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Pi-Donor Intercalate Polymers: Synthesis, Charge-Transfer Interactions, and Applications

When low-ionization-potential organic donor molecules D *such as tetrathiafulvalene, ferrocene, or triarylpyrazolines are chemically attached to a polymer backbone, a number of interesting and potentially useful phenomena are observed in films of the resulting polymers. For example, chemical oxidation, irradiation, or electrochemical treatment of these materials leads to a series of polymers, poly*$[D_x(D^+A^-)_{1-x}]$, *where* D *is the polymer-coupled organic molecule, x is the extent of oxidation, and* A^- *is the charge-compensating anion. Depending on the nature of the bound donor group, these polymers exhibit two kinds of electronic interactions between donor sites which are of charge-transfer origin. These phenomena are responsible for several important properties of this new class of materials that make them interesting as polymer-modified electrodes, as semiconducting polymers, and as high-resolution electron-beam (or x-ray) resists.*

Introduction

Although study of the electronic properties of organic solids has been of interest for more than 30 years [1], it has only been over the last decade that this truly interdisciplinary field has blossomed, with a diverse variety of organic materials currently being investigated [2] in laboratories around the world. Of central importance in the motivation for studying these novel solids has been the consideration that organic materials offered a degree of synthetic variability not found with more traditional materials, which could enable control over scientifically interesting or potentially useful properties by means of systematic structural modifications. The purpose of this article is to describe a relatively new class of organic solids, pi-donor polymers, which may offer a rather high degree of desirable synthetic variability. The preparation of these materials, their unusual electrochemical and conduction properties in thin-film form, and possible applications will be discussed. In addition, their properties will be compared and contrasted with related organic and inorganic solid state materials.

Background

• *Crystalline ion-radical salts*

Almost all known organic molecules exist naturally with their electronic spins paired. However, some organic species called pi donors [3], D (see Fig. 1 for structures), can transfer an electron in the presence of appropriate acceptor molecules such as tetracyanoquinodimethane (TCNQ) [4] or halogens, to form compounds which contain the oxidized, stable cation-radical D^+. In some cases, such as for the donor tetrathiafulvalene (TTF), the salts which result from this charge transfer crystallize in segregated stacks of the donor molecules, giving rise to high electrical conductivity and other interesting physical properties [5].

A large number of salts of TTF and other donors with various acceptors have been prepared, and it has been observed that the crystallization of these salts into this desirable mode of stacking is determined by the nature of the molecular constituents and that the resulting structures can only exist over very narrow composition ranges [6]. In practice, this has limited the ability to obtain structure-property data to alloys [7] composed of isostructural [8] donors, or to other organic materials [9] present as dopants in amounts not large enough to disrupt the stacking structure of the host lattice. Single crystals [10] of these materials, often unobtainable, are routinely required for physical measurements in order to avoid complications due to grain boundaries present in polycrystalline samples.

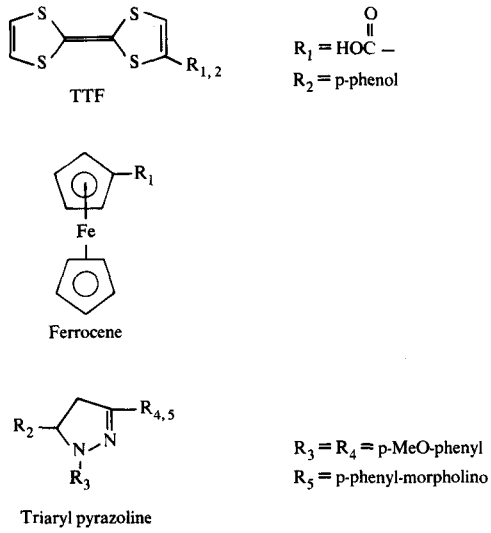
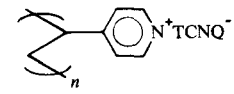


Figure 1 Molecular structure of monofunctionalized pi donors discussed in this paper. Names of unsubstituted compounds are given below the structures.

An alternate approach to the design of electronically interesting organic solids is the use of organic polymers with backbones that force the subunits into electronic contact with one another. One way of accomplishing this is with polymers in which the organic repeat units are covalently attached to one another to form the polymer backbone. Several examples of this kind of polymer with simple repeat units, *i.e.*, polyacetylene [11] and polypyrrole [12], are known, but attempts at synthesizing polymers of this kind with TTF or analogous donor repeat units forming the main chain have not been successful [13], largely because of the intractability (*i.e.*, insolubility) of the resulting materials.

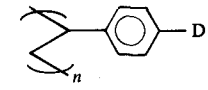
Another way to achieve interesting electronic effects in polymeric materials is to combine the favorable film-forming and mechanical properties of flexible, insulating polymer chains with the self-organizing behavior of organic donors. This takes advantage of the latter's potential for site-site interactions as cation-radicals. Such systems would be structurally amorphous but would have considerable synthetic degrees of freedom. It would clearly be desirable [14] to modify the electronic properties of the polymers without sacrificing mechanical properties; however, previous approaches have been only moderately successful in achieving these goals. For example, in the earliest work, $TCNQ^-$ anion radicals were ionically bound to a poly(vinyl pyridinium) backbone [15] [see Structure (I)] to form an acceptor polymer whose conductivity could be increased a millionfold by doping (20% by weight) with neutral TCNQ.



(I)

In another approach, it was shown [16] that electronically insulating polymers such as polycarbonates or polyesters could be made as conductive as 10^{-8} $(\Omega\text{-cm})^{-1}$ by molecularly dispersing mixtures of tri-p-tolylamine donor cation-salt and the neutral donor in the polymer film. In both these cases, "molecular doping" was successfully used to control and vary the conductivity of the polymer matrix. However, the generality of these approaches is limited by the solubility of the dopant in the host matrix, and (as in the TCNQ case just discussed) by the tendency of the unbound ions to crystallize at higher loadings. In addition, experimental phenomena involving contact with a liquid phase (see below) are necessarily precluded due to extraction of the dopant.

In contrast, our materials approach involves polymers in which the donor species D is chemically attached to a polystyrene chain [see Structure (II)] by a covalent



(II)

linkage. As opposed to the molecularly doped systems, the density of the bound donors in a film of such a polymer is determined by structural details such as molecular weight, copolymer composition, and chain stereochemistry. As might be expected, this enables considerably higher donor densities to be achieved than in the doping cases. In addition, problems due to solubility or migration of the donor species are avoided because the donors are physically anchored to the polymer chain.

Introduction of ion-radicals into the polymer matrix is accomplished by oxidation of the bound donor species. Typical pi-donor molecules can be oxidized by using chemical oxidants [17], photochemically [18], or electrochemically [19] and, as we shall see next, these methods can also be used to oxidize the chemically (covalently) anchored donors, both in solution and in solid-film form. Controlled oxidation of the polymers in thin-film form is particularly desirable for ease in studying the resulting solids and leads to a number of useful phenomena.

For introduction of the donor cation-radicals onto the polymeric donor [poly(D), Structure (II)], the range of possible compositions resulting from a thin-film oxidation process of the bound neutral donors can be represented as

$$\text{poly(D)} \xrightarrow{\text{oxidation}} \text{poly}(D^+A^-)_x(D)_{1-x}\,, \qquad (1)$$

Table 1 Experimental conditions for preparation of pi-donor polymers.

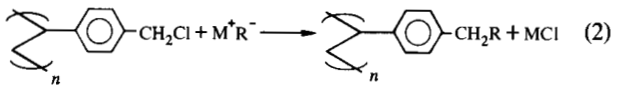
Monomer[a]	*Metal*[b]	*Experimental conditions*[c]		*Temp.* (°C)	*Polymer coverage*[e] (%)
		Solvent	*Reactant ratio*[d]		
TTF (R_1)	Cs	DMF	1.1	80	87
"	Cs	DMF	0.30	80	30
TTF (R_2)	K	THF	1.1	65	69
Ferrocene (R_1)	Cs	DMF	1.1	80	60
Triaryl pyrazoline (R_2, R_3 = 4)	K	THF	1.1	65	85
"	K	THF	0.55	65	51
Triaryl pyrazoline (R_2, R_3 = 5)	K	THF	1.1	65	65
"	K	THF	0.55	65	47

[a]For substituents in parentheses see Fig. 1.
[b]Cesium salt prepared from CsOH; potassium salt prepared from KH, by reaction with donor [34].
[c]Salt and poly(vinylbenzylchloride) stirred in solution at temperature indicated for 24 hours, followed by repeated precipitations into H_2O.
[d]Mole ratio of salt to polymer used.
[e]Percent reaction as determined by elemental analysis.

where x is the fraction of ionized donors, D is the polymer-coupled donor molecule, and A is a charge-compensating anion. In principle, the polymers designated in Eq. (1) should form a series of partially oxidized materials over the complete composition range $0 < x \leq 1$, from the neutral polymer ($x = 0$) to the fully oxidized ($x = 1$) species. Therefore, for stable polymer-bound cation radicals [20], it should be possible to designate x and A^- by appropriate choice and control of the oxidation procedure. This suggests that with physical properties dependent on the value of the composition parameter x and the chemical nature of A^-, structure-property relationships [21] can be examined by controlled variation of these parameters. External control over these variables (*i.e.*, with light or electrochemically) to allow (reversible) modification of properties makes materials of this kind relevant to technologically important applications such as information display [22], energy conversion [23] and storage [24], electrocatalysis [25], and lithography [26].

Synthesis of pi-donor polymers and preparation of films

The donor polymers were prepared by reacting alkali salts of the monofunctionalized pi donors [27] (Fig. 1) with a poly(vinylbenzylchloride) backbone; see Eq. (2). In all of the coupling reactions, yields were high (>60%), indicating that side reactions or site inaccessibility was not a serious problem.



(2)

The high reactivity allows copolymers (donors at lower than 100% coverage) to be prepared (see Table 1) and prevents polymer degradation or insolubilization by allowing the coupling reactions to proceed under very mild conditions. In the absence of these complications, an advantage of this preformed polymer reaction is that product polymer molecular weight for a given coverage can be explicitly determined by the molecular weight of the reactant poly(vinylbenzylchloride). We have confirmed this and also determined that the reactivity patterns of Table 1 are substantially unaffected by increasing the molecular weight of the starting polymer [28]. This is significant because recent attempts to synthesize TTF pendant polymers directly from vinyl derivatives of this donor have been unsuccessful due to problems of low molecular weight [29] or cross-link-induced insolubility [30] of the product polymers.

In contrast to this case, the polymers described here are stable and very soluble in typical organic solvents such as tetrahydrofuran (THF), dimethylformamide (DMF), methylene chloride (CH_2Cl_2), etc. This high solubility is useful in their purification and solution characterization. In addition, their high solubility allows films to be prepared using common spin-coating [31] procedures. In this technique, the polymer solution is placed on a substrate which can be rapidly spun, causing the solvent to evaporate and leaving the solid polymer film. Polymer film thickness can be readily varied by changing polymer solution concentration or spin rate. For the polymers discussed here, good-quality films could always be formed in thicknesses from ≈10 nm to several micrometers.

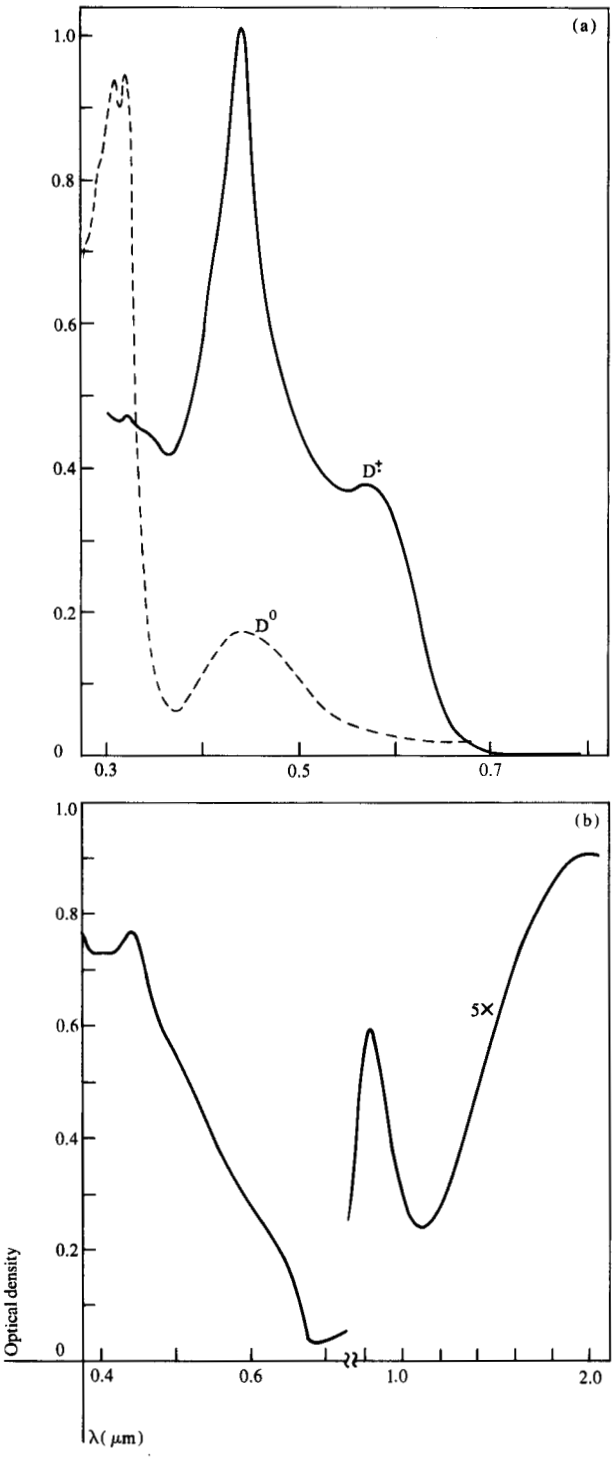


Figure 2 (a) Electronic spectra of partially oxidized (D^+) TTF (R_1) monomer (——) *vs.* the neutral (D^0) TTF monomer (---). (b) Electronic spectrum of the TTF (R_1) polymer. The absorptions from ≈0.75 to 2.0 μm have been enhanced by five.

Cooperative electronic interactions

The saturated framework of the polystyrene-based polymer systems precludes the possibility of all but weak electronic cooperative interactions along the basic polymer chains. This is confirmed in the ultraviolet spectra of the neutral donor polymers, which resemble those of unbound donors in dilute solution, as has been observed for other pendant polymers [32]. Nevertheless, under certain conditions electronic interactions between the pendant groups of these polymers can be very strong. Once these polymers were oxidized to the stable cation-radical state, we were able to identify two modes of site-site charge-transfer electronic interactions for the bound donor species which result in nontrivial physical phenomena for solutions and thin films. The electronic properties of dissolved polymers are discussed first; a subsequent section examines their properties in solid, thin-film form.

Table 2 Electrochemical properties of pi donors and related pi-donor polymers.

Monomer	I_p^a (eV)	$E_{1/2}^b$ (V *vs.* SCE)	*Polymer coverage* (%)	$E_{1/2}^c$ (V *vs.* SCE)	δ^d (mV)
TTF (R_1)	6.95	0.46	100	0.52	200
Ferrocene (R_1)	6.9	0.68	60	0.74	60
Triaryl pyrazoline (R_2, R_3 = 4)	—	0.54	85	0.60	100

[a]For unsubstituted donors by mass spectroscopy, see C. E. Klots, R. N. Compton, and V. F. Raaen, *J. Chem. Phys.* **60**, 1177 (1974).
[b]In CH_3CN solvent (0.1N TEAP).
[c]Polymers dissolved in DMF solvent (0.1N TEAP).
[d]Peak width at half height.

When dissolved, donor-functionalized polymers can be electrochemically oxidized (partially or fully) in solvents such as DMF or THF. Their electrochemical oxidation potentials are found to be very similar to those of the dissolved non-polymer-bound monomers (Table 2). This suggests that there are no major changes in donor ionization potential [33] due to their being bound to the polymer chain. However, on closer examination, TTF polymers are found to exhibit electronic effects not previously observed.

For the TTF polymer, we observed significantly broadened cyclic peak shapes [34] not seen for the other pendant polymeric donors or the TTF monomers in solution. In addition, the optical and infrared spectra for the oxidized polymers revealed further important differences. Whereas the oxidized [35] pyrazoline or ferrocene polymers showed spectra characteristic of the *unbound* donor cations, the partially oxidized TTF polymer showed new spectral absorptions at 2 μm and 0.8 μm which are not observed for the monomeric TTF cation (Fig. 2).

Drawing analogies from work on crystalline TTF salts in the solid state [36, 37], these absorptions can be assigned to the dication dimer D_2^{2+} (0.8 μm) and a mixed-valence aggregate $(D_2^+)_n$ with absorption at 2 μm. These assignments are also consistent with the results of a spectrophotometric titration experiment (Fig. 3), where the relative intensities of these two optical transitions are found to depend on the amount of oxidant added due to the differences in the stoichiometric dependence on TTF cation concentration for each type of absorbing aggregate.

Subsequent work on spin-coated thin films (to be discussed) has established [34, 38] that mixed-valence aggregate absorptions are observed only when the oxidation is performed under conditions where the polymer chains are relatively mobile (*i.e.*, in contact with a swelling solvent). This leads to a physical picture in the TTF polymers in which dimeric aggregates are always observed upon oxidation, but aggregation into more extended mixed-valence arrays requires pendant group and polymer backbone motion to allow proper orientation of the bound TTF species. Other consequences of significant internal motion in these polymer films are discussed in later sections of this paper.

The formation of ionic aggregates within a polymer phase can be expected to have important consequences for their optical, electrochemical, and electrical properties. The specific molecular properties which encourage aggregate formation in the TTF case but discourage it for the polymeric ferrocene and pyrazoline systems are not well understood at present. However, it may be that the natural tendency of donors such as TTF to self-stack as mixed-valence arrays in crystalline environments [36, 37] can also be expressed when bound in high concentration to a polymer backbone. If so, other carefully chosen pi donors could show the same phenomena.

Electrochemical intercalation

As just described, the pi-donor polymers can be oxidized in solution chemically or electrochemically to form stable cation-radical polymers. For convenience in studying these polymers, and for most applications, material in solid-film form rather than in solution is desirable. We have found that chemical reagents such as chlorine (Cl_2) or bromine (Br_2) can be used to oxidize solid films of these donor polymers; however, the results are generally unsatisfactory due to problems of reversibility and inhomogeneous donor-cation distributions. Stronger oxidants like arsenic pentafluoride (AsF_5) [39] are unacceptable because their higher oxidizing power produces the donor dication D^{2+} and because their corrosive nature makes these reagents experimentally difficult to handle.

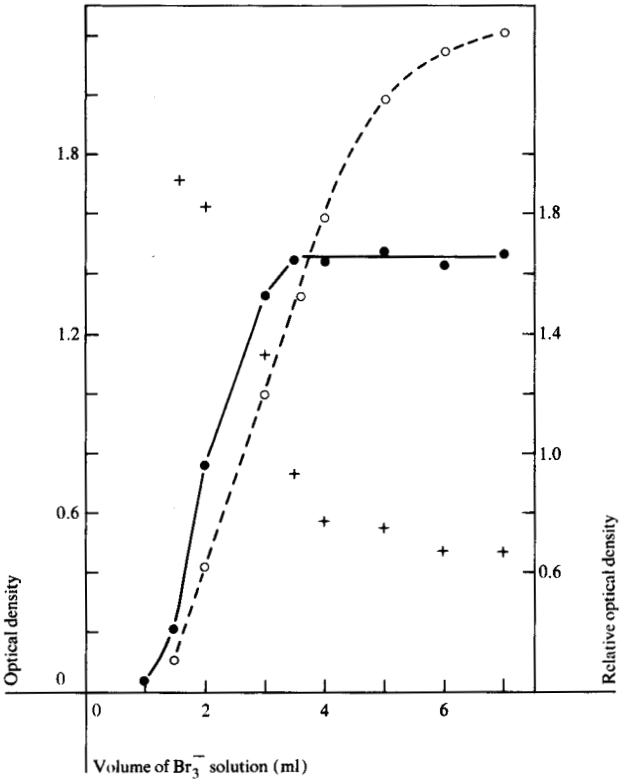


Figure 3 Effect of increasing the polymer oxidation level (given as the volume of a 5×10^{-3}M solution of Br_3^- added to the neutral TTF polymer solution) on the solution absorption at 0.8 μm (---) and 2.0 μm (——). A plot (+) of the relative absorptions (2 μm/0.8 μm) is also given.

The disadvantages of chemical oxidants can be overcome in electrochemical oxidation because the extent of oxidation and type of charge-compensating anion can be controlled by specifying the applied voltage and electrolyte and by measuring the amount of charge passed. Electrochemical oxidation has become a widely used technique for the preparation of controlled-stoichiometry [40, 41] crystalline TTF donor salts. However, when we began this work, it was not clear how useful this technique could be for performing controlled oxidations on polymer films thicker than a few monolayers due to expected problems of charge transport from/to an ostensibly immobile phase and the electrode.

Recently we discovered, however, that charge transport through thick polymer films is, in fact, possible. We found that films of the TTF polymers, when coated onto Pt electrodes and immersed in acetonitrile, a nonsolvent for the polymer, could be reversibly oxidized [42] electrochemically, yielding cyclic voltammograms which appear very similar to those for the polymer dissolved in solution

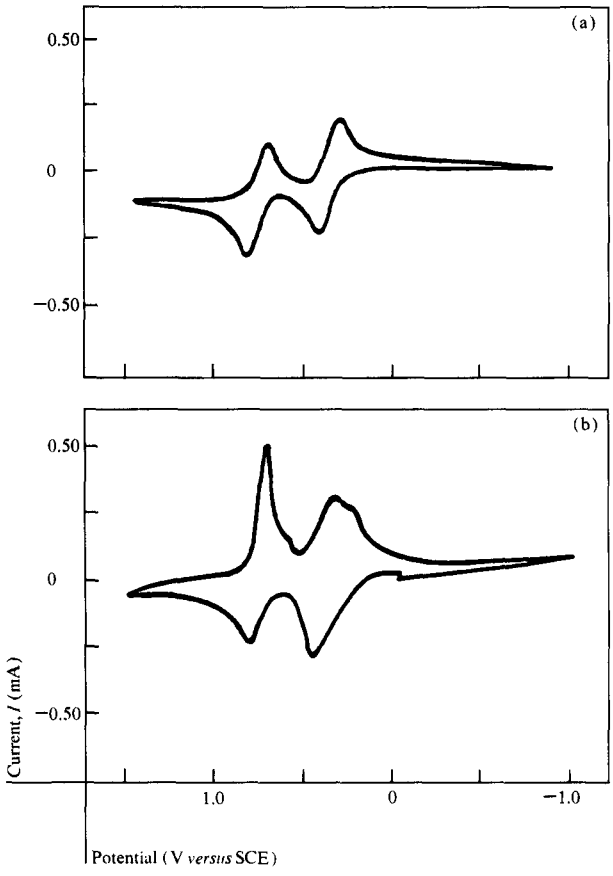


Figure 4 Comparison of the cyclic voltammograms in CH_3CN/0.1N TEAP (tetraethylammonium perchlorate) obtained for (a) a 10^{-3}M solution of TTF and (b) an 0.04-μm film of TTF (R_2) polymer. The potential is *vs.* a standard calomel electrode (SCE).

(Fig. 4). Although the bound TTF molecules are prevented from physically diffusing to the electrode in the solid polymer film, there exists efficient electronic "contact" between the TTF polymer films and the underlying Pt electrode. The data shown in Fig. 5 indicate a linear relationship between polymer film thickness and the amount of electrochemical charge passed. In conjunction with other data relating thickness to absolute numbers of TTF sites, these experiments showed that even in films as thick as 1 μm, all TTF sites could be reversibly oxidized.

Subsequent experiments have demonstrated the generality of this effect in other polymers. All donor polymers [43] in Table 1 can be oxidized over the complete range of available stoichiometries [$0 < x \leq 1$; see Eq. (1)]. The parameter x and the charge-compensating anion (A^- = ClO_4^-, PF_6^-, BF_4^-, etc.) are determined by the applied oxidation potential period and by the electrolyte. The efficiency of electronic contact between the bound donor and the metal electrode appears to be high and independent of the polymer coverage, type of donor [44], and method of film preparation [45]. Furthermore, the oxidized polymer compositions appear relatively stable in the solid state as observed from absorption spectra [22] and electron spin resonance [46] measurements.

The formation of the cationic polymer series poly-$[(D^+A^-)_x(D)_{1-x}]$ [see Eq. (1)] and the ability to completely oxidize it ($x = 1$) require the ability to create positively charged holes in the polymer bulk and to charge-compensate them through the intercalation of anions from the external solution phase. In contrast to the chemical oxidation process in which diffusion of an oxidant to a given site is followed by an electron-transfer reaction, electrochemical oxidation requires somewhat different kinds of transport processes. Specifically, electron transfer at a given potential occurs at the metal electrode-polymer interface to oxidize the closest polymer-bound donor forming a cation-radical. To be able to completely oxidize the polymer film, the hole generated in this way at that interface must diffuse into the polymer bulk, recreating neutral donor sites near the electrode which can be reoxidized. At the same time, anion diffusion into the polymer film from the external solution is required to maintain charge neutrality. The intercalation process is thermodynamically reversible and occurs without major structural reorganization, as can be seen from the symmetrical nature of the cyclic voltammetry waves [42–45]. In these aspects, it is similar to intercalation in numerous inorganic [47] solids. However, weaker electronic interactions in the polymer systems, as well as the fact that intercalation occurs between polymer chains rather than between crystal planes, are important differences between the polymeric and crystalline materials.

Information on the hole-transport process has been obtained from studies on TTF polymer films. In contrast to all other known polymer film donor systems [44–45], cyclic voltammetry of thin TTF polymer films shows evidence for significant broadening of the first oxidation wave (Fig. 6). Detailed examination [42] of the optical changes occurring as a function of applied potential (Fig. 7) showed that broadening was due to the growth of mixed-valence aggregates at potentials ($E_{1/2}$ = 0.23 V) lower than that required to oxidize the TTF molecule ($E_{1/2}$ = 0.34 V), confirming the results of solution studies (see previous discussion).

Mixed-valence aggregation usually leads to relatively highly conducting [36, 37] crystalline organic salts. With the TTF polymer, films which exhibit spectral evidence for these aggregates have dc conductivities [38] which are

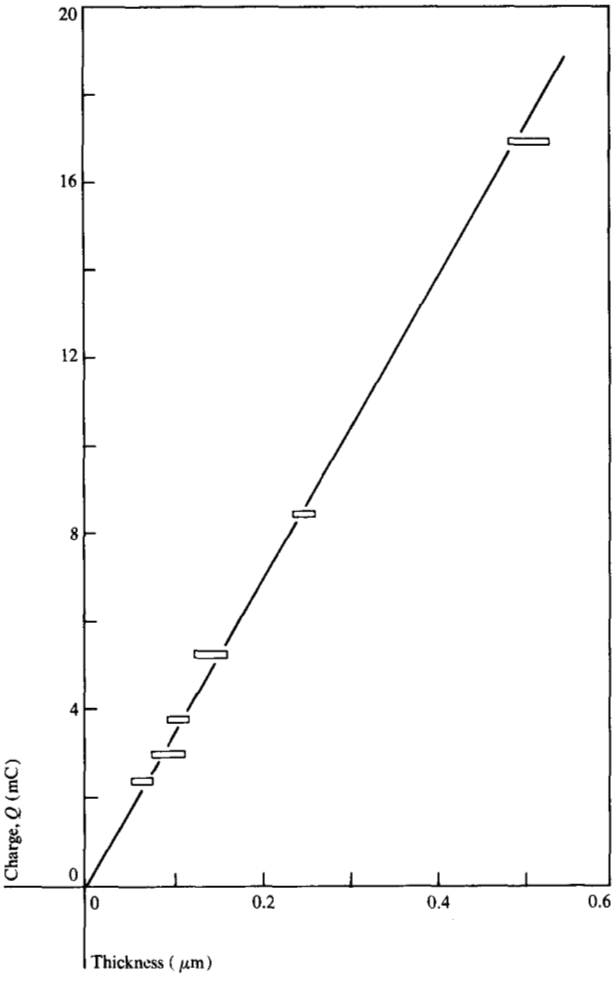


Figure 5 Charge injected at 0.65 V (*vs.* SCE) as a function of the thickness for films of the TTF (R_1, 30% coverage) polymer.

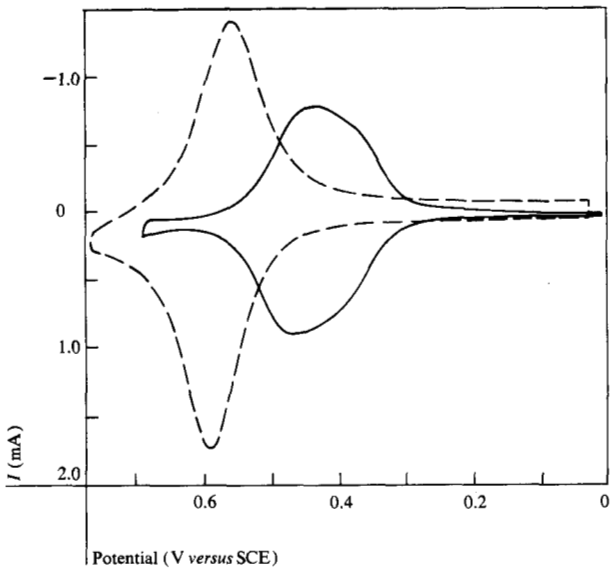


Figure 6 Cyclic voltammograms for 0.3-μm films of the pyrazoline (R_3, 51% coverage) polymer (---) and the TTF (R_1, 30% coverage) polymer (——); 0.1N TEAP, CH_3CN solvent. Sweep-rates are 50 (TTF) and 200 (pyrazoline) mV/s.

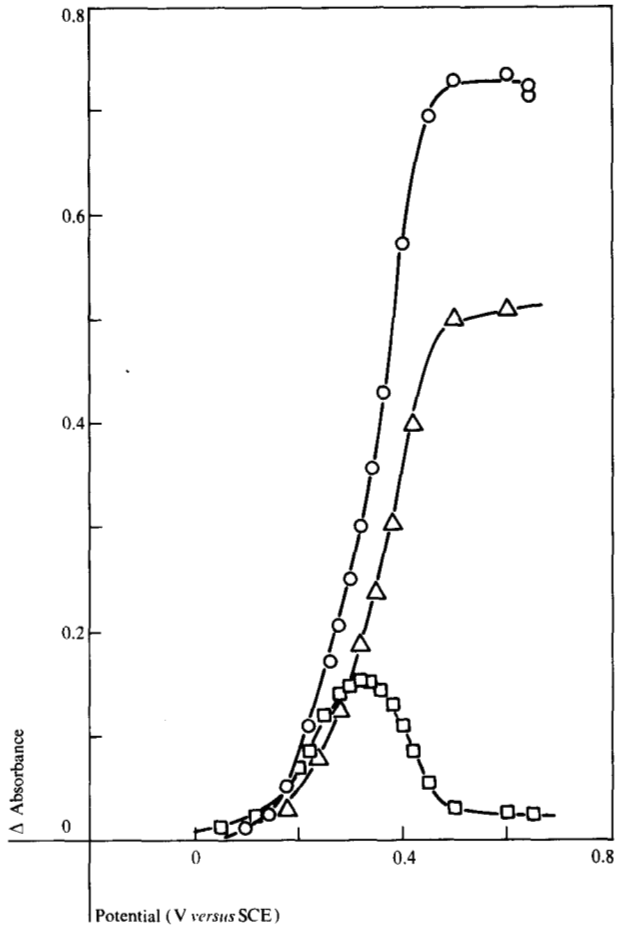


Figure 7 The change in absorbances of TTF polymer films as a function of the potential (V *vs.* SCE) at 1.805 μm (□, TTF_2^+), 0.820 μm (△, TTF_2^{2+}), and 0.393 μm (○, TTF^+).

at least six orders of magnitude higher than the neutral polymer films. However, the narrow voltage range for existence of aggregates (Fig. 8) and the significantly broader voltage range for TTF polymer film electroactivity (Fig. 4) clearly indicate that electrochemical intercalation does not require solid state electrical conductivity. This is consistent with the observation that most of the polymer electrochemistry investigated to date has involved materials which are poorly conducting at best.

Electrochemical charge transport

Bulk polymer film oxidation, which begins at the electrode-polymer film interface, appears to involve [27c, 42, 43] a phonon-assisted hopping process between localized states. This is a sufficiently general mechanism for (weak) site-site electronic interaction to be applicable to the different kinds of polymers which exhibit electro-

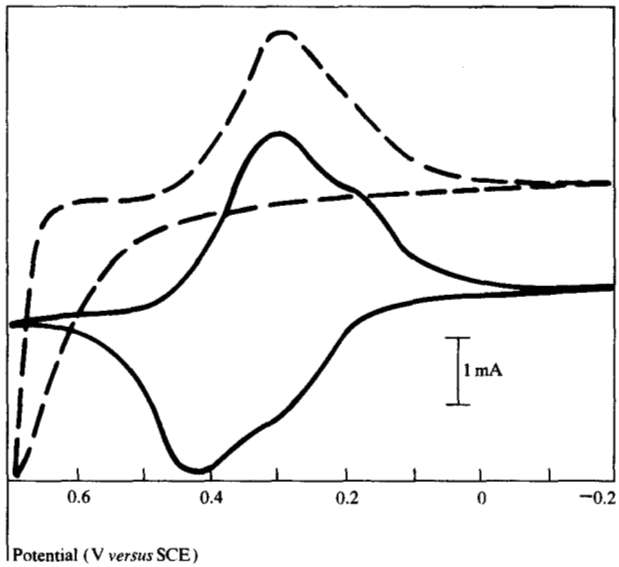


Figure 8 Cyclic voltammograms of an 0.5-μm TTF (R_2, 69% coverage) polymer film before (---) and after (——) doping so that the polymer density is reduced by 50%; 0.1N TEAP, CH_3CN, sweeprate of 100 mV/s.

chemical intercalation. Charge transport is known to occur in this way in some molecularly doped [32, 48] and covalently modified [49] photoconductive polymer systems. For dry films of the neutral TTF polymer, admittance measurements performed over wide frequency (10^{-3} to 10^{+6} Hz) and temperature (2.6 to 316 K) ranges indicate that electronic conduction here occurs [50] by classical hopping over barriers with a height distribution caused by a random spatial site distribution. The hopping conductivity mechanism probably also provides the basis for hole charge transport and allows electrochemical intercalation to proceed over the entire composition range, even for thick films.

Transition metal oxides such as WO_3 [51] or iridium oxide [52] are semiconductors which in thin-film form exhibit electrochemical intercalation reactions similar to those just described. Although their dc conductivities (when doped) are orders of magnitude higher than for the pi-donor intercalated cation-radical polymers, the transition times [53] for electrochemical charge injection in both these materials are comparable, around 40 mC/s. For WO_3 the rate-limiting step has been shown to be ion-transfer [51] at the film-electrolyte interface. Since electrical conduction in most of the inorganic systems is so high, ionic conduction might be expected to be the rate-limiting step.

The situation for the polymer films is more complex. For instance, it is likely that the intrinsically low electronic charge-carrier mobilities typically measured for (dry) organic films of this kind are substantially increased under the influence of absorbed solvent, the presence of which is known [54] to speed up the internal motion of pendant groups attached to polymer chains. However, rapid internal motion would also be expected to permit diffusion of ions into the amorphous polymer matrix. Thus, in the organic case, rates for electronic and ionic processes are related to the same structural factors. For some polymer systems, therefore, it may not be entirely clear which process is rate-limiting.

A variety of experimental data obtained on the pi-donor polymer films supports this physical picture. That there is substantial internal motion in the solvent-contacted polymer films is shown by the growth of mixed-valence aggregates [34, 42] and by the observation of electrochemically induced interchain dimerization [55] reactions. In addition, we have observed polymer film morphology changes [56] after electrochemical intercalation by means of mechanically determined film thickness profiles and microscopic examination of the polymer film surface.

Large variations in oxidation over-potential [43] were measured for the series of polymers (Table 1) as a function of changing the pendant donor, the percent functionalization, and the conditions of film preparation. Subsequently, we observed that this range of electrochemical behavior correlated very well with diffusion coefficients measured [56] for dyes diffusing out of the respective polymer films when these were put into contact with the electrochemical solvent. This connection between electrochemical kinetics and permeability was shown to be dependent on polymer free volume in the following manner. Artificially decreasing the density of a polymer, while keeping all other materials' variables constant, was found to dramatically change the kinetic behavior of a TTF polymer film. In Fig. 9 is shown the decreased over-potential and distortion of the cyclic voltammogram after (solid line) the TTF polymer film density was decreased [43, 56] by doping. Similar results were observed in going from high- to low-coverage polymer films. If electron transfer rates were being affected by the decreased density, the opposite results would be expected since according to the hopping model slower rates should result as the distance between localized sites increases.

These results on the TTF systems are consistent with charge-compensating anion migration as the rate-determining step in polymer film oxidation. Confirming evi-

dence [42, 43] for this interpretation was obtained from a study showing that the oxidation rate of the TTF films depends on the identity of the electrolyte anion and its concentration. Although the TTF polymers were the only ones showing mixed-valence absorption and electrical conductivity enhancement, they were among the slowest [22, 43] films studied in terms of electrochemical oxidation rates, thus reconfirming the lack of correspondence between these two parameters. For the faster pyrazoline and ferrocene films (Table 1) there was no evidence for the kind of phenomena [42, 43] (electrolyte and doping effects, "break-in" with electrochemical cycling) which, for the TTF-polymer films, indicated simple ion-transfer rate limitations. These data suggest that variables including pendant donor type, percent functionalization, and method of film preparation all have effects on the kinetics of electrochemical intercalation through their influence in modifying polymer film morphology. For the kinetically faster polymers just referred to, further work is necessary to help define how each of the transport processes contributes to the net observed kinetic behavior of the films.

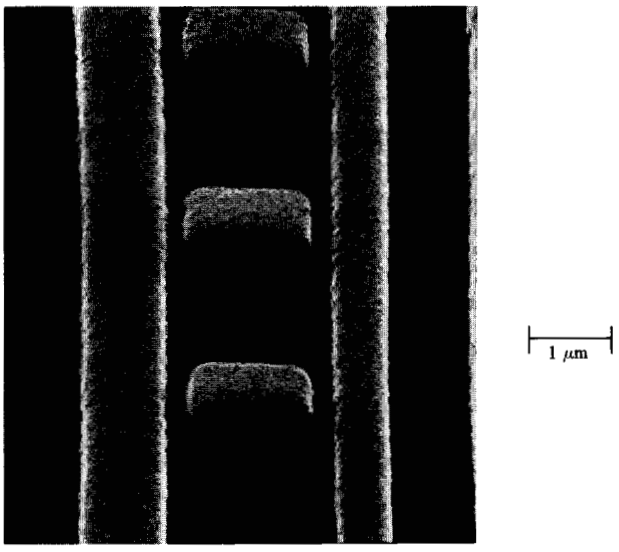


Figure 9 Remaining polymer pattern [TTF (R_1) polymer on a Si substrate] after doping with halocarbon, 10 $\mu C/cm^2$ e-beam exposure, and washing with a nonpolar solvent. Polymer film thickness is 0.6 μm.

Photochemical intercalation

The TTF donor in solution can also be oxidized by light [18] in the presence of halocarbon acceptors such as CCl_4 or CBr_4, forming halide salts; see Eq. (3). Spectro-

$$TTF + CBr_4 \xrightarrow{h\nu} TTF^+Br^- + CBr_3^\cdot \qquad (3)$$

scopic evidence for the formation of a ground-state complex (TTF)(CBr_4) was obtained [18], suggesting that charge transfer occurs from the TTF to the halocarbon upon absorption of light, yielding the TTF^+ and CBr_4^- ions. Breakage of the carbon-halogen bond to form $CBr_3^\cdot$ + Br^- results in a donor-cation salt and prevents back reaction to the neutral reactants.

If the same photochemical reaction were affected in TTF polymer films, light could be used to introduce (polymeric) TTF cations in the absence of chemical oxidants and solvents. We found that TTF polymer films with up to 200 mole percent CBr_4 could be spin-cast without crystallization of the halocarbon. Irradiation of these TTF-acceptor films in their charge-transfer bands turns the films a darker color, with an increase in the characteristic spectral absorptions of TTF^+ with irradiation time. Thus, formation of the photoactive complex in the polymer film followed by irradiation results in production of the cation in the polymer matrix. In addition, the number of cationic centers and their spatial distribution in the film can also be readily controlled [38] by light intensity and its wavelength distribution. We have also found that irradiation causes changes in the film's solubility, with the irradiated, and therefore ionic, portion of the film becoming insoluble in nonpolar organic solvents. The additional finding that other sources of radiation such as x-rays and e-beams can be used to induce ion formation and differential solubility has made the TTF polymers of potential interest as high-resolution lithographic resists (see next discussion).

Applications

The pi-donor polymers described here are a new class of materials whose novel mechanical, film-forming, and electronic properties are currently the subject of increasing study. Because they possess a combination of interesting chemical and physical properties, in addition to a degree of synthetic generality not readily achieved in more traditional materials, they may find utility in a variety of practical applications. These can be broadly classified as electronic, modified-electrode, and lithographic applications. Besides the spin-coating procedure discussed in this work, polymers of this type have also been deposited as thin films by dip-coating [57], electrodeposition [45(b), 55], and plasma-polymerization [45(c)] procedures. In general, adhesion of these polymers to metal, semiconductor, and insulating substrates is excellent.

It is generally understood that disordered organic materials of this type do not show very high electrical conduc-

tivity. However, the ability to deposit the polymers on large-area and/or flexible substrates, combined with semiconductivity (after doping) in the 10^{-4} to 10^{-8} $(\Omega\text{-cm})^{-1}$ regime may make them useful as antistatic [58] agents. In addition, by using these materials to introduce known quantities of stable cation radicals into films of polymeric photoconductors [59], it may be possible to achieve precise control and modification over useful photoconductivity properties.

A major application of pi-donor polymer films is likely to be in modifying the optical, electrocatalytic, or chemical properties of electrode surfaces. Such modified [60] electrodes have generated considerable interest recently because of their potential utility in energy conversion (prevention of photocorrosion in liquid-junction solar cells [23]) and storage devices (batteries [24]), in electrocatalysis [25], in electrochromic [22, 61] displays, and in the sensing (ion-controlled diodes [62]) and adsorption [63] of dissolved ions. Films of high active-site density with mixed electronic and ionic transport, as just described, are required in all of these applications. Except for electrochromic displays, where the voltage-induced color change of the polymer film between two or more differently colored oxidation states is of interest, all of the other phenomena involve electrochemical interaction with solute species dissolved in an external electrolyte. Thus, for these applications an additional requirement is that the polymer film act as an electronic mediator between electroactive solute species and the underlying metal electrode. Depending on the material, this can often be achieved [42, 43] with thin films (<100 nm). In several applications, moreover, steady-state operation of the device may make the kinetics of intercalation a relatively unimportant consideration. From an ultimate performance point of view, the maximum mobilities obtainable in these systems have probably not yet been achieved. However, work to date suggests that the inorganic materials which exhibit intercalation probably have no fundamental speed advantages over organic materials.

As discussed in the previous section, oxidation of the TTF polymer films can be observed when halocarbon acceptor-doped films are irradiated with light. We subsequently found that e-beam and x-ray irradiation were equally effective in oxidizing the film, thereby forming cations and changing the film solubility in nonpolar solvents [26].

Pattern quality and resolution using this lithographic [26] process are observed to be extremely high (Fig. 9). Among other important qualities of these new resists is that no solvent-induced swelling occurs in the insoluble exposed polymer region. The generation of differential solubility in this way, rather than by the usual chemical crosslinking, represents a new direction in resist materials [64] research. Studies of the variation of lithographic parameters with polymer properties promises to be an exciting area for future research.

Conclusions

Electroactive organic donor molecules bound to polystyrene backbones form novel thin-film solids with several interesting physical properties, some of which have potential technical utility. The process which is central to this behavior is the introduction of stable cation-radicals into solid films of these materials by chemical, electrochemical, or photochemical means. The oxidized and intercalated polymers exhibit modified optical, electronic, electrochemical, and solubility properties which make them interesting for various processes. In some cases, these materials exhibit phenomena due to electronic interactions between the polymer-bound cation radicals, such as aggregation or electrochemical charge transport, which are not as yet completely understood. The synthetic ability to modify materials' variables, for example by changing the donor, percent functionalization, or backbone molecular weight, suggests that the interesting and useful properties of these new polymer systems may be amenable to optimization by systematic structural modification.

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