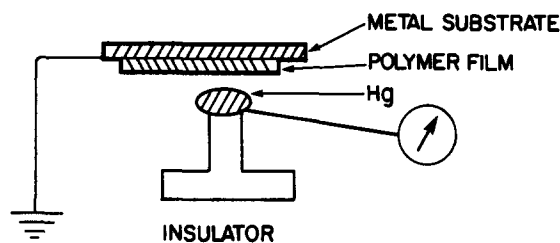


Figure 7 Mercury contact charging apparatus

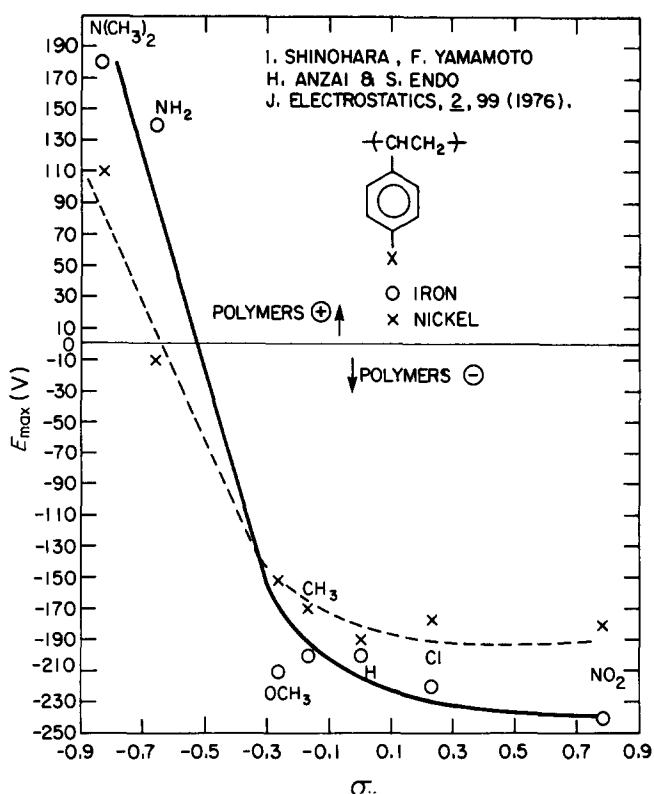
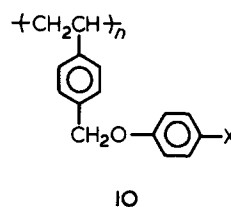


Figure 8 Contact potential versus Hammett substituent constant for substituted polystyrenes

Modification of cellulose to give a series of polymers of structure 9 was also carried out²³. They exhibited a correlation of negative charging with electron accepting substituents such as NO₂ and positive charging with electron donating substituents such as OH.

The rationalization of these correlations is accommodated by the following arguments and model. It has been shown that in both the gas and solution phases molecular orbital energy levels are in general directly proportional to Hammett or related substituent constants. Thus, ionization potentials^{24,25} and electron affinities, as deduced from reduction potentials²⁶⁻²⁸, are directly dependent upon the nature of the substituent. In organic solids these energy levels are modified only by the polarization energy and are thus only shifted relative to the isolated molecule^{29,30}. The direction of charging is believed to be exponentially governed by the energy barriers to electron exchange between the Fermi level of the metal and the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO), the smaller energy gap, of course, determining

the direction of charge exchange (Figure 9)^{12,19}. Thus, in a series of compounds which all acquire the same sign of charge, the logarithm of the extent of charging is directly proportional to the energy gaps between the metal Fermi level and the appropriate MO, hence also proportional to the substituent constant σ (Figure 10). This model predicts that the slope of the Hammett plot [\log (charge level) vs. σ] will be opposite the sign of charge acquired by the organic film; this is in fact observed^{18,19} (see Figures 6 and 8).



Further exploration of this relationship utilized series 10, which was prepared from 8, X=CH₂Cl³¹. A Hammett plot of the charging results is shown in Figure 11.

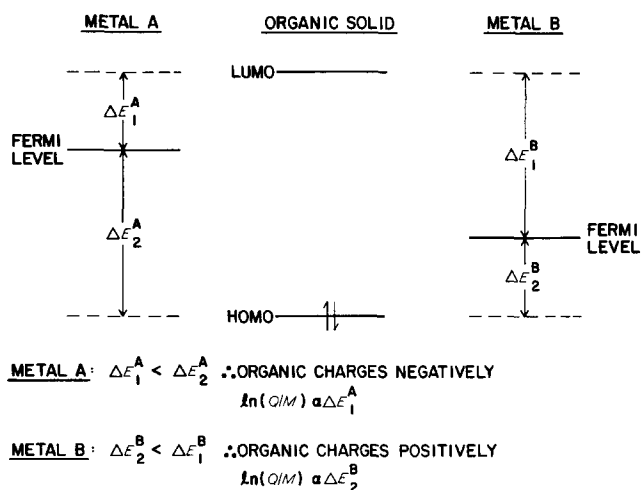


Figure 9 Model of triboelectric charging of organics based upon molecular orbital energy levels

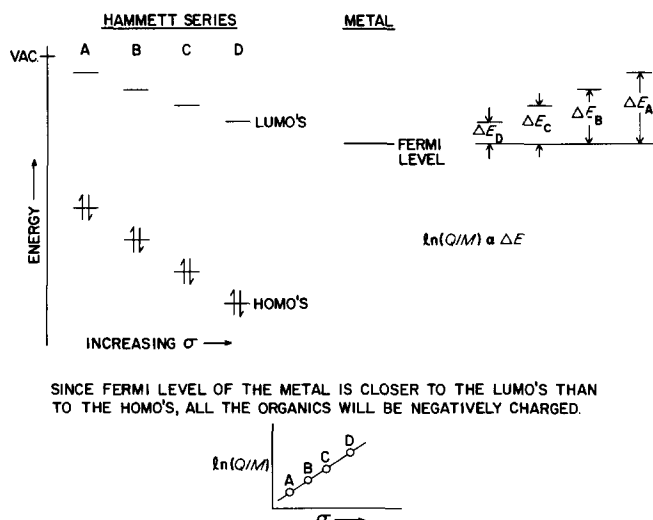


Figure 10 Consequence of model of Figure 9: dependence of triboelectric charge upon Hammett substituent constant for a homologous series

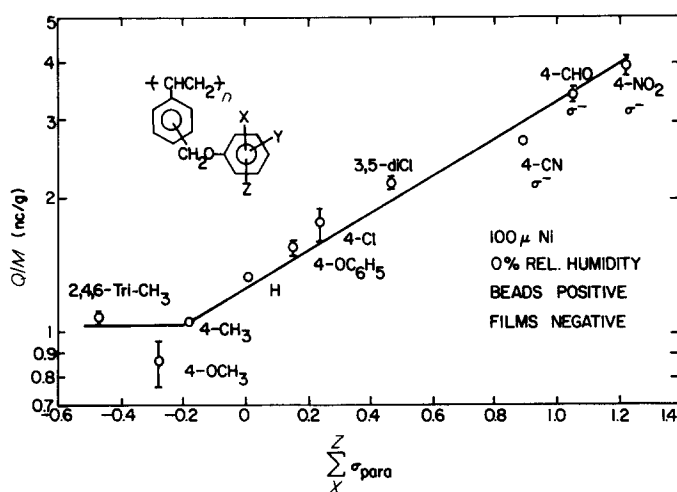


Figure 11 Triboelectric charge versus Hammett substituent constant for poly(*p*-substituted phenoxyethylstyrenes)

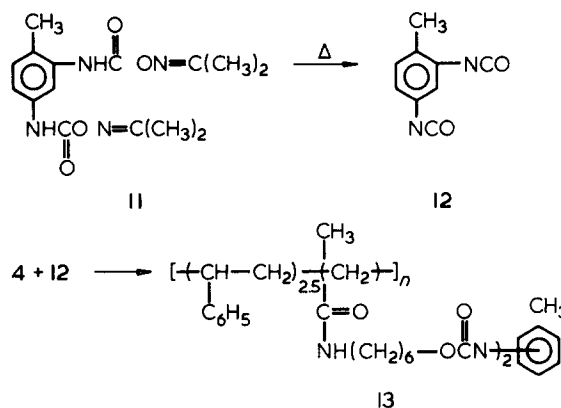
The invariant negative charging of the polymers, followed by a linear increase as σ increases, is expected on the basis of the energetic model presented above. Since interactions between chains and even between the pendant groups are very weak, the charging is believed to be governed by localized molecular states³². In this case each monomer unit possesses two aromatic chromophores. The negative charging of the polymer will thus be dominated by the aromatic moiety with the more accessible orbital, i.e., the more stable lowest unoccupied molecular orbital (LUMO), or greater electron affinity (EA). In polymer 10, assuming no interaction between the two aromatic rings, the energy of the LUMO of the ring attached to the polymer backbone is invariant, while the energy of the LUMO of the other ring decreases²⁴, i.e., EA increases with σ . At low σ the EA of the first ring dominates and no effect of changing X is observed. Then the two EA's become identical and finally EA of the second ring becomes greater and begins to dominate, hence the increase in charging with σ .

Several exceptions to the general correlation of charging with energy levels or substituent constants have been noted. These occur for moieties such as phenols and carboxylic acid^{18,33}. A possible explanation is that the mechanism of charging for these structures is ionic in the presence of water (due to H⁺ transfer) while for other moieties the mechanism is electronic. This is in accord with observations of higher negative charging values observed than would have been predicted based on substituent constants. It is also supported by the fact that acids' charging capacities change dramatically upon thorough drying¹⁴. Another explanation is that substituent constants for hydroxy and carboxyl, which are derived from solution data, do not hold in the solid state. They have been shown to be in error when applied to the gas phase²⁵.

Chemical modification in the bulk of polymeric solids

In some cases bulk modification of the polymer in the solid state is an alternative. Radiation chemistry is one well known but poorly characterized method of doing this. Let us consider a classical chemical reaction in the bulk in terms of its effect upon triboelectric charging. The hydroxy functionalized polymer 3 was cast as a film from a solution containing the acetone oxime blocked

diisocyanate 11. Blocked diisocyanates are commonly employed as *in situ* diisocyanate sources³⁴; variation of the blocking agent affords a variety of deblocking temperatures. The polymer film was examined triboelectrically and incrementally heated at a temperature high enough to liberate the diisocyanate 12, which in turn reacts with the hydroxy groups of the polymer, converting them to urethane linkages 13. The results are shown in Figure 12. The triboelectric charging changes smoothly with time. In fact, the triboelectric charging can be used to follow the reaction and established its pseudo first order character¹². That is, once more the charging is directly proportional to the extent of reaction. Moreover, the urethane charges less positively than the alcohol in keeping with results described above for esters and amides.



Chemical modification of polymer surfaces

Oxidation of polystyrene surfaces has been shown to increase the negative charging capacity linearly (Figure 13)^{35,36}. Introduction of carbonyl containing functionalities (acceptor groups) is known to occur³⁷. Oxidation in the absence of ultraviolet light is relatively slow³⁶. Ultraviolet photooxidation is fast³⁷. It forms the basis of imaging systems that operate upon the change in triboelectric charging capacity. Imagewise exposure of polystyrene to ultraviolet light in air leads to the generation of carbonyl functionality. Exposure of the polystyrene to mercury causes the imaged areas to become negatively charged. This electrostatic image is then developable as

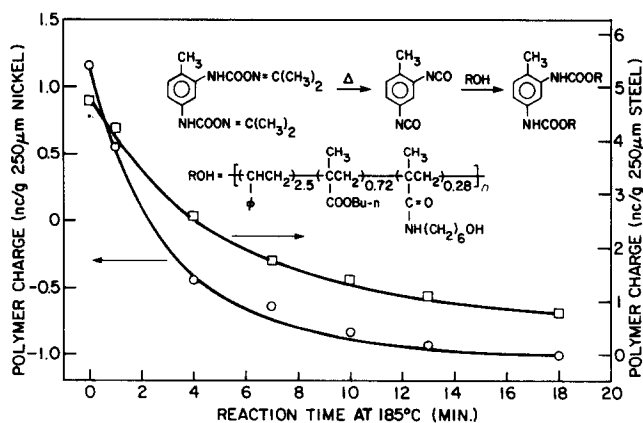


Figure 12 Triboelectric charge versus heating time for blend of blocked diisocyanate and hydroxyl-containing polymer

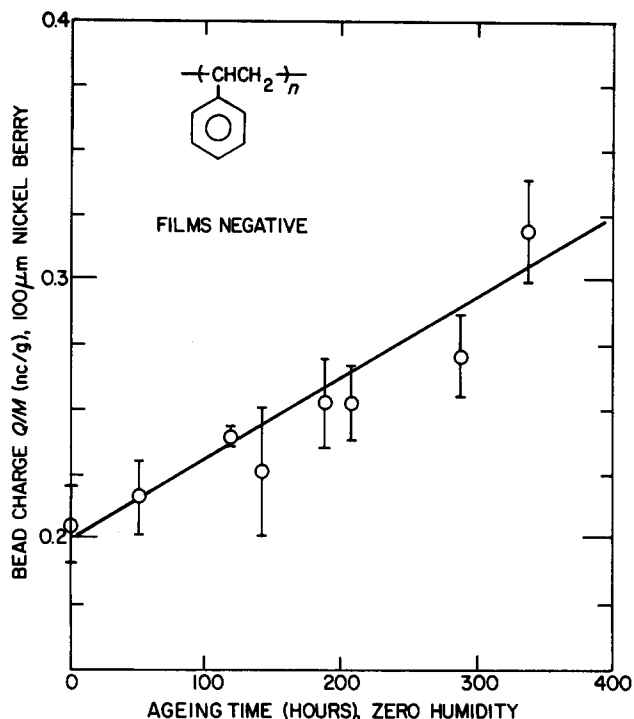


Figure 13 Triboelectric charge versus air exposure-time of freshly cast polystyrene film

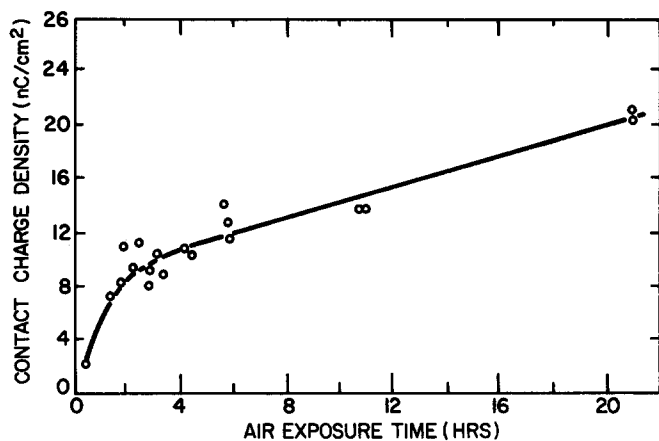


Figure 14 Triboelectric charge versus air exposure time of branched polyethylene

been studied in detail⁴². This system provides an example of the complexities of the solid state of such highly polar polymers. The triboelectric charging of a series of ion exchanged sulphonated polystyrenes (14) has been studied as a function of extent of sulphonation. Sulphonation was carried out using 100% H₂SO₄. The films were then ion exchanged to completion with aqueous solutions of the cations⁴³.

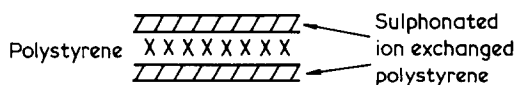
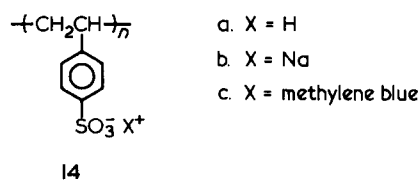
A plot of *Q/M* versus extent of reaction for the sulphonic acid itself (14a) is given in Figure 16. Note that the ultimate charging level becomes insensitive through a maximum value with many oscillations. The curve is reproducible. The initial strong increase in charging must be due to the great propensity of the styrene-sulphonate groups for charging negatively and the fact that they are on the surface of the film. To understand the remainder of the curve one must consider the results of surface energy and e.s.c.a. (electron spectroscopy for chemical analysis⁴⁴). In Figure 17 are shown plots of these results along with the triboelectric charging results⁴⁵. Note the similarities of the curves, both with regard to the ultimate plateauing as well as the maximum and attendant oscillation. While a detailed explanation has not been put forth, it is apparent that associative forces of the polar functionalities alter the extent of aggregation and the average depth of the aggregates from the surface. The results suggest that at higher sulphonation levels the styrene-sulphonate moieties are able to reorient during the ion exchange process, yielding more and probably higher order aggregates. The complicated triboelectric charging dependence probably reflects changes in both the charging propensity of the styrene-sulphonate moieties of the aggregates and variation in their depths.

Other cations display similar, though somewhat less complicated, behaviour. In Figures 18 and 19 are shown *Q/M* versus extent of sulphonation for fully exchanged films containing Na⁺ (14b) and methylene blue (14c). Other ions give similar results. The plateau levels of Figures 16–19 indicate that the charging method of Figure 2 probes a depth of about 1.5 μm, in rough agreement with other estimates by a different technique⁴⁶.

described above³⁸. Alternatively the hydroperoxy groups can be treated with SO₂ to yield sulphate groups. The polar sulphate groups are developable by a number of electrostatic methods³⁹.

Oxidation and ozonization of branched (unsaturated) polyethylene lead to very similar results, i.e., enhanced negative charging capacity (Figure 14)^{36,40}. Oxidation of coal is similar in effect⁴¹. In all of these cases, since triboelectric charge is limited to a region near the polymer surface, the charging increases smoothly and then reaches a plateau value after a certain extent of reaction. This is reasonable on the basis of the model shown in Figure 15, in which the dependence of the charge contribution of a given site on its distance from the surface of the film is an asymptotic function.

Sulphonation of free-standing films of polystyrene has



As a means of providing (1) verification of the model of triboelectric charging based on molecular orbital energy levels, the (2) a means of controlling the triboelectric charging, polystyrene was sulphonated as outlined above to a degree that corresponded to a point well out on the plateau of plots such as Figure 19, i.e., $E = 2 \times 10^{-4}$ moles/g. These films were then completely ion exchanged with a series of dyes of various structural

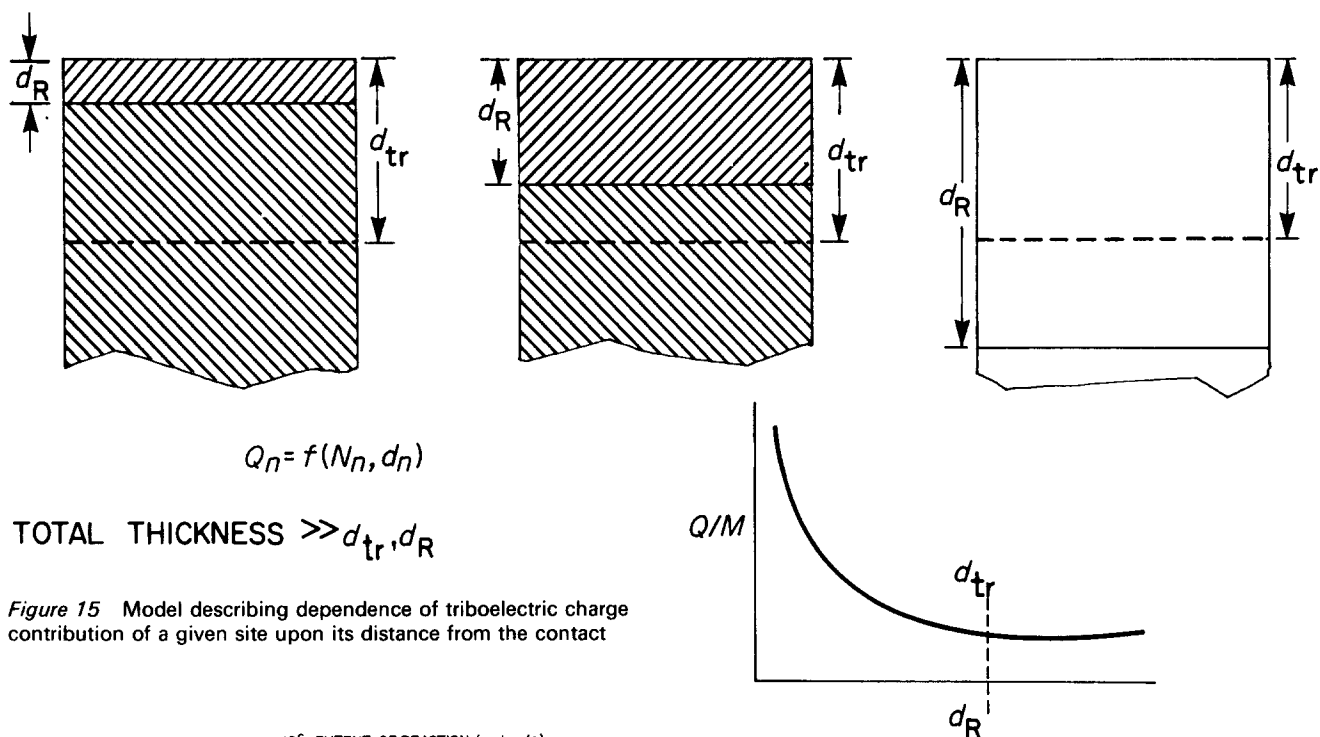


Figure 15 Model describing dependence of triboelectric charge contribution of a given site upon its distance from the contact

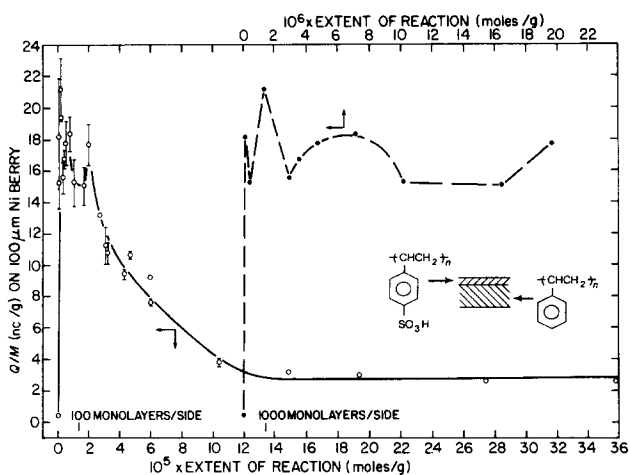


Figure 16 Triboelectric charge versus extent of sulphonation of free standing polystyrene films

types. The dyes were selected such that there was no relationship between the HOMO and LUMO energies as determined by electrochemical potentials (Figure 20). Based upon the model, triboelectric charge exchange may be likened to electrochemistry (Figure 21). The difference is that in electrochemistry the applied voltage is varied to probe the difference in potential between the reference electrode and the HOMO for oxidation and the LUMO for reduction, while the triboelectric charging is related to the difference in these energy levels. Thus, as in electrochemistry, variations of the Fermi energy of metal bead should allow one to probe both HOMO and LUMO states. The point in energy at which the charging is zero corresponds to the midpoint between the HOMO and LUMO. Conversely, if the metal is constant and the energies of the HOMO's and LUMO's of a series of polymer films are varied, the point of zero charging corresponds to the Fermi level of the metal bead. The results for such an experiment are shown in Figure 22 as a plot of Q/M versus $(E_{1/2}^{OX} + E_{1/2}^{RED})/2$ of the cationic dyes. The Fermi

level of the metal determined in this way is somewhat less than the reported value.

This same technique has been applied to the substituted polystyrenes (8), as shown in Figure 23 using

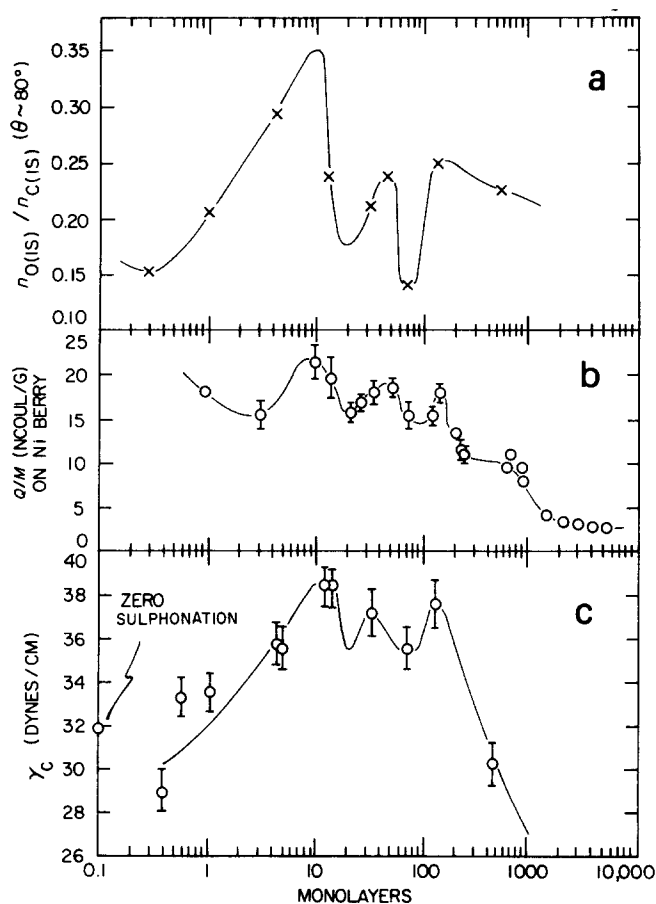


Figure 17 Oxygen to carbon ratios (e.s.c.a.), triboelectric charge and surface energy (γ_c) versus amount of polystyrene sulphonate formed on free standing polystyrene films

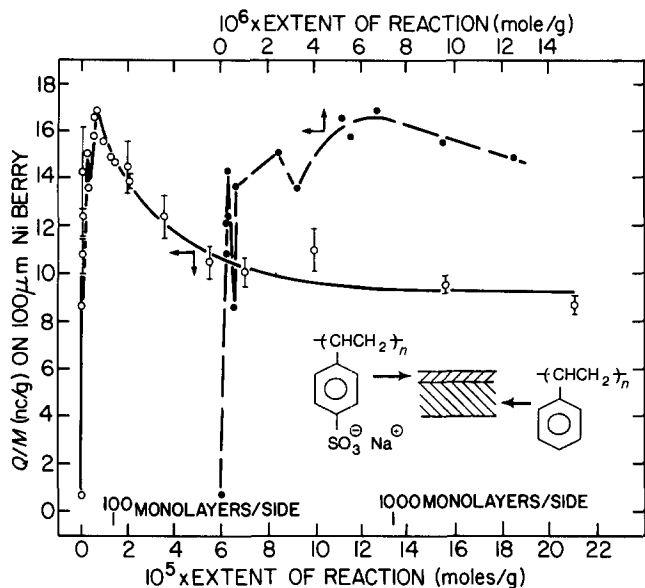


Figure 18 Triboelectric charge versus extent of sulfonation for sodium ion exchanged, sulphonated free standing polystyrene films

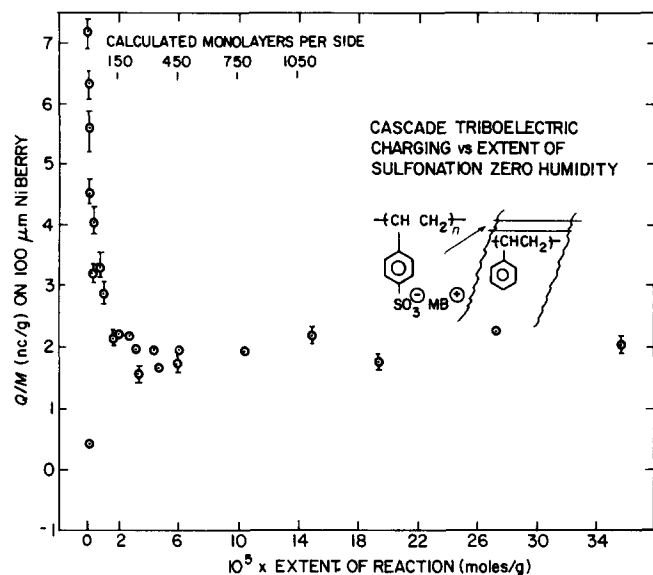


Figure 19 Triboelectric charge versus extent of sulphonation for methylene blue exchanged sulphonated free standing polystyrene films

values of $(EA + IP)/2$ derived from substituted benzenes. Again, the determined value of the Fermi level is slightly low relative to reported values.

The discrepancy between Fermi levels determined in this way and other reported values is accommodated by the fact that the energy levels (HOMO and LUMO) are not discrete but are distributions. Since the number of electrons transferred is small³², the tails of the distributions are important. For many of the dyes used in this study the solid state energy distribution is reported to be 0.7 eV wide⁴⁷. The Fermi levels determined are lower by ~0.3 eV than reported, in good agreement with this distribution width, as shown schematically in Figure 24. This in no way affects the arguments made above.

Conclusions

The work summarized in this section leads to the

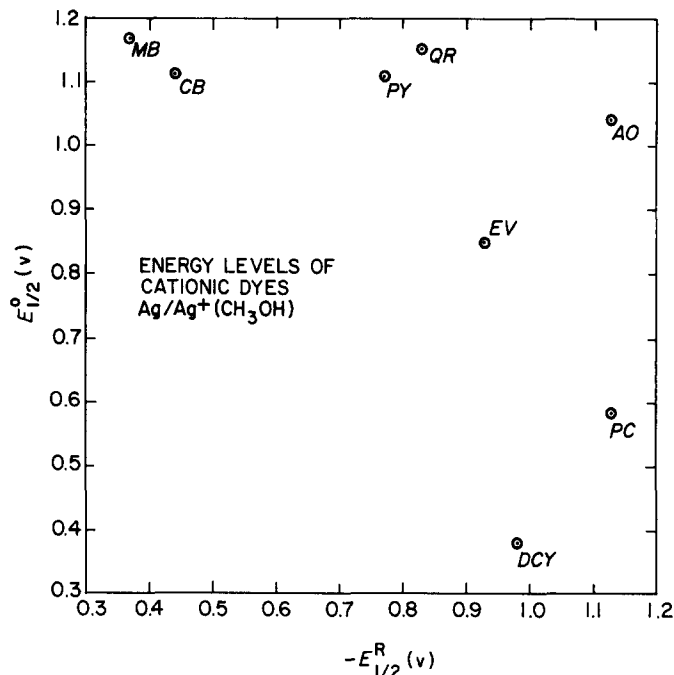


Figure 20 Plot of reduction potential versus oxidation potential for a series of cationic dyes (MB=methylene blue, CB=Capri blue, PY=pyronin, QR=quinaldine red, EV=ethyl violet, AO=acridine orange, PC=pinacyanol; DCY=dicarbocyananine)

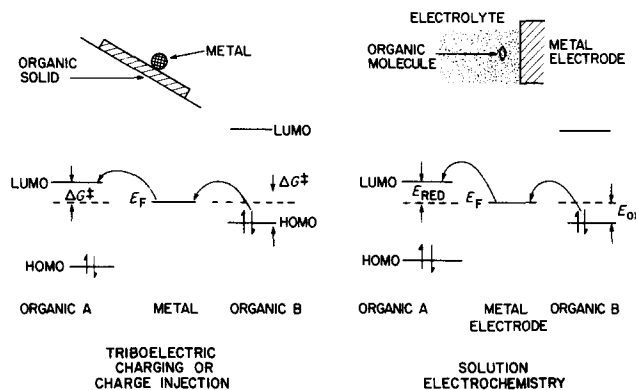


Figure 21 Analogy between triboelectric charging and solution phase electrochemistry

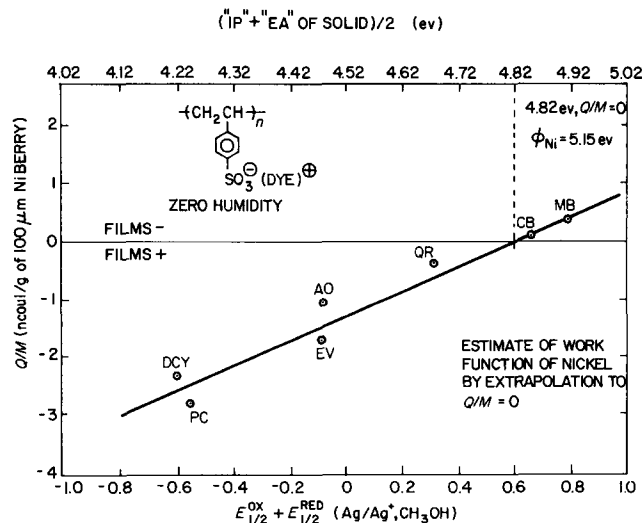


Figure 22 Triboelectric charge versus half the sum of reduction and oxidation potentials of cationic dyes bound to films of sulphonated polystyrene

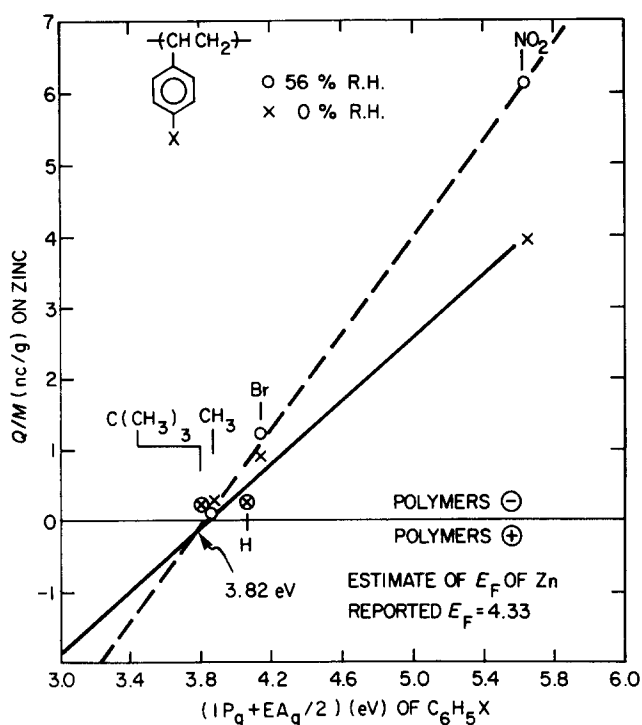


Figure 23 Triboelectric charge of substituted polystyrene versus half the sum of the ionization potential and electron affinity of analogous substituted benzene

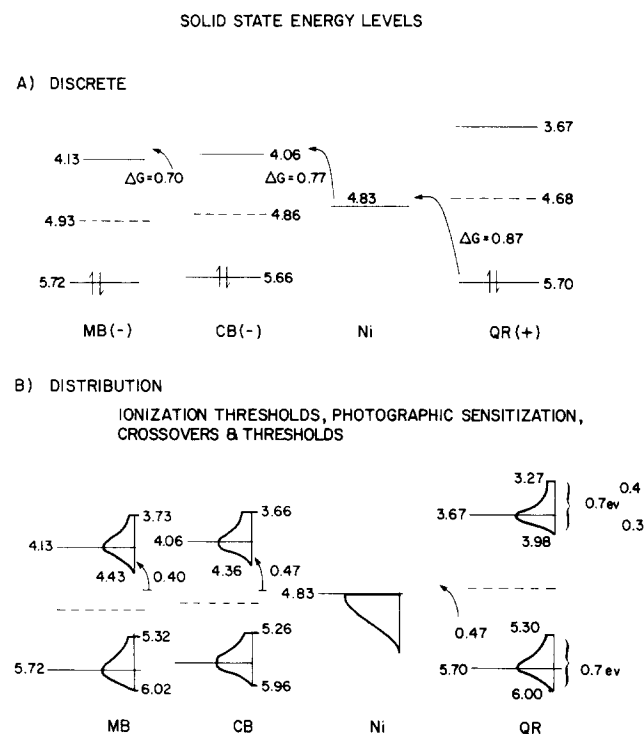


Figure 24 Solid state energy levels: (A) idealized, discrete levels; (B) actual, distribution of levels (see Figure 19 for key to dye abbreviations)

following conclusions regarding the utility of chemical modification for alteration and control of triboelectric charging of insulating polymers

(i) With weakly or moderately polar functionalities the triboelectric charging is directly proportional to the extent of reaction, whether the reaction is carried out in solution, on the polymer surface or in the polymer bulk.

With strongly polar moieties such as sulphonate groups, the relationship is more complex.

(ii) The direction and magnitude of triboelectric charging is understood in terms of molecular orbital energy levels of the constituents, enabling rational choice of the type of functionality to be introduced or altered to achieve the desired direction and level of charging.

PHOTOCONDUCTIVE POLYMERS

As noted in the section above, photoconductivity is one of the commercially significant photoresponses of polymeric systems. It is fundamental to xerography⁸, as well as a number of related processes. Photoconductivity has been well studied from a scientific point of view⁴⁸, but a review of the underlying features is perhaps appropriate here in order to orient the reader.

Photoconductivity is defined as a significant increase (by a factor of $\geq 10^3$ to be of practical utility) in the conductivity under illumination. This increase is attributed to an increase in the number of charge carriers (electrons or holes) as a direct result of electronic excitation. Thus, the phenomena necessary for photoconduction are: (1) photogeneration of charge carriers and (2) transport of charge carriers. These two phenomena can be treated separately both functionally in practice and in theory and we shall do so here insofar as possible. In cases where detailed analyses were not available, results will be discussed in the section dealing with transport. By functional definition photoconductivity is generally discussed only for systems of low [say $< 10^{-10}$ (ohm cm)⁻¹] dark conductivity. This section likewise will deal only with such systems.

Chemical modification to alter photogeneration

Two objectives for the chemical modification of polymers with respect to the photogeneration process have been pursued: (a) extension of the spectral response and (b) increase in efficiency. These objectives have been reached in two ways. First, addition of a small molecular 'dopant' can be utilized. This subject will be included here, because there is an electron transfer reaction between the dopant and the transport polymer matrix. Second, the polymer can be chemically modified in the more classical sense.

Addition of 'small molecules' to polymers. This approach is the oldest one and dates back at least forty years to 1941, when Szent-Gyorgyi examined the effect of a cyanine dye upon the photoconductivity of a protein⁴⁹. Dyes are commonly employed to extend the spectral response (sensitization) of photoconducting polymers, such as poly(*N*-vinylcarbazole) (15), into the visible range. These include rose bengal, methyl violet, methylene blue, pinacyanol, etc.⁵⁰⁻⁵². In general, the action spectrum, i.e., the wavelength dependence of the conductivity, roughly follows the electronic absorption spectrum of the dye (Figure 25). It is now generally accepted that the sensitization process involves electron transfer between the excited state of the dye and the polymer transport matrix. As schematically shown in Figure 26, the direction of electron transfer depends upon the relative energy levels of the dye and the polymer. Most systems transport holes more readily

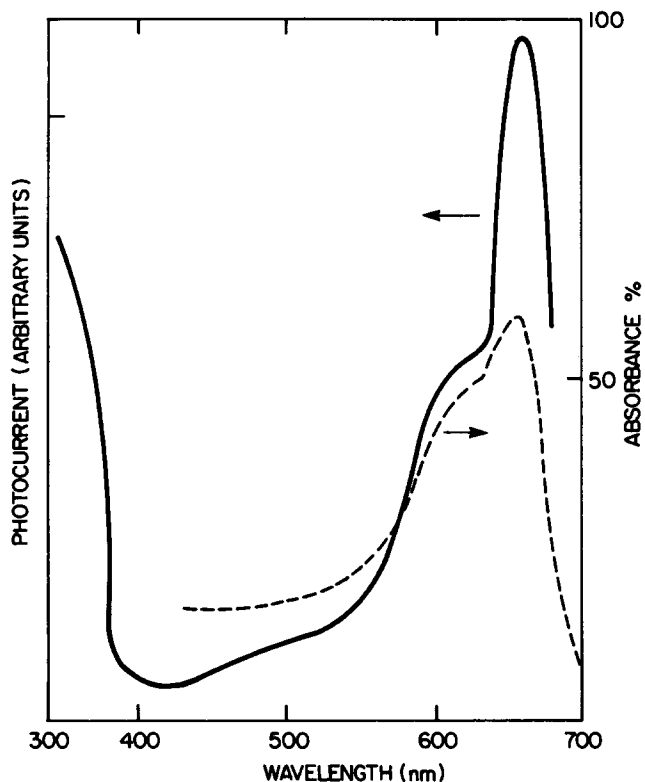
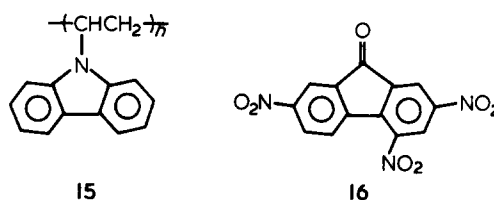


Figure 25 Wavelength dependence of absorption of a dye (methylene blue) and the photoconductivity of polyvinylcarbazole sensitized by the dye

occurs between the dye and the polymer and this results in a decrease in photoconductivity⁵⁴. This problem can be overcome by the addition of acceptor molecules such as tetracyanoethylene or chloranil. The addition of the acceptor causes a new band to appear in the action spectrum; the band is attributed to the formation of the anion radical of the acceptor. These observations are accommodated by the scheme of Figure 27.

Another way to improve photogeneration of charge carriers is to add acceptor molecules to a hole transporting polymer such as poly(vinylcarbazole) (PVK) (15). The donor-acceptor interaction between the polymer and the dopant leads to a 'charge transfer' band in both the absorption and action spectra. 2,4,7-Trinitro-9-fluorenone (TNF) (16) in PVK has been widely studied over a range of molar ratios⁵⁵. The mechanism of photogeneration is considered to be formation of the radical anion-radical cation pair upon excitation in the presence of an electric field. The transport properties of the system are discussed below.



A systematic study of the effect of molecular orbital energy levels of acceptor dopants on the photogeneration efficiency of PVK has been carried out⁵⁶. It was found that the logarithm of photogeneration efficiency is directly proportional to the ease of reduction of a series of cyano compounds, as shown in Figure 28. This is in accord with the proposed mechanism involving electron

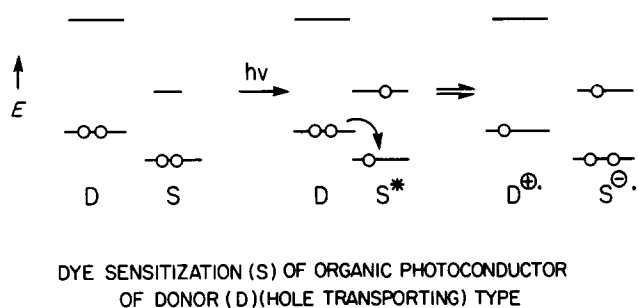


Figure 26 Electron transfer mechanism of sensitization of photoconduction for an acceptor type dye and a donor photoconductor

than electrons (see below), so that electron transfer from the polymer to the excited dye is the situation usually encountered in practice. As can be seen in the Figure, for hole transport the electron is injected into the highest occupied molecular orbital (HOMO) of the excited state of the dye. This, of course, can only occur when one of the electrons occupying this energy level has been excited (Pauli exclusion principle).

The separation of the resultant cation radical-anion radical ('hole-electron') pair is facilitated by an electric field that has been applied to the photoconductor (see Figure 1). The geminate recombination rate of such pairs is less, the higher the applied electric field (Onsager theory⁵³).

The photogeneration efficiency is sometimes concentration dependent⁵¹. The dye species may also serve as a trap in the transport process in dispersed systems⁵¹. Another problem associated with sensitization of this type is that over the long term a photochemical reaction

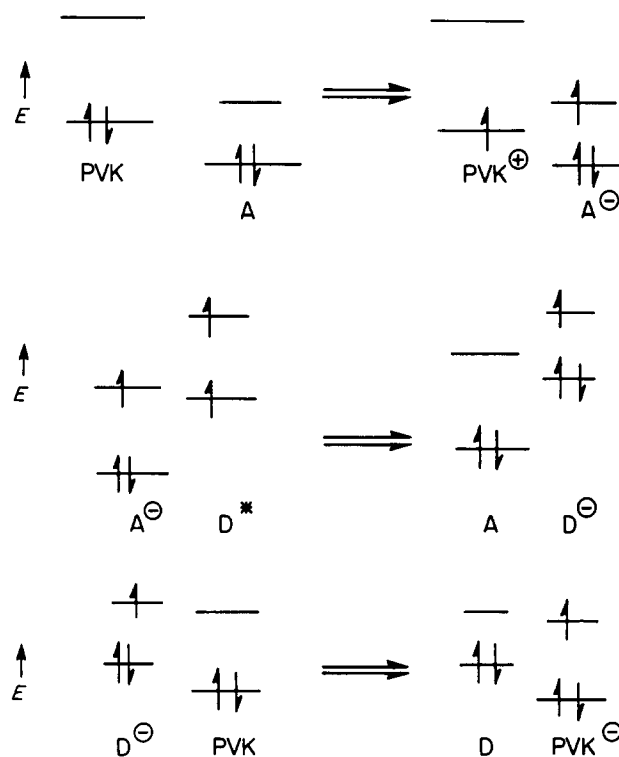


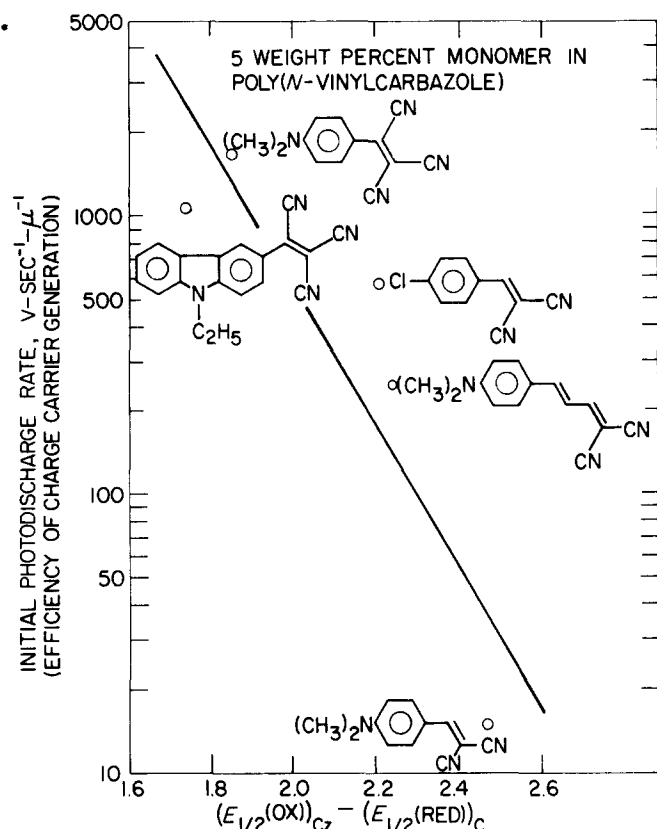
Figure 27 Mechanism of dye sensitization in the presence of an acceptor

transfer from donor (PVK, constant) to acceptor, whereby the rate, i.e., the photogeneration efficiency, is dependent in exponential fashion upon the electron affinity (ease of reduction) of the acceptor, that is, to the energy gap between the donor and acceptor (Figure 29).

This situation may not always result when one looks at the overall photoconduction process, as has been reported^{57,58}. This is due to opposing effects on photogeneration and hole transport⁵⁹; see discussion below, for example, for the effect of TNF on hole transfer in PVK. A complicating factor is partial incompatibility of the dopant and matrix leading to phase separation. Molecular shape effects have also been proposed to

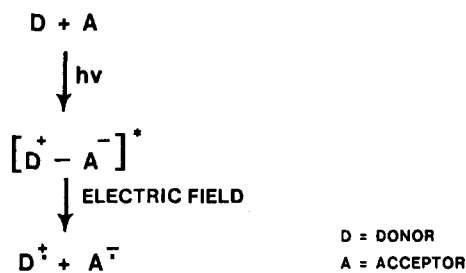
account for such observations⁵⁸. Another complication is increased dark conductivity of the charge transfer complexes^{57,59}.

Classical chemical modification. Sensitization of poly(vinylcarbazole) (15) has been achieved in the following manner. PVK films on a metal substrate were sulphonated on the surface. These sulphonated PVK (17) films were then cationically dyed with methylene blue to yield (18)⁶⁰. Methylene blue is known to sensitize PVK to the visible region of the spectrum^{51,52}. However, when applied as a surface layer the dye is readily abraded away. The chemical bonding of the dye to the PVK alleviates this problem. The photogeneration efficiency (per photon) was found to depend upon the extent of sulphonation/dyeing, being greatest for lightly sulphonated/dyed films⁶⁰. This methodology allows a measure of flexibility in that the dyeing step can be applied using any of a number of cationic dyes. This allows one to select the spectral range of interest.



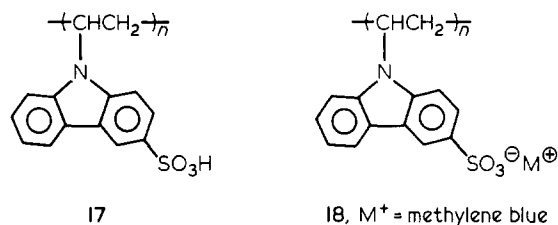
J. E. KRUDER, W.W. LIMBURG, J.M. POCHAN, D. WYCHICK, J. CHEM. SOC., PERKIN TRANS. II; 1643 (1977)

Figure 28 Photogeneration efficiency of solid solutions of acceptors in poly(*N*-vinylcarbazole) versus the difference between oxidation potential of *N*-ethylcarbazole and reduction potential of acceptor

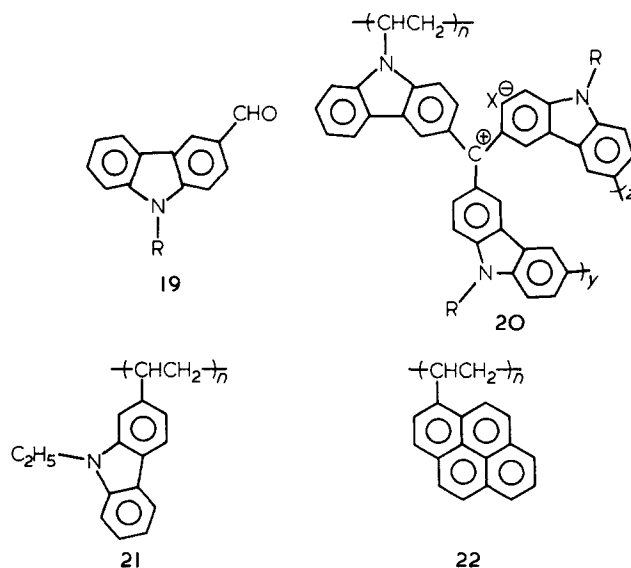


PHOTOGENERATION OF CHARGE CARRIERS FROM DONOR - ACCEPTOR SYSTEMS

Figure 29 Electron transfer model of sensitization of donor photoconductors by acceptors

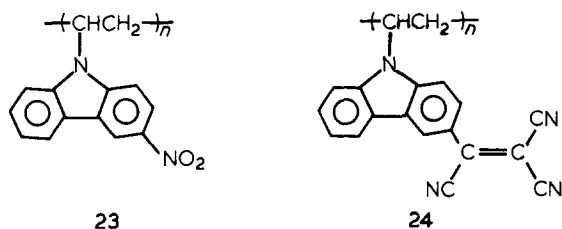


Another means of sensitization is the introduction of dye moieties into the bulk of the polymer by chemical modification. One example of this is the formation of dyes of the triarylmethane type by acid catalysed condensation of *N*-alkylcarbazole-3-aldehydes (19) with electron rich polymers⁶¹. For example, reaction of PVK with (19) is claimed to yield coloured polymer of structure (20). Other electron rich polymers cited were poly(vinylcarbazole) isomers such as poly(*N*-ethyl-2-vinylcarbazole) (21) as well as polyvinylpyrene (22) and the like. The resultant polymers absorb throughout the visible spectrum (to 750 nm) and the action spectrum reflects this in extended spectral range of photoconduction.

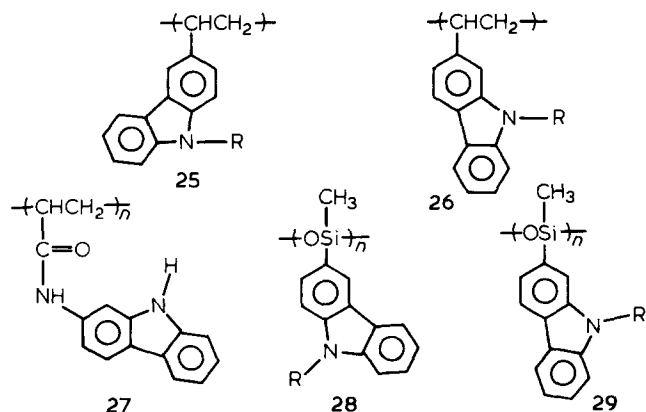


As noted above, the doping of hole transporting, donor polymers with electron acceptors results in extended spectral sensitivity as well as enhanced photo-generation efficiency. There are, however, problems associated with this approach. These problems stem from the tendency for the dopant molecules to aggregate in the solid state, leading to difficulty in achieving homogeneous dispersions and ultimately phase separation at high loadings. Chemical modification of the polymer matrix circumvents these problems.

PVK (15) has been the most studied system in this regard. Nitration of PVK leads to partial conversion to poly(*N*-vinyl-3-nitrocarbazole) (23)⁶². This polymer is yellow and hence its spectral response extends well into the visible. A 'charge-transfer' interaction between the nitrocarbazole and carbazole moieties of the resultant copolymer is credited with bringing about the enhanced photoconductivity⁶² relative to PVK itself via increased photogeneration of charge carriers.



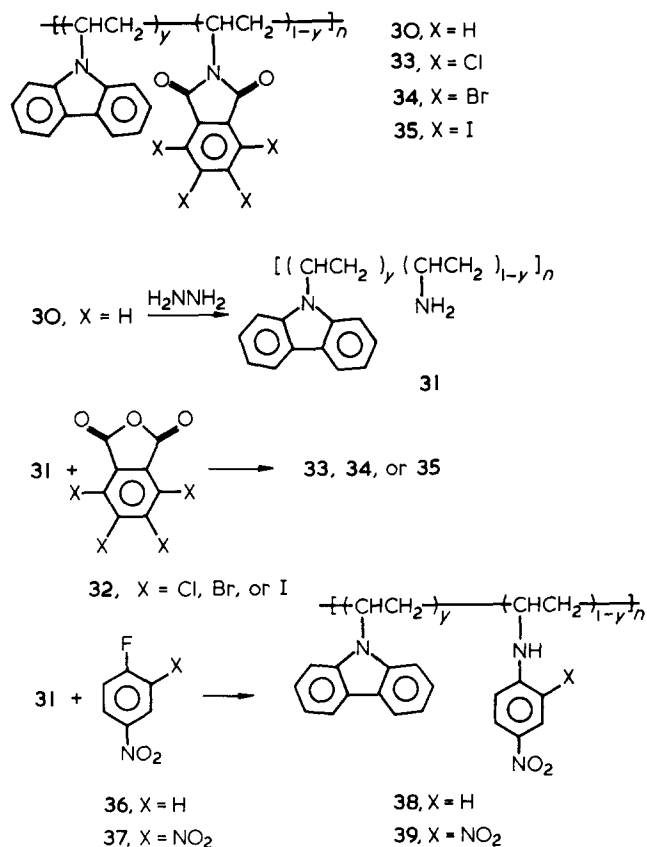
Reaction of PVK (15) with tetracyanoethylene in dimethylformamide leads to the formation of 3-tricyanovinylcarbazole moieties (24)⁶³. Two effects on photogeneration are again observed: (1) increased spectral response out into the visible range (~620 nm) and (2) enhanced photogeneration efficiency⁶³. The process can be controlled to afford random copolymers having various proportions of the tricyanovinylated functionality (24) up to ~50%. The photogeneration efficiency increases with the proportion of 24. Application of this technique to other hole transporting polymers such as 25-29 is also reported to yield the corresponding tricyanovinyl derivatives⁶⁴. Thus, this technique appears to be of general applicability for improving the spectral response and charge carrier photogeneration efficiency of hole transporting systems. Moreover, due to the radical quenching ability of such acceptor structures⁶⁵, these polymers could not be prepared by direct polymerization techniques. This emphasizes an advantage of the chemical modification approach, namely the ability to prepare otherwise inaccessible polymers.



Copolymers of *N*-vinylcarbazole and acceptors have been studied to achieve similar ends as by chemical modification. One such system is the copolymer 30 with *N*-vinylphthalimide. This particular system has been chemically modified to yield useful derivative systems⁶⁶. Treatment of 30 with hydrazine yields poly(*N*-vinylcarbazole-co-vinylamine) (31). Preparation of such an amino polymer is possible only by chemical modification. Compound (31) then affords the opportunity to manipulate significantly the spectral sensitivity and charge photogeneration efficiency by carrying out chemical reactions on the amino group. Two distinct reactions were studied toward these ends. First, 31 was reacted with a series of tetrahalophthalic anhydrides (32) to yield the tetrahalophthalimide polymers (33-35), which are derivatives of 30⁶⁶. Second, reaction of 31 with *p*-nitrofluorobenzene (36) and 2,4-dinitrofluorobenzene (37) yielded the copolymers poly(*N*-vinylcarbazole-co-*N*-vinyl-4-nitroaniline) (38) and poly(*N*-vinylcarbazole-co-*N*-vinyl-2,4-dinitroaniline) (39)⁶⁶.

The hydrazinolysis reaction of 30 to 31 is quantitative⁶⁶. Conversions are not given for the reaction of 31 to form 33-35, but presumably these are nearly quantitative. In general $y=0.5$ to 0.99, which yields a wide range of compositions. However, in 30 it was found that $y \sim 0.75$ was optimal in terms of charge carrier photogeneration efficiency.

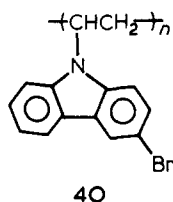
Conversion of 30 to derivatives 33-35 achieves the goal of extended spectral range by moving the absorption tail further into the visible. However, the initial photocurrent, taken as a measure of the charge carrier photogeneration efficiency is less for 33-35 than for the parent 30. This situation also holds for derivatives 38 and 39, which show enhanced spectral range, but diminished photogeneration efficiencies. The lower photogeneration efficiencies have been attributed to confor-



mational problems^{66,67}. In fact, the efficiencies for series 30, 33–35 are in the order H>Cl>Br>I. This is consistent with increasing size of X.

A plot of initial photocurrents *versus* the covalent radii of the substituents is nearly linear, supporting such an argument, in spite of the fact that the electron affinity undoubtedly increases for the series H, Cl, Br, I⁶⁷. In contrast, however, the expected higher electron affinity of the dinitroaryl group of 39 relative to the nitroaryl function of 38 overcomes the greater steric bulk in 39 to cause enhanced initial photocurrent in 39 relative to 38. In fact, 39 is very similar to PVK (15) in this respect⁶⁶. Thus, as might be expected, in polymers whose active chromophores are close to the backbone, steric interplay can sometimes lead to situations in which the conformational requirements for effective 'charge transfer' complexation are not met, in spite of favourable energetic relationship between the donor and acceptor.

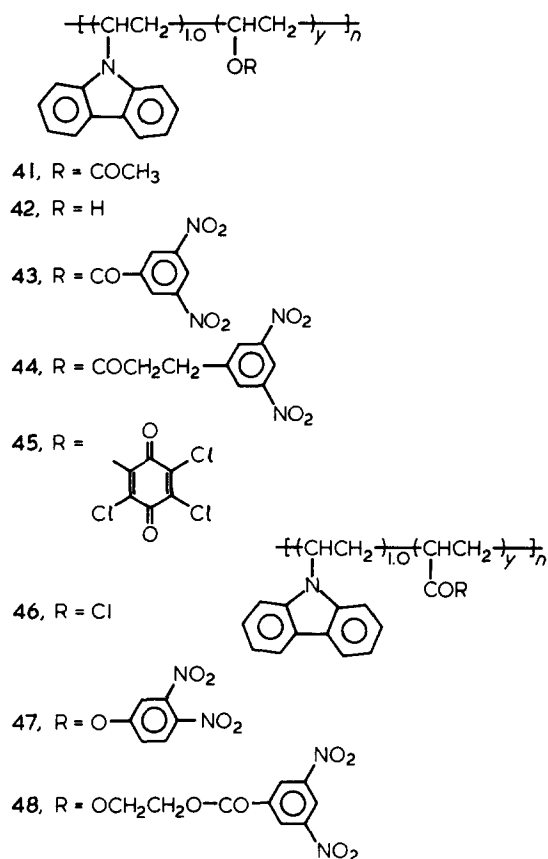
In a detailed study of brominated PVK (40) utilizing carrier photogeneration measurements coupled with X-ray diffraction results this conformational problem has been clearly identified⁶⁸. The photogeneration efficiency of the brominated polymer was shown to be a factor of two or more lower than that of PVK itself over a range of applied electric fields. The X-ray structure of 40 differs from that of PVK and this difference has been attributed to steric effects of the bromo substituent. The decreased photogeneration efficiency of 40 is thus linked to this conformational complication. This work is in conflict with earlier reports of enhanced photoconductivity in 40^{69,70}.



Another interesting series of experiments, designed to improve photogeneration efficiency, involves reactions of *N*-vinylcarbazole copolymers of vinyl acetate or acryloyl chloride⁷¹. Reaction of copolymer 41 with base yielded the vinyl alcohol copolymer 42. Subsequent reaction of 42 with 3,5-dinitrobenzoyl chloride afforded the benzoate 43. Photogeneration efficiencies were not measured, but 43 containing 40–55% of the dinitrobenzoyl moiety (i.e., $y=0.67$ to 1.22) discharged as rapidly as PVK doped with 10% by weight chloranil. Copolymer 44, in which the dinitrobenzoyl group is attenuated to some extent by the ether-type oxygen to which it is bonded shows no photodischarge for $0 < y < 0.15$. Reaction of 42 with chloranil led to copolymer 45. This copolymer with $y=0.20$ showed improved photodischarge relative to PVK itself, but was not as rapid as PVK doped with chloranil.

The acryloyl chloride copolymer 46 was reacted with 3,4-dinitrophenol to afford the copolymer 47⁷¹. 47 could not be prepared directly by free radical polymerization, presumably due to the stability of the radical derived from the dinitrophenyl acrylate. The discharge rate of 47, $y=0.25$ was slow, again indicative of low photogeneration efficiency. This was again attributed to the presence of the ether oxygen on the dinitrophenyl ring. In an attempt to test this idea, copolymer 48 was

synthesized from 46 and the appropriate alcohol. 48, $y=0.11$ shows a photodischarge rate comparable to that achieved with chloranil doped PVK, but lower than that of 43. This is to be expected since in 48 the acceptor group is removed from the polymer backbone and hence from the carbazole group. Moreover, the acceptor group of 48 has considerable conformational flexibility, which can detrimentally affect charge transfer interaction with the carbazole donor.



Interestingly it now appears that most of the photogeneration of charge carriers in PVK itself arises because of 'impurities' on the surface⁷². Such impurities are likely the result of oxidation and are therefore acceptors. Results on carefully purified PVK indicate a lower photogeneration efficiency⁷³. Use of X-rays to cause excitation in the bulk of the PVK sample results in much lower photogeneration efficiencies than does ultraviolet radiation⁷⁴. More detailed studies also establish the clear intervention of 'surface states' in the photogeneration process. Thus, in some cases adventitious chemical modification of polymers also leads to improved properties.

Chemical modification to alter transport properties

The features of transport that have been addressed by chemical modification of polymers are (1) the majority carriers (holes or electrons) and (2) the rate of transport (carrier mobility). Hole transport is defined as a process in which cationic species are involved. This is schematically shown in Figure 30. The bottom part of the Figure shows a radical cation formed near the anode of the applied electric field. By a series of electron transfers the positive charge migrates to the cathode where it is neutralized. Electron transport involves anions. As shown in Figure 31 a series of electron transfers moves a

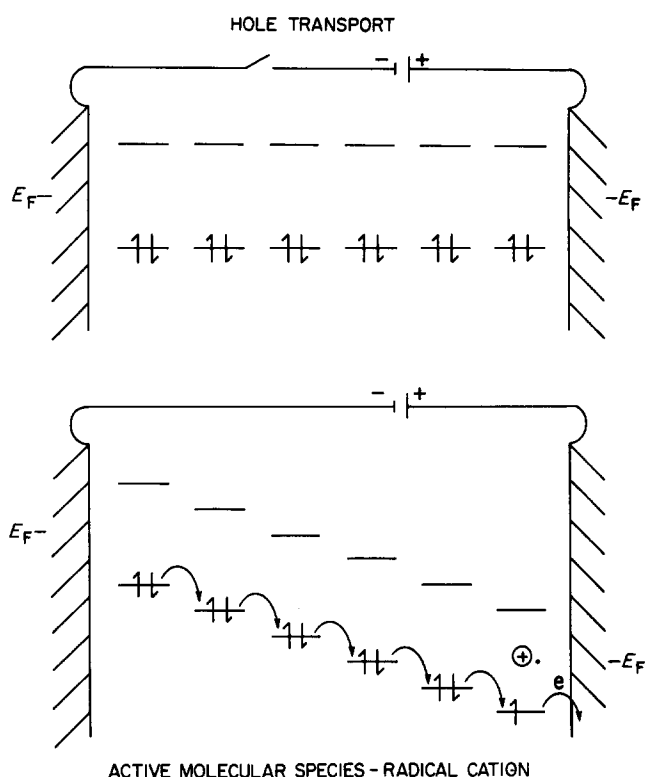


Figure 30 Schematic description of a hole transport system. The upper panel shows the energy levels of the HOMO's and LUMO's in the absence of an applied electric field. The bottom panel depicts the energy levels in an applied field and the migration of the positive charge by means of a series of electron transfer steps between cation radicals

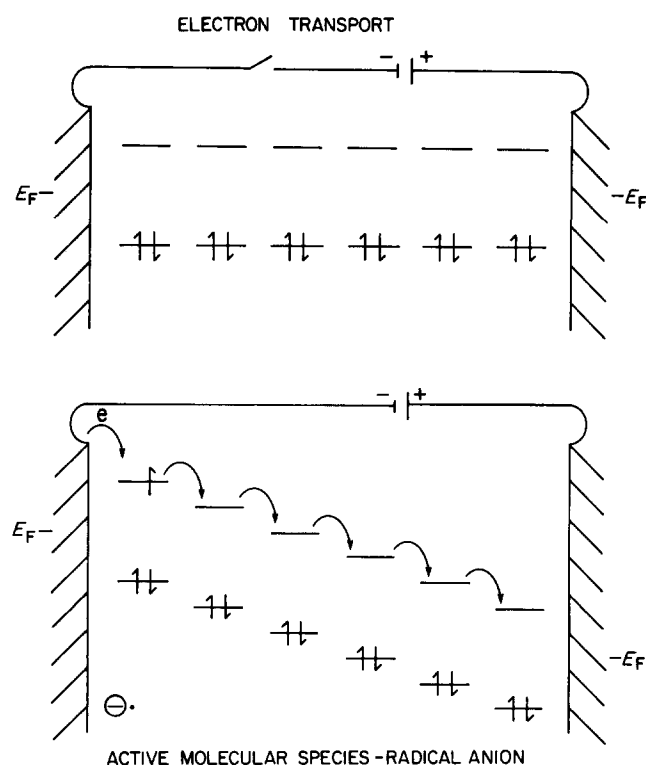


Figure 31 Schematic representation of an electron transport system. The upper panel shows the energy levels of the HOMO's and LUMO's in the absence of an applied electric field. The bottom panel depicts the energy levels in an applied field and the migration of the negative charge via a series of electron transfer steps between anion radicals

negative charge from the cathode to the anode where it is neutralized. The sign of the majority carriers can thus be controlled by consideration of ionization potentials and electron affinities, low values of the former being desirable for hole transport and high values of the latter for electron transport. The rate of transport (carrier mobility) is related to the concentration of the active transport species and the barrier to electron transfer (orbital overlap, etc.). Mechanical property improvements in the polymeric transport matrix are also an important objective. As in the above section, two methods have been applied: (1) addition of dopants to polymers and (2) actual modification of the macromolecular structure. In the former category we will only be concerned with cases in which the polymeric matrix plays an active role and the dopant causes a change in electronic structure by means of electron transfer, complexation, etc. Use of inert polymers as binders for active monomeric transport species^{50,75} will not be discussed.

Addition of 'small' molecules to polymers. This technique has been widely applied because of its apparent simplicity. The driving force for this work has been to provide electron transporting systems, rather than to enhance the mobility of hole transport. The reason for this is that addition of donors to hole transporting polymer matrices leads to diminished hole mobility due to trapping of the positive charges by the dopant donor molecules at low concentrations⁷⁶. At high concentrations low ionization potential dopants become the active hole transport states and the polymer matrix becomes the site of trapping of positive charges⁷⁷.

The addition of monomeric acceptors to PVK to bring about charge transport via anionic states (electron transport) has been well studied^{78,79}. The electron mobility of TNF doped PVK is shown in Figure 32. Also shown is data for TNF in an inactive polymeric matrix⁷⁵. As can be seen, the curves are identical, meaning that the PVK does not participate in the transport process.

For hole transport (conduction via cationic states), as shown in Figure 33, the TNF acts not only as a diluent to the active matrix, but also removes some of the carbazole units from participation in the transport process via charge transfer complexation⁸⁰. This is in contrast to the electron transport in which both free and complexed TNF are active⁷⁸. Once again these findings probably reveal the sensitivity of hole transport in PVK to conformational factors that interfere with intramolecular overlap of carbazole orbitals.

In summary, addition of donors to hole transporting polymers leads to either a decrease in carrier mobility or no effect. Addition of strong acceptors results in enhanced electron mobility at the expense of hole mobility, but the polymer matrix does not play an active role.

Classical chemical modification. Chemical modification of polymers has been employed extensively to alter transport characteristics. As noted in the introduction to this section, literature which discusses photoconductivity without explicit reference to either charge carrier generation or charge transport will also be summarized here.

Polyacenaphthylene (49) has been nitrated to varying extents, from 8-41%⁸¹, presumably yielding the nitroderivative 50. The parent polymer 49 is only slightly

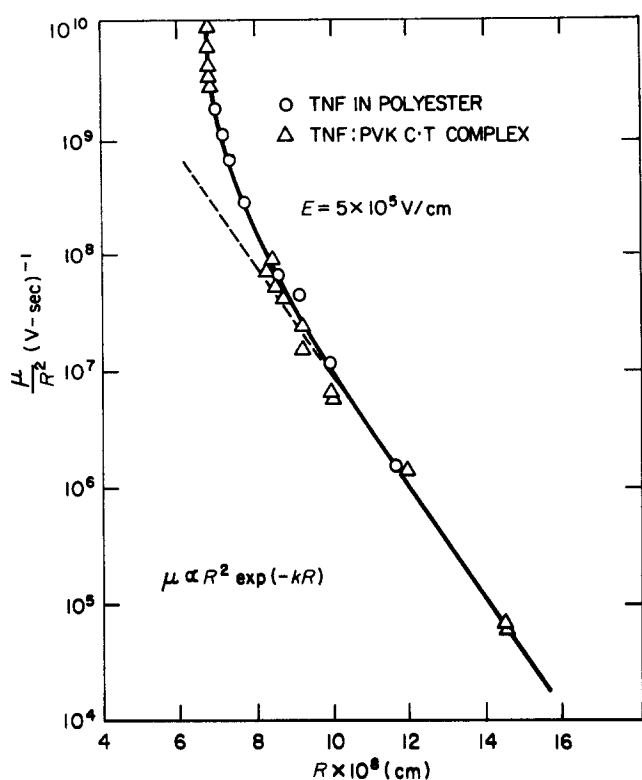
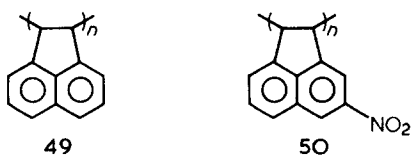
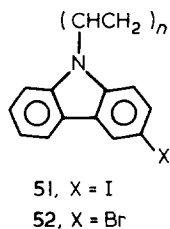


Figure 32 Electron mobility normalized to square of separation distance versus separation distance of 2,4,7-trinitrofluorenone dispersed in polyvinylcarbazole and polyester matrices

photoconductive, reaching its maximum current after 200 s of constant illumination. The partially nitrated polymers (**50**) reach much higher current levels (100×) but reach a maximum current more slowly (1000–1500 s). The authors argue that the nitrated acenaphthene moiety acts as an electron trap, hence the slow rise⁸¹. The increase in photoconduction is attributed to the formation of a charge transfer complex between nitrated and nonnitrated acenaphthene chromophores, but no evidence is given to support this view.

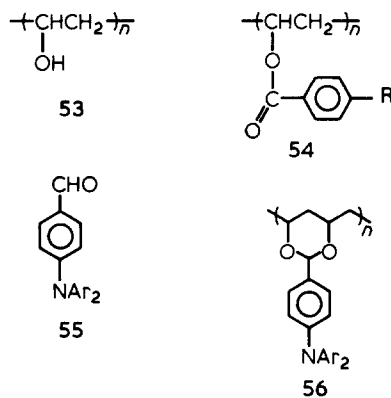


Poly(vinylcarbazole) (**15**) has been chemically modified. Complete iodination and bromination of PVK to **51** and **52**, respectively, have been claimed to yield photoconductive polymers^{69,70,82}.



A number of photoconductive polymers has been prepared by chemical modification of readily available

polymers with a view toward retention of desirable mechanical and solubility features, while fostering good transport characteristics. One example of such a common polymer is poly(vinyl alcohol) (**53**). Reaction of **53** with aromatic acid chlorides yields **54**, which is claimed to be photoconductive in cases where $R = NAr_2$ ⁸³. Reaction of **53** with an aldehyde containing a triarylamine function (**55**), followed by esterification of residual hydroxyl groups yields a copolymer of **53** and **56** in varying proportions. The copolymers are also photoconductive⁸³.



Formation of acetals of poly(vinyl alcohol) and poly(vinyl acetate) copolymers from aldehyde derivatives of pyrene and carbazole also leads to photoconductive compositions⁸⁴. For example, reaction of copolymer **57** with 1-pyrenecarboxaldehyde leads to copolymer **58**. Other pyrenealdehyde derivatives were also made in this manner. Reaction of **57** and *N*-ethylcarbazole-3-carboxaldehyde yielded copolymer **59**. These polymers were tested for hole transport properties

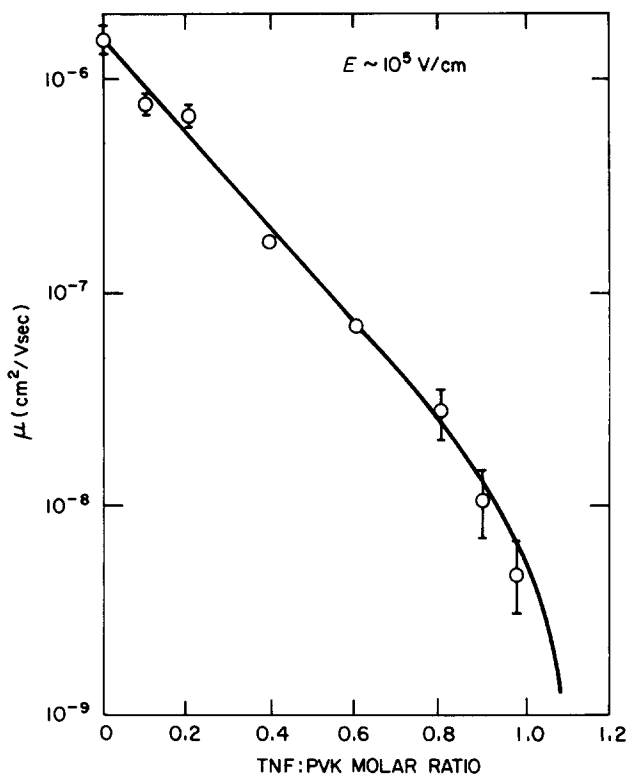
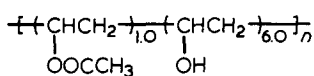
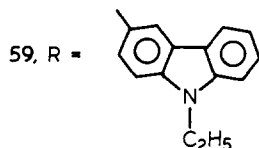
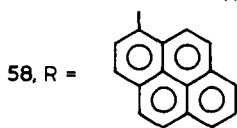
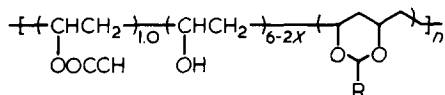


Figure 33 Hole mobility as a function of composition of PVK/TNF

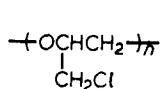
by use of a selenium photogenerator layer. Relative to PVK or polyvinylpyrene these polymers have improved mechanical properties.



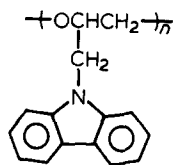
57



Polyepichlorohydrin (60) has been subjected to nucleophilic attack by carbazyl anion to yield polymer 61. This polymer possesses hole transport properties equivalent to PVK, while retaining the desirable mechanical properties of the epoxy family of polymers⁸⁵. In similar fashion, nucleophilic attack of the carbazyl anion upon poly(vinylbenzyl chloride) (62) yielded the benzylcarbazole polymer 63⁸⁶.

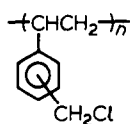


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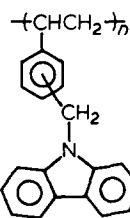


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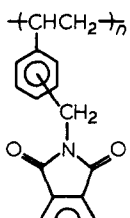
It was also possible to prepare similarly by means of the phthalimide anion a copolymer of 62 containing 85 mole % of units of structure 64⁸⁶. Unfortunately, it was not possible to prepare a 1:1 copolymer of 63 and 64 by sequential reaction due to a photochemical reaction of the intermediate polymer⁸⁷. Compound 63 by itself did not transport holes⁸⁸; this can be attributed to the high degree of conformational freedom of the carbazole moieties and their distance from the polymer backbone, which result in poor intrachain overlap of carbazole moieties.



62

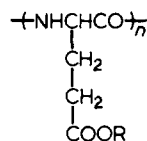


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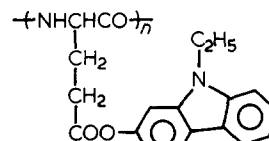


64

Transesterification of poly(γ -alkyl-L-glutamates) (65) with alcohols containing carbazole, naphthalene and anthracene moieties is claimed to afford photoconductive polyglutamates with α -helical structure⁸⁹. 66 is an example of the type of molecular structure formed.

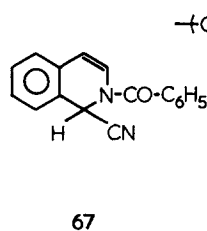


65 (R = CH₃, C₂H₃ - etc)

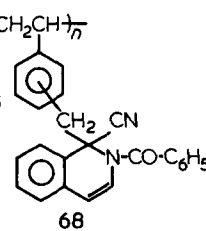


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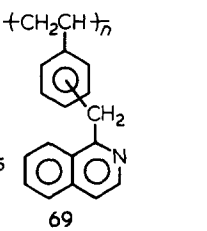
The difficulty in polymerization of monomers containing many fused aromatic rings has been mentioned above. This factor has provided impetus for some of the chemical modifications described above. It also was the driving force behind the modification of poly(vinylbenzyl chloride) (62) and derivatives by Reissert compounds such as 67, or its quinoline analogue. The basic concept involved the utilization of an azaaromatic polycyclic system and its nitrogen functionality to generate the Reissert compound, which as its anion could serve as a nucleophilic reagent for attack on suitable polymeric substrates. Following coupling to the polymer the polycyclic system's full aromaticity could be restored. These concepts are demonstrated by reaction of 62 and 67 to yield 68, which upon basic hydrolysis yields the rearomatized isoquinoline polymer 69⁹⁰. Similarly, the polymeric aldehydes 70⁹¹ and 71⁹² derived from 62 react with the Reissert compound 67 to yield the polymeric isoquinoline ester derivatives 72 and 73⁹². Quinoline Reissert compounds have also been examined and are found to be less reactive toward these polymeric electrophiles⁹⁴. The aldehyde polymer 71 has been condensed with 3-amino-N-ethylcarbazole to afford the polymeric carbazole anil 74⁹⁵. The isoquinoline polymers 69, 72 and 73 are inactive matrices for hole transport⁸⁸. Likewise, the anil polymer 74 is inactive.



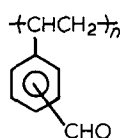
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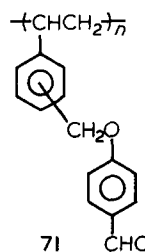
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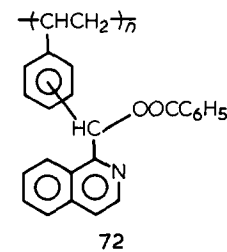
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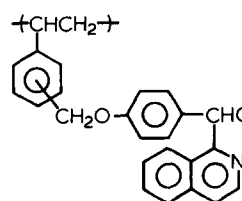
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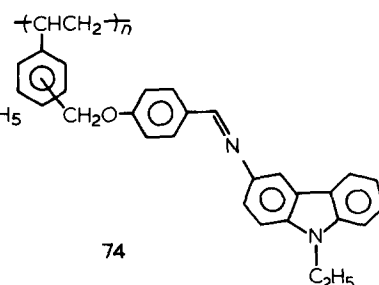
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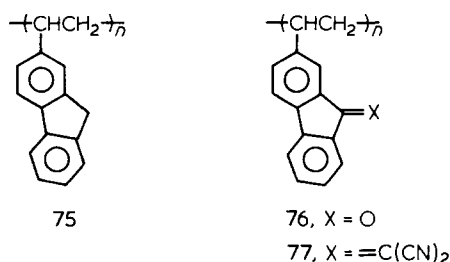
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These results corroborate the studies cited earlier in that they indicate a lack of overlap of the pendant aromatic chromophores when they are removed from the polymer backbone by more than one or two intervening atoms.

There have been attempts to prepare electron transporting polymers by chemical modification. These attempts were occasioned by the difficulty in synthesizing polymers containing strong electron accepting functionality. In order to synthesize such systems, poly(2-vinylfluorene) (**75**) was oxidized to poly(2-vinylfluorenone) (**76**), though only 90% conversion could be accomplished⁹⁶. The desired polymer **76** was in this instance able to be prepared by polymerization of the vinylfluorenone monomer. The polymer showed very low electron mobility⁷³. Reaction of **76** with malononitrile led to incorporation of units **77** into the polymer; however, above ~50% conversion solubility was lost⁹⁶. These solubility problems precluded the evaluation of the electron transporting characteristics of the polymer⁷³.



Conclusions

Photoconductivity and its component processes, charge generation and charge transport, can be controlled by chemical modification of polymers.

(i) The spectral range associated with the charge photogeneration process can be controlled by (a) addition of dyes or acceptor molecules, and (b) surface or bulk attachment of dyes or acceptor functionalities onto the polymer.

(ii) The charge transport process can be influenced in terms of the sign of the majority carriers and the rate of transport. Addition of small molecular dopants can control the sign of the charge carriers, independent of the polymer matrix. Introduction of functionalities with low ionization potential, such as carbazole, triarylamine, pyrene, by chemical reaction of functional polymers is successful in generating hole (cationic) transporting systems. To date no useful electron (anionic) transporting systems have been prepared in this manner.

(iii) Chemical modification also is useful in improving the mechanical properties, particularly, solubility, film formation, flexibility and impact resistance, of photoconductive polymer systems.

CONDUCTIVE POLYMERS

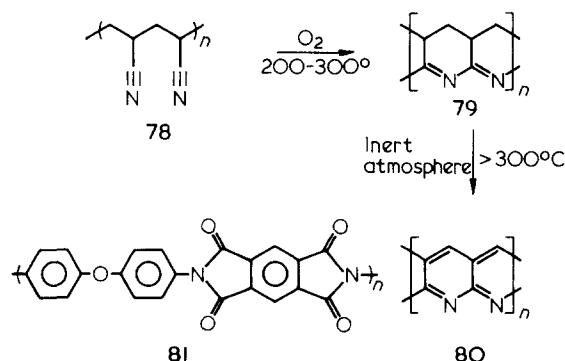
Interest in electrically conductive polymers stems from the potential for combining in one material the advantageous properties of polymers and the electrical properties of semiconductors and/or metals. The advantageous properties of polymers are their mechanical properties (flexibility, stretchability, impact resistance, etc.), their ease and low cost of preparation, especially compared to

semiconductors and metals and the ease and low cost of their fabrication, again in comparison to semiconductors and metals. An especially attractive possibility is the ability to vary the conductivity of a polymer at will by chemical modification. This, for example, could allow the generation of a range of electrical behaviour from the insulator to the semiconductor to the metallic region. The ability to carry out such chemical manipulations in an areawise pattern on thin polymer films could revolutionize the electrical/electronic industry.

The quest has been a fitful one dating back many years. Chemical modification of polymers has played and continues to play a central role in these efforts. The aims are to increase the conductivity of an insulating polymer in a controlled manner. Basically there are two directions these efforts have taken: (1) pyrolytic modification of polymers and (2) non-pyrolytic chemical transformations. These two avenues will be addressed separately. In each case the discussion will be confined to processes leading to polymers exhibiting conductivities in excess of 10^{-10} (ohm cm)⁻¹.

Pyrolytic modification of polymers

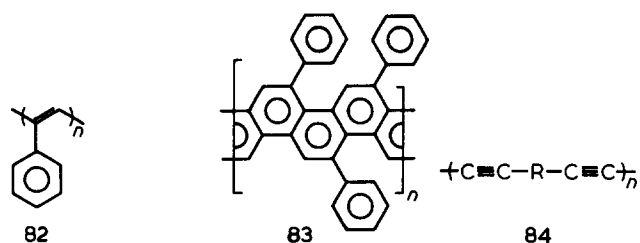
Polymer pyrolysis is one of the oldest ways of generating conductive materials. In general, the product polymers have not been well characterized in terms of molecular structure. One system which has been well studied is poly(acrylonitrile) (**78**). Pyrolysis takes place in three stages. The first stage is achieved by heating at 200°–300°C in the presence of oxygen⁹⁷. This stage results in closure of six membered rings via formation of conjugated imino functionality (**79**)^{98,99}. The second stage process at >300°C in an inert atmosphere results in dehydrogenation of the backbone, leading to a fully conjugated ladder polymer structure (**80**). Formation of extended planar graphitic structures is believed to occur at temperatures above 600°C by loss of NH₃ or HCN^{98,99}. The conductivity can be controlled by the temperature of pyrolysis. In the 400°–500°C range conductivities (σ) ranging from 10^{-10} up to 10^{-3} (ohm cm)⁻¹ can be achieved. By carrying out stage 3 in the presence of AlCl₃ at 900°C a conductivity of 20 (ohm cm)⁻¹ has been reported for the resultant 'black Orlon'⁹⁸.



Poly(*N,N'*-*p,p'*-oxydiphenylene)pyromellitimide (Dupont Kapton[®]) (**81**) has also been well studied. Its vacuum pyrolysis proceeds in three stages^{100,101}. Stage one occurs at ~600°C and results in loss of CO and intramolecular cyclization to small aromatic systems.

The conductivity remains in the insulator range. Stage 2 takes place at $\sim 700^\circ\text{C}$ and results in formation of larger aromatic structures having conductivities of $\sim 10^{-7}$ (ohm cm) $^{-1}$ or greater. Stage 3 at $\sim 800^\circ\text{C}$ forms more extended network aromatic (graphitic) structures of high conductivity, ~ 20 (ohm cm) $^{-1}$. Electron spin resonance spectroscopy demonstrates the evolution of free radical sites during the pyrolysis^{101,102}. Moreover, the line-width decreases at higher temperatures, indicating a higher degree of delocalization¹⁰². Interaction of these free radicals with acceptors can lead to formation of 'holes' (positive ions) via electron loss from the polymer. Donor interaction with the free radicals can convert them to 'electrons' (negative ions). These charged centres then may be the active species in the conductive process. This is a generally applicable model and more will be said regarding these free radical sites in a succeeding section.

Pyrolysis of a number of other polymers yields materials with conductivities in excess of 10^{-10} (ohm cm) $^{-1}$. These are listed in Table 1.



Pope has classified pyrolysis of organic polymers into component reactions depending upon temperature¹¹².

Stage 1 ($< 350^\circ\text{C}$): Loss of volatile adsorbed species.

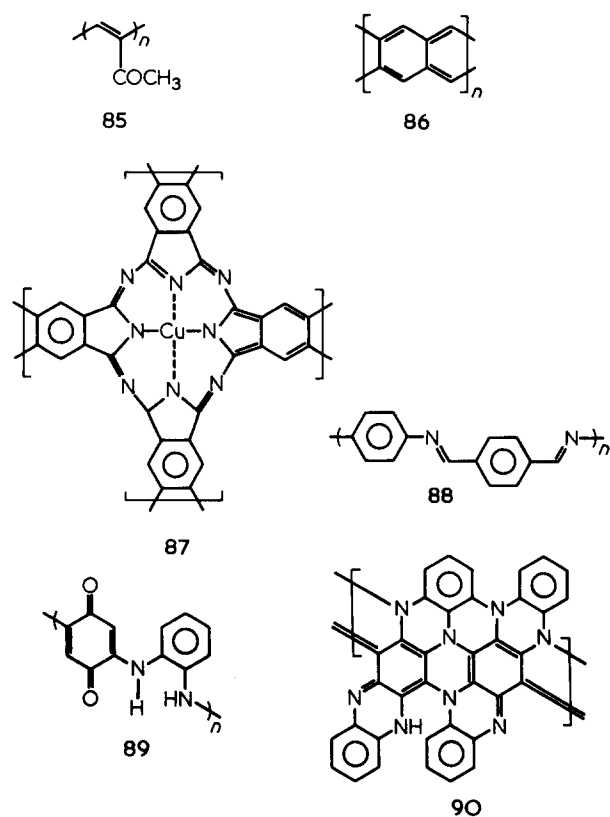
Stage 2 (400°C – 600°C): Single C–C bonds, C–Cl, C–I, C–Br, C–O bonds broken with formation of condensed aromatics and free radicals.

Stage 3 ($> 600^\circ\text{C}$): Loss of H_2 from aliphatic portions, yielding larger condensed aromatic plates with fewer free radical sites.

This scheme is consistent with X-ray¹¹³, infrared^{112,114} and e.s.r.¹¹⁵ measurements on a variety of polymeric substrates. Thus, most polymers when pyrolysed give electrically conductive materials, the only variables being the precise temperatures and the yields.

Non-pyrolytic chemical modification

In this section once again a distinction will be made with regard to chemical modification in the classical sense of changing the molecular structure and doping or the addition of molecules whose function is to alter the polymer by charge transfer interaction.



Classical molecular modification. The objective of most polymer modifications with regard to conductive polymers has been the generation of conjugated polyene structures. A number of avenues have been explored toward this goal. Dehydrohalogenation of poly(vinyl halides) (91) to polyenes has been well studied. As expected elimination of HI is faster than that of HBr which in turn is more facile than that of HCl¹¹⁵. A number of bases have proven effective for poly(vinyl chloride) (91a), including alkoxides¹¹⁷, phenoxides¹¹⁸, amines¹¹⁹, sodium hydroxide¹²⁰ and metal amides¹²¹. As calculated on a statistical basis by Flory¹²² only 86% of the chlorine atoms can be eliminated¹²³. This leaves saturated carbon atoms in the backbone (92, X=Cl). Thermal dehydrohalogenation is presumably not subject to this restriction because it is autocatalytic. The autocatalysis arises from the greater lability of the allylic chlorine atoms as double bonds form. Thus, the polyene chain can propagate regularly down the polymer backbone¹²⁴. Hydrohalic acids can catalyse the thermal process¹²⁵.

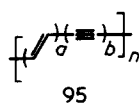
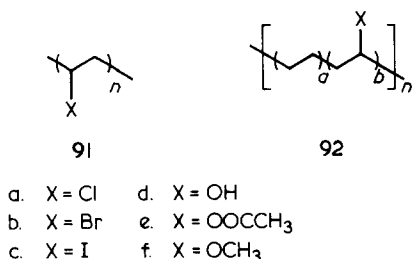
Dehydrochlorination of other chlorinated polymers^{126,127} such as poly(vinylidene chlorofluoride) (93)¹²⁸ can also be affected. Poly(vinylidene chloride)

Table 1 Conductive polymers formed by pyrolysis of polymers

Starting polymer	Pyrolysis conditions	Proposed product	Conductivity (ohm cm) $^{-1}$	References
Poly(phenylacetylene) (82)	300°C – 700°C	83	$< 5 \times 10^{-2}$	100, 103
Polyynes (84)	200°C – 600°C	?	< 2	104–106
Poly(acetylacetylene) (85)	400°C – 870°C	86	$< 10^2$	107
Poly(copper phthalocyanine) (87)	300°C , 10^{-2} Torr	$-\text{CO}_2$, H_2O , N_2 , NH_3	0.14	108
Metal-containing ion exchange resins	700°C – 1200°C	—	< 100	109
Polymeric Schiff base (88)	500°C	?	6×10^{-2}	110
Polyaminoquinones (89)	350°C	90	10^{-7}	111

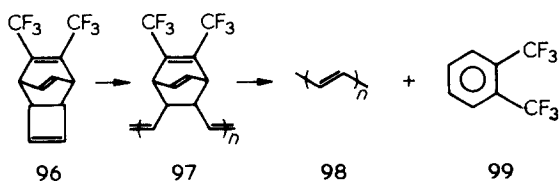
(94) thus yields a polyene containing polyene units (95)¹²⁰.

Polyenes can be formed by elimination of water from poly(vinyl alcohol) (91d)¹²⁹, by elimination of acetic acid from poly(vinyl acetate) (91e)¹²⁹ and by elimination of methanol from poly(methyl vinyl ether) (91f)¹²⁶, though these processes are less facile.

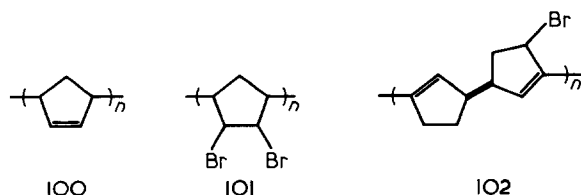


The conductivities of the polyenes prepared by the above processes are not generally reported and are, therefore, presumed to be low, due to limited conjugation lengths.

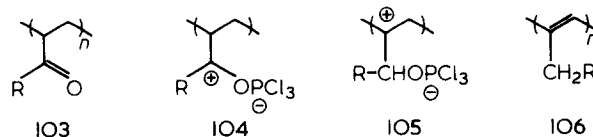
The synthesis of polyacetylene (98) by means of elimination of a larger fragment in a retro-Diels Alder type process was recently reported¹³⁰. Polymerization of 7,8-bis(trifluoromethyl)tricyclo[4,2,2,0^{2,5}]deca-3,7,9-triene (96) to polymer (97) was achieved by ring opening of the cyclobutene ring. Thermal treatment of (97) *in vacuo* led to elimination of 1,2-bis(trifluoromethyl)benzene (99) and polyacetylene (98). The electrical conductivity of the product upon doping is identical to that of polyacetylene films prepared directly and doped¹³⁰.



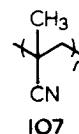
Another interesting polymer modification involves poly(cyclopentadiene) (100). Bromination of the polymer in solution causes a series of colour changes from yellow to yellow-green to blue-black as hydrogen bromide is evolved. The reaction is believed to involve the initial formation of the dibromide adduct (101), followed by spontaneous dehydrobromination to the conjugated polyene (102). The insoluble black polymer had a conductivity of 10⁻⁶ (ohm cm)⁻¹.



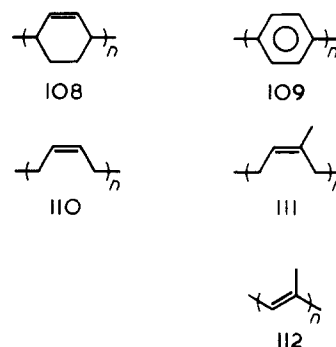
Reaction of films or solutions of poly(alkyl vinyl ketones) (103) with phosphoryl chloride, leads to polymer films with conductivities of 10⁻² to 10⁻⁵ (ohm cm)⁻¹.¹³² Production of a conjugated polyene backbone (106) was proposed, presumably occurring via (104) and (105).



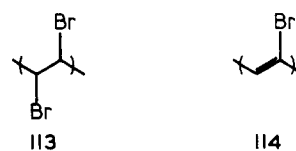
Polyacrylonitrile (78) can be converted to a ladder polymer with conjugated imino functionalities (79) by radiation treatment. Likewise, exposure of polymethacrylonitrile (107) to radiation causes polymerization of the cyano groups yielding a ladder polymer analogous to (79).



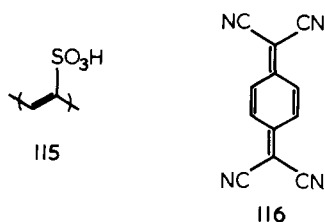
Another category of modifications of polymers is dehydrogenation, which generates conjugated polyene structures. These are, in general, limited to reactions in solution. For example, poly(1,3-cyclohexadiene) (108) yields poly-*p*-phenylene (109)¹³³. Polybutadiene (110), polyisoprene (111) and even polystyrene (8, X = H) have been converted to polymers containing units such as (98), (112) and (82)¹³⁴.



In a few instances polymers that are already polyenes have been chemically modified in order to alter chemical reactivity or physical properties. For example, films of polyacetylene (98) can be treated with bromine to yield the dibromo derivative (113), presumably. Then 113 can be dehydrobrominated to yield a polyene containing ~20% of the brominated unit (114)¹³⁵. This polymer is a semiconductor [10⁻⁵ (ohm cm)⁻¹] that can be doped to high conductivity¹³⁵.



A second example of chemical modification of a polyene is the treatment of polyacetylene (98) with SO₃, yielding what is believed to be the sulphonated derivative (115)¹³⁶. The conductivity was about 10⁻¹ (ohm cm)⁻¹.



'Doping' of polymers with 'small' molecules. The doping of semiconductors to achieve desired electronic properties is well known. The doping of polymers for the purpose of achieving good electrical conductivity has until recently been pursued less diligently. The earliest efforts seem to have taken place in the early 1960's. The charge transfer complexation of polymers was shown to result in enhanced conductivity. A number of the more conductive species are listed in Table 2. The enhanced conductivity may be attributed to the presence of cations and anions formed via electron transfer from the donor species to the acceptor. Transport of the charge may then occur via either cationic (holes) or anionic (electrons) states. Good charge transfer does not ensure high conductivity because of the influence of other factors on the transport process(es). In the case of the TCNQ (116) salts the ratio of TCNQ⁻ to TCNQ⁰ has been found to control the conductivity, which is relatively insensitive to the nature of the polymer, as can be seen from Table 2. This has the advantage of allowing one to fine tune other physical properties to some extent¹⁴⁴.

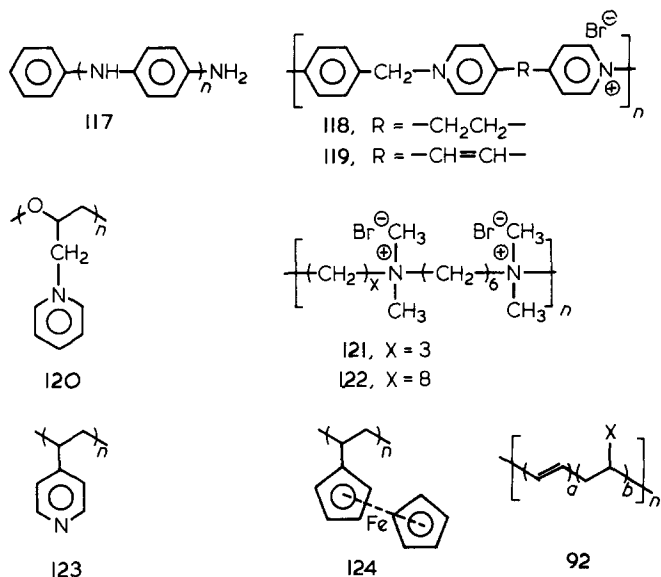


Table 2 Doping of non-conjugated polymers to achieve electrical conductivity

Polymer	Dopant	Conductivity (ohm cm) ⁻¹	Reference
117	I ₂	10 ⁻¹	137
118	TCNQ ^a	10 ⁻²	138
119	TCNQ ^a	10 ⁻²	138
120	TCNQ ^a	10 ⁻²	139
121	TCNQ ^a	10 ⁻³	140
122	TCNQ ^a	10 ⁻³	140
123	I ₂	10 ⁻⁴	141
15	I ₂	10 ⁻⁴	142
124	Chloronil	10 ⁻⁶	143

^a TCNQ = tetracyanoquinodimethane

From the early 1960's until the late 1970's very little work appeared in the literature on conducting polymers. In 1974 Shirakawa reported the polymerization of acetylene *in situ* to a free-standing insoluble, flexible film¹⁴⁵. Previously this had been available only as an insoluble infusible powder¹⁴⁶. The availability of polyacetylene (98) in film form sparked a rebirth in efforts to prepare conductive polymers and chemical modification by doping, has played a central role in this burgeoning area.

Doping of polyacetylene powder by a variety of dopants led to altered conductivity as was reported in 1968¹⁴⁷. The recent work on polyacetylene film has extended the number of dopants and the level of conductivity achievable¹⁴⁸. The results for a number of dopants are given in Table 3. Doping techniques include exposure of the films to the vapours of dopants such as I₂, H₂SO₄, AsF₅ and SbCl₅ or to solutions of dopants such as I₂, sodium naphthalide and NO₂SbF₆. Electrochemical oxidation of polyacetylene is a useful doping technique as well. In this manner the counter ion incorporated is the anion in the electrolyte solution, e.g., ClO₄⁻, I⁻, BF₄⁻. Metal-like conductivities are achievable starting from either the *cis* or *trans* isomers which have conductivities of ~10⁻⁹ and 10⁻⁵ (ohm cm)⁻¹, respectively. The effect of dopant level on conductivity is shown in Figure 34; a sharp increase is followed by a plateau region. Thus, conductivity can be controlled by controlling the dopant concentration.

Other polyenes can also be converted to a highly

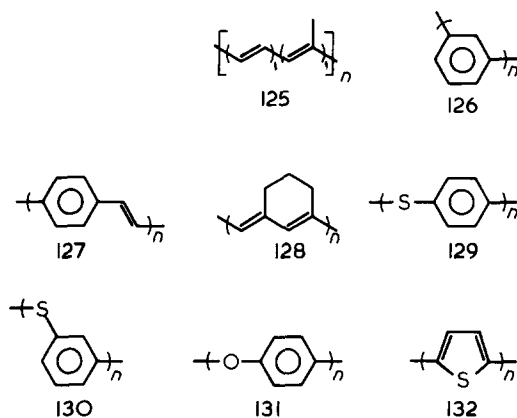


Table 3 Doping of polyacetylene films¹⁴⁸

Dopant	Equiv. per double bond	Conductivity ^a (ohm cm) ⁻¹ (25° C)
None	None	<i>cis</i> : 1.7 × 10 ⁻⁹ <i>trans</i> : 4.4 × 10 ⁻⁵
I	0.50 0.40	<i>cis</i> : 360 <i>trans</i> : 160
AsF ₅	0.28 0.20	<i>cis</i> : 560 <i>trans</i> : 400
IBr	0.30 0.24	<i>cis</i> : 400 <i>trans</i> : 120
Na	0.42 0.56	<i>cis</i> : 25 <i>trans</i> : 80

^a *Cis* and *trans* denote preponderant starting isomer and do not imply the geometry of the doped polymer

conductive state by treatment with appropriate acceptors and/or dopants. These results are summarized in Table 4.

The increased conductivity of some of these polymers can be rationalized in terms of the interactions of free radical sites with the dopant molecules, be they donors or acceptors. As mentioned in the section on pyrolytic polymers, interaction of free radicals with acceptors leads to cationic states and interactions with donors leads to anionic states, because of the fact that the free radical energy levels are higher in regard to donor levels associated with double bonds (Π states) and lower in energy compared with Π^* states. It is also possible that there is some involvement of Π or Π^* states.

The free radical sites in polyacetylene arise during thermal isomerization of the *cis* (**133**) (as formed at -78°C) to *trans* (**98**) isomer as conclusively shown by e.s.r.¹⁵⁸. They are therefore believed to be due to conformational barriers to coplanarity of the polyene. The free

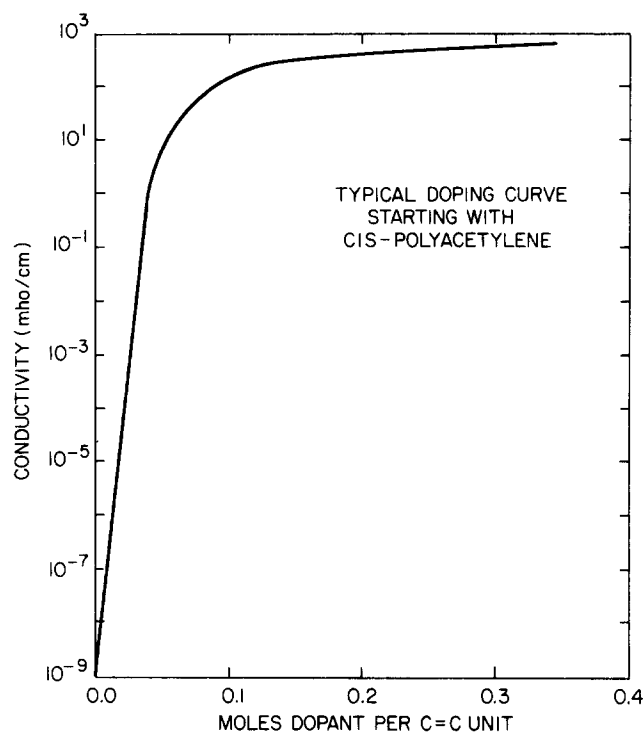


Figure 34 Typical conductivity versus dopant concentration curve starting with *cis*-polyacetylene

Table 4 Doping of other polyenes

Polyene	Dopant	Equiv. per double bond	Conductivity (ohm cm) ⁻¹ (25°C)	Reference
112	AsF ₅	—	10 ⁻³	149
125	AsF ₅	—	40	149
109	AsF ₅	0.13	500	150, 151
109	Na	0.19	3000	150, 151
126	AsF ₅	0.33	10 ⁻³	152
127	AsF ₅	0.19	3	153
128	I	0.5	0.1	154
129	AsF ₅	0.33	1	155
130	AsF ₅	0.33	10 ⁻²	155
131	AsF ₅	0.13	10 ⁻³	155
132	I	0.15	0.1	156
79	I	>0.05	70	157

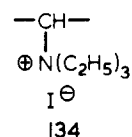
radicals have a g value indicative of a nearly free electron¹⁵⁸, however, so that they are delocalized. Doping thus results in a delocalized ion. Doping of the predominantly *cis* polymer is believed to cause conversion to the *trans* isomer. Doping of the *trans* polymer results in a drastic reduction in the number of free spins in the polyene¹⁵⁹.

In some cases the doping process is accompanied by more profound structural changes in the polyene backbone. For example, treatment of polyacetylene with increasing amounts of bromine results in a maximum in conductivity¹⁴⁸. This is attributed to addition of bromine to double bonds, thereby diminishing the degree of conjugation. While oxygen dopes polyacetylene, the doping is followed by incorporation of oxygen into the polymer and loss of conductivity¹⁶¹. At compositions up to $(\text{C}_2\text{H}_2\text{O}_{0.14})_n$, however, it is still possible to obtain high conductivity values by doping¹⁶². Since oxygen interacts with the free radical sites these results are a clear indication of their importance in the doping process.



The time and temperature of *cis-trans* isomerization strongly influence not only the conductivity of the resultant *trans*-polyacetylene (**98**), but also the ultimate poly(methylacetylene) (**112**) there are very few free spins poly(methylacetylene) (**113**) there are very few free spins and the conductivity upon doping reaches only 10^{-3} (ohm cm)⁻¹.¹⁴⁹ Only by incorporation of acetylene to form copolymers can the number of free spins in the undoped state and the conductivity upon doping be increased.

Treatment of iodine doped polyacetylene with triethylamine leads to incorporation of the amine, presumably as quaternary ammonium units (**134**)¹⁴⁸. The conductivity was $\sim 10^{-1}$ (ohm cm)⁻¹. Similar results were reported for an electrochemically oxidized polyacetylene with ClO_4^- as the counterion¹⁴⁸.



Poly(1,6-heptadiyne) (**128**) presents interesting contrasts to polyacetylene in its doping behaviour. Iodine doping results in a maximum in conductivity as a function of time at room temperature (Figure 35)¹⁶³. At -78°C the conductivity increases smoothly¹⁶³. E.s.r. studies reveal that the number of spins increases upon exposure to iodine¹⁶³. These results are accommodated by formation and persistence of radical cations due to their non-degenerate nature. Shown in Figure 36, abstraction of an allylic hydrogen atom by I \cdot would lead to an increased number of free spins. Further, the HI formed could add to double bonds, thus shortening the conjugation lengths and decreasing the conductivity. Yet another reaction of the allylic radical is its rearrangement to **135**, which again is not conjugated along the polymer backbone. This latter process can be observed thermally with the undoped polymer¹⁶⁴. Interestingly, exposure of polyacetylene to iodine vapour for extended

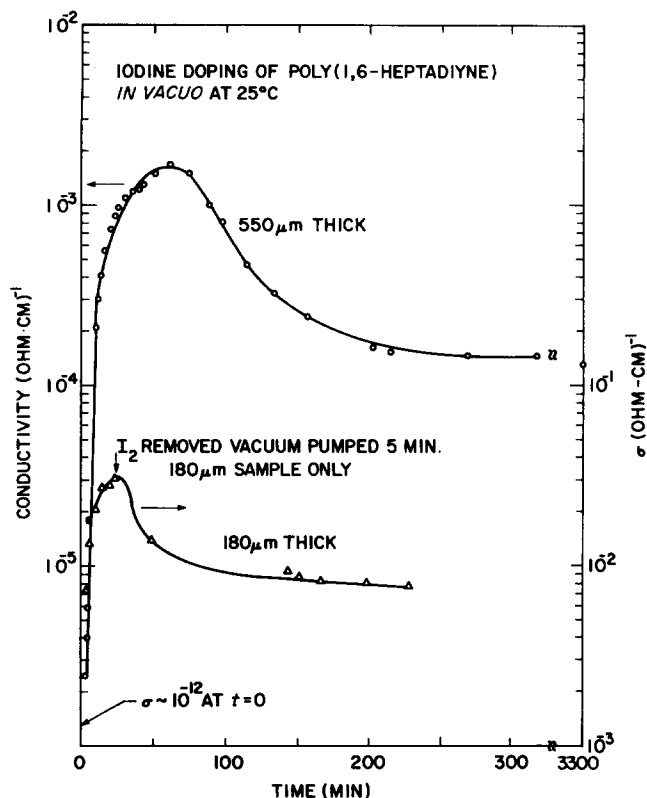


Figure 35 Conductive versus iodine exposure time for a film of poly(1,6-heptadiyne)

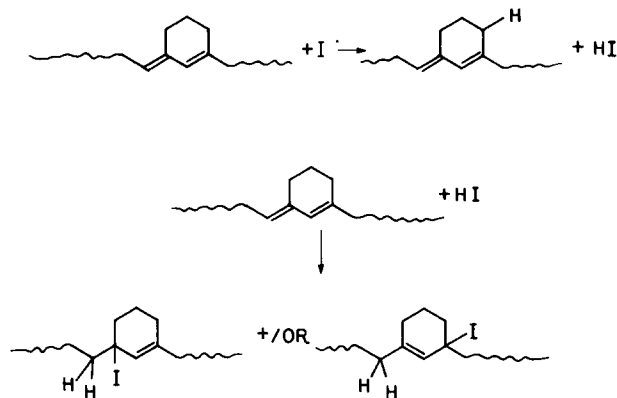
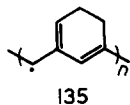


Figure 36 Rationalization of observed conductivity maximum and increased free radical population during iodine doping of poly(1,6-heptadiyne)

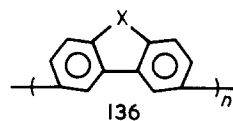
periods of time also results in a fall-off in conductivity¹⁶². It is tempting to ascribe this behaviour to a similar reaction sequence involving allylic hydrogen atoms located at crosslink sites in the polyacetylene.



Oxygen treatment of poly(1,6-heptadiyne) (128) results in an initial increase in conductivity of several orders of magnitude followed by loss of conductivity^{162,165}. The process is similar to that observed in polyacetylene, but is about an order of magnitude faster.

Detailed examination of the AsF₅ treatment of

poly(phenylene sulphide) (129) and poly(phenylene oxide) (131) indicates that the dopant, a powerful Friedel-Crafts catalyst, causes cyclization to structures such as (136)¹⁶⁶.



Research in this area of conductive polymers is currently aimed toward stable processable systems. At present none of the systems discussed is stable under ambient conditions both before and after doping. The molecular structural changes that have been found to accompany doping in some cases are most likely deleterious in the long term and will receive more attention.

Conclusions

Electrical conductivity of polymers can be achieved by chemical modification in the following ways:

(i) Pyrolysis of a range of polymer structures at temperatures up to 900°C yields polymers comprised of extended aromatic rings, approaching a graphitic structure. Conductivities up to 20 (ohm cm)⁻¹ are achieved.

(ii) A variety of elimination reactions can be employed to produce polyenes from a range of functional polymers. In general these processes produce polyenes with short conjugation lengths. In most cases conductivities are not reported; apparently only low conductivity levels (less than 10⁻⁸ (ohm cm)⁻¹) are achieved.

(iii) Treatment ('doping') of conjugated polyene or ionic polymers with monomeric acceptors or donors is a convenient method of controlling conductivity over the range ~10⁻¹⁰ to 10³ (ohm cm)⁻¹.

In many cases deleterious chemical modification occurs. Oxidation and chemical rearrangement to non-conjugated and/or less conductive structures are examples. Such processes require further study.

SUMMARY

In this review the chemical modification of polymers for alteration and control of three distinct electrical properties has been summarized. In the area of triboelectric charging chemical modification of polymers has been advantageously employed for the fundamental investigation of the structure-property relationships as well as for the synthesis of polymers useful in the xerographic copying process. In view of the ever-changing technology associated with copiers having greater speed, better resolution, etc., it is likely that chemical modification will continue to be employed for the generation of useful developer materials. Manipulation of photoconductive properties of polymeric systems either by addition of monomeric dopants or by macromolecular structural modification has played a central role in the development of a generation of organic photoconductors for replacement of selenium based systems, which suffer from the costs and poor mechanical properties associated with metals. Again, the desire to improve organic photoconductors in terms of speed, lifetime and mechanical properties seems certain to ensure the im-

portance of chemical modification of polymers in this area. Conducting polymers are now under intense scrutiny, following the rebirth of interest in them. Chemical modification, as concerns both the ability to control conductivity as well as to eliminate deleterious reactions with air, water or dopants, will continue apace in the quest for a practically useful system.

Clearly the electrical properties of polymers are subject to manipulation by chemical means. With the increasing energy costs of refinement and processing of metals, the use of polymers as replacement for metals is likely to continue. Discovery and commercial development of totally new families of polymers appears to be very unlikely. This then means that increasingly, old well known polymers will be asked to do new jobs. Chemical modification of polymers in this light will be of increasing importance in the chemist's arsenal of methodologies.

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