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Polyimides: Versatile Specialty Polymers

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ABSTRACT: Polyimide specialty polymers are finding growing usage in applications such as high temperature, thermally stable insulators and dielectrics, coatings, adhesives, and high performance composites. To add to this already rich field of polyimide functions, we wish to review recent research from our laboratory which features the photoconductive and electrochemical behavior of polyimides, areas which have not as yet been widely explored. The first area of research, which illustrates polyimides as electrochemically active materials, is the recent work of S. Mazur and S. Reich. It deals with the specially controlled deposition of very thin silver layers, or certain other metal layers, into a polyimide film prepared from 4,4′-oxydianiline and pyromellitic dianhydride. This is achieved by coating the polyimide film, $\sim 10\,\mu\text{m}$ thick, onto a cathode. The cathode is placed in an electrolyte solution containing silver ion. A potential is applied between the solution and the cathode, resulting in the diffusion of silver ions towards the cathode. At steady state, when the flux of electrons (moving away from the cathode) equals that of the silver ions, a well defined, particulate, dense silver layer, $\sim 0.1\,\mu\text{m}$ thick, is deposited within the polyimide film. It is shown that the position and thickness of the metal layer as well as its geometrical shape can be controlled very precisely. The second area of research, photoconductivity in polyimides, is the work of S. C. Freilich. It is found that addition of electron donors, such as dimethylaniline, to Kapton® polyimide film results in an enhancement of the photocurrent generated by as much as five orders of magnitude when compared to the undoped polymer. The mechanism of the enhancement is shown to be the result of radiation absorption by a charge transfer complex formed between the added electron donor and the imide portion of the polymer backbone. Excitation is followed by rapid and complete electron transfer from the donor to pyromellitimide to yield the radical anion of the polymer and the radical cation of the donor. These ion pairs are demonstrated to be the carriers of the photocurrent. They also undergo rapid back electron transfer, and the geminate recombination process is consistent with an Onsager model analysis.

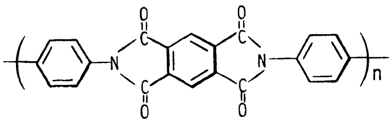
KEY WORDS Polyimides / Metal / Polyimide Films / Electrodeposition / Microcircuitry / Silver Electrodiffusion / (Polyimide) Photoconductivity / (Polyimide) Charge Transfer Complexes / (Polyimide) Ion Pair Conduction / Enhanced (Polyimide) Photoconductivity / Electroactive Polyimides /

During the past 25 years there has been growing interest in polyimides, a class of specialty polymers which are having a substantial impact on a number of advanced technologies. Polyimide specialty polymers are finding growing usage in applications such as high temperature, thermally stable insulators and dielectrics, coatings, adhesives, and high performance composites. Market areas include aerospace, microelectronics, heavy duty equipment, computers and medical devices. The versatility of polyimide-based high performance materials is providing incentive for accelerating R&D activity in many directions.[1]

Fundamental to most of today's applications is the unusual heat resistance and thermal stability of polyimides, with useful retention of properties at temperatures up to 400°C. The earliest and most widely used polyimides have a structure derived from reacting pyromellitic dianhydride with bis(4-aminophenyl) oxide ether. Products based on this structure were first pioneered by the Du Pont Company in the early sixties and include Kapton® polyimide films, Pyralin® polyimide coatings prepared from polyamic acid solutions, Pyralux® copper clad laminates, and Vespel® parts and shapes as structural composites. There is a wide variety of products produced by other companies, as well, and in particular those which combine the imide configurations with other structures to convey specific desired properties. This is exemplified by the Ultem® polyetherimides introduced by General Electric Company in 1982, which feature thermoplastic processibility together with many properties associated with polyimides.[1] Ube Industries Ltd. is also marketing a family of polyimides of novel compositions, designated as Upirex® R, S, and C, respectively. Among the most recent developments are thermoplastic matrix polymers, used as matrix resins in the manufacture of Avimid* K and N prepregs, introduced by du Pont for use in high performance composites.[2]

To add to the already rich field of polyimide investigations, we wish to review some recent research from our laboratory which features the electrochemical and photoconductive behavior of polyimides, fields which have not as yet been widely explored. In particular, we wish to review the recent work of Mazur and Reich[3,4] and of Freilich.[5] Although this work is still in an early stage, it speaks to areas of new potential utility for polyimides.

I. ELECTROCHEMICAL DEPOSITION OF METAL INTERLAYERS IN POLYIMIDE FILMS



The first research area, which illustrates the potential utility of polyimides as electrochemically active materials, is the recent work of Mazur and Reich.[3,4] It deals with the spacially controlled deposition of very thin silver layers, or of certain other metal layers, into a polyimide film prepared from 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA). This is achieved by first coating the polyimide film, 5 to 10 μm thick, onto a cathode. The cathode is placed in an electrolyte solution containing silver ion. A potential is applied between the solution and the cathode, resulting in the diffusion of silver ions towards the cathode. At steady state, when the flux of electrons (moving away from the cathode) equals that of the silver ions, a well defined, particulate, dense silver layer, 0.05 to 0.5 μm thick, is deposited within the polyimide film. Both the position and thickness of the metal layer can be controlled very precisely, as is discussed below.

In order to attain the necessary degree of permeability, the polyimide films were prepared under relatively mild conditions. The precursor ODA/PMDA polyamic acid was cast on a variety of electrodes, *e.g.*, glassy carbon, platinum, or tin oxide coated glass. The reaction to form the polyimide was completed by exposure to acetic anhydride in pyridine, followed by vacuum drying at 100°C. The resulting clear films displayed optical and infrared spectra virtually identical to polyimides prepared by high temperature dehydration.[6]

In cyclic voltammetry experiments, it was demonstrated that the polyimide, when prepared as above, can be reduced in stages by one and two electrons per repeat unit in the polymer. The reduction potentials occur at -0.73 and -1.13 V *vs.* SCE, respectively. These reductions are reversible and virtually

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* Du Pont trademark.

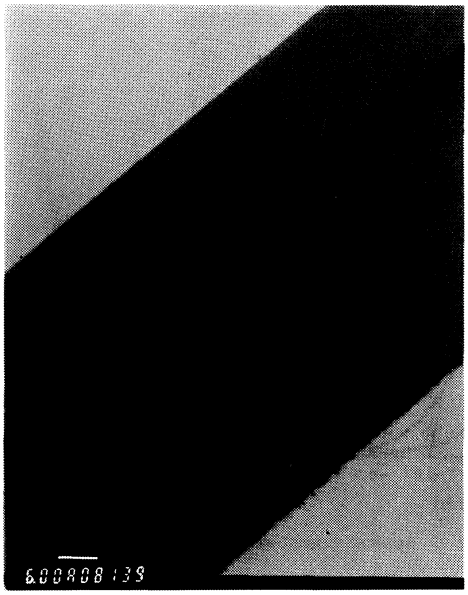


Figure 1. Transmission electron micrograph of silver layer in polyimide film. Upper, dense part of layer faces solution side. Bar in lower left indicates 1 μm scale.

complete, and are accompanied by color changes from the original yellow, to blue (charge: -1), and to rose (charge: -2).

Since the reduction potential of certain metal ions, *e.g.*, Ag^+, Cu^+, and Au^+, is less negative than that of the ODA/PMDA polyimide, the polymer anions are capable of reducing these metal ions to give metallic interlayers which can be deposited in a spacially controlled manner. In a typical experiment, an electrode coated with an ODA/PMDA film, 9 μm thick, was exposed to a *N*,*N*-dimethylformamide solution containing 0.10 M KPF_6 and 0.010 M $AgBF_4$. At a potential of -1.30 V *vs.* Ag/Ag^+ and after several minutes, 0.35 mg cm^{-2} of Ag had been deposited. The silver layer appeared highly reflective when viewed from the solution side, and black when viewed from the cathode side. Transmission electron micrography of the silver layers showed silver particles, 150 Å average diameter in two kinds of morphology. A dense interlayer (*ca.* 0.4 μm thick) faces the solution side of the film while additional particles are diffusely distributed towards the cathode side (Figure 1). The volume fraction of the silver in the dense interlayer was about 0.7. Its electrical conductivity was high, approximately 400 fold less than for bulk silver metal.

A simple model to describe the reduction and deposition process at the steady state postulates that the metal interlayer is formed in a plane when the metal ion flux equals the opposing electron flux. By combining Fick's first law and the Nernst equation, one can show that

$$\frac{t}{d}=1+\frac{D_{\mathrm{m}}K_{\mathrm{s}}(\mathrm{M}^+)_{\mathrm{s}}}{D_{\mathrm{e}}(\mathrm{e})_0},$$

where

$$(\mathrm{e})_0=\frac{(\mathrm{P})\exp\left(\frac{nF}{RT}(E^0-E)\right)}{1+\exp\left(\frac{nF}{RT}(E^0-E)\right)} \qquad (1)$$

where, t is the film thickness; d is the distance from cathode to metal layer; D_{e} and D_{m} are effective diffusion coefficients for electrons and metal, respectively; K_{s} is an equilibrium constant for sorption of metal ions by the polymer at solution concentration $(\mathrm{M}^+)_{\mathrm{s}}$; $(\mathrm{e})_0$ is the concentration of electron carriers at the cathode surface; and, (P) the total volume concentration of polymer functional groups. By using two adjustable parameters, E^0 and $D_{\mathrm{m}}K_{\mathrm{s}}/D_{\mathrm{e}}$, a very good fit for the position of the interlayer, d/t, as a function of applied potential, E, and metal ion solution concentration, (M^+), is obtained (Figure 2).

As is evident from eq 1 above, by varying E or $(\mathrm{M}^+)_{\mathrm{s}}$ in the course of an experiment the position of the interlayer may be varied in a controlled manner. It is also possible to deposit multiple interlayers at different positions within the film. The thickness of the interlayers can be controlled by adjusting the rate and time for deposition. High resolution two-dimensional patterns within the metal layer may also be obtained by employing suitable

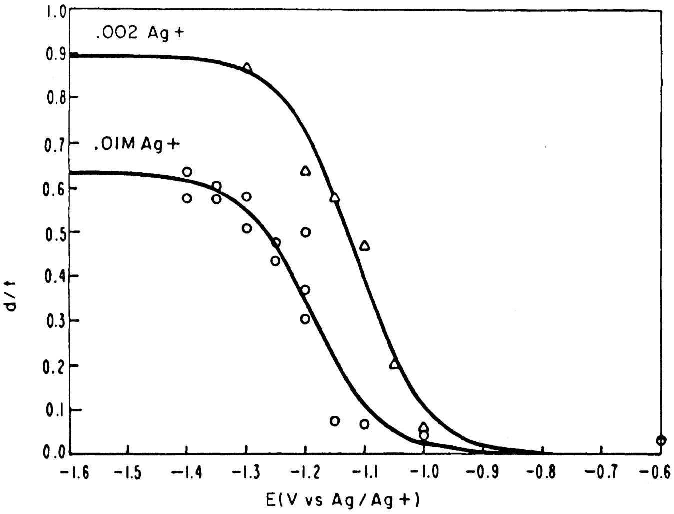


Figure 2. Position of silver layer (*t*/*d*) in polyimide film *vs*. applied potential (*E*) for two silver ion concentrations. Points are experimental; curves calculated by eq 1.

masks on either side of the polymer film. Thus, virtually all spacial characteristics of the metal interlayer can be controlled with good precision, providing a potentially powerful new technology for thin polymer/metal films.

II. PHOTOCONDUCTIVITY IN POLYIMIDES

Amorphous selenium is well recognized as a photoconductive material with established applications for electrophotography.[7] Organic photoconductors are not as well developed, although effective organic, polymeric photoconductors have been described, in particular trinitrofluorenone–poly(vinyl carbazole).[8] Previous work has also shown that Kapton® polyimide film is somewhat photoconductive in the presence of high electric fields.[9] Freilich of our laboratory has recently studied this phenomenon in some depth and has been successful in enhancing the photoconductivity of Kapton® to a large degree by the addition of suitable electron donors.[5] This work is reviewed in more detail below.

The three principal steps in photoconduction of a system are: excitation, charge carrier generation, and carrier transport. We will consider each of these in turn.

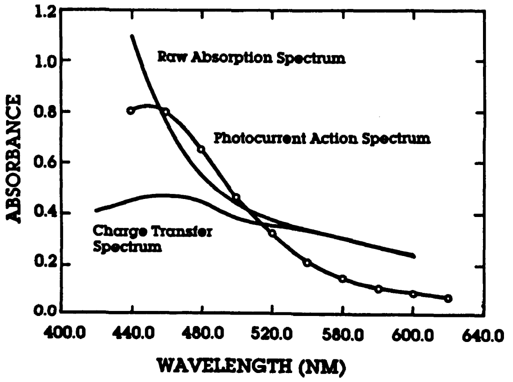
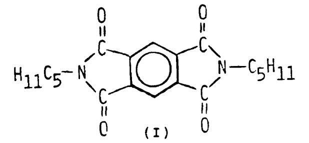


Figure 3. "Raw absorption spectrum" of Kapton® polyimide film containing 7.6% by weight of dimethylaniline (DMA), and "charge transfer spectrum" obtained by subtracting absorption of polyimide. Photocurrent action spectrum is also shown.

When an electron donor, such as dimethylaniline (DMA), is added to a Kapton® polyimide film (by exposing the film to a 4 M solution of DMA in methylene chloride), the color of the polyimide film changes markedly. Figure 3 shows a spectrum obtained for a Kapton® film containing 7.6% DMA by weight. The difference spectrum of the donor loaded film and the original film displays a well defined maximum at 480 nm which will be demonstrated to be a charge transfer transition. The corresponding charge transfer complex will be shown to be essential to the donor enhanced photoconductivity of Kapton®.

Because Kapton® is an intractable material, a model system was employed to simulate the nature of the charge transfer complex. The following imide was prepared:



(I)

When this compound is dissolved in methylene chloride it displays absorption maxima at 315 and 306 nm. Addition of DMA results in a broad transition maximum of 468 nm, similar to the one shown in Figure 3. The complex can be shown to be one-to-one with $K_{eq}=0.54$ l mol^{-1}.

When other electron donors are used, as shown in Figure 4, a shift in the charge transfer absorption maximum occurs. This shift is linear with ionization potential of the donor, and is well represented by $h\nu_{ct}=aI_p+b$, as proposed by Mulliken's charge transfer theory.[10] These results are strongly supportive of the formation of charge transfer complexes in these Kapton®/electron donor systems.

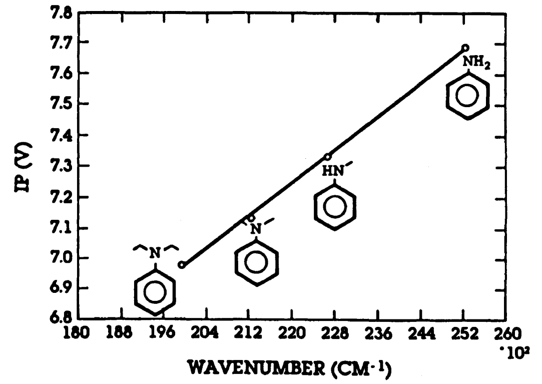


Figure 4. Ionization potentials of various donors (structures shown) *vs.* absorption maxima of charge transfer complexes between donors and model polyimide (structure I) in methylene chloride.

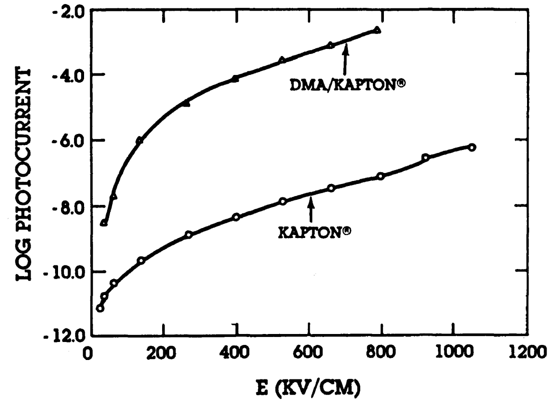


Figure 5. Photocurrent of Kapton® polyimide film and film containing 7.6 wt% DMA, upon irradiation at 480 nm, *vs.* applied potential, *E*.

As mentioned earlier, Kapton® is weakly photoconductive. However, when an electron donor, *e.g.*, DMA, is added, photocurrent generation is increased by some five orders of magnitude, as shown in Figure 5. In this experiment, a 0.3 mil Kapton® film contained 7.6% by weight of DMA and was illuminated at the charge transfer complex absorption maximum of 480 nm. The action spectrum of this system is shown in Figure 3, indicating that maximum photoconductivity occurs at this absorption maximum. This observation strongly suggests that the charge transfer complex is responsible for the generation of charge carriers in these systems.

The charge carriers are envisioned as resulting from an electron transfer process from the donor to the polyimide to give the corresponding ground state contact ion pairs. To elucidate this formation of ion pairs, picosecond absorption flash photolysis was employed. Irradiation of the imide, I, (0.1 M) and DMA (1 M) in methylene chloride resulted in the formation of a transient species within 35 ps of excitation. This transient, having maxima at 728 and 659 nm, is virtually identical to the imide radical anion formed through electrochemical reduction, as discussed in Section I. A corresponding similar experiment on Kapton®/DMA yielded a very similar spectrum (maximum 731 and 653 nm). The decay of this species is multi-exponential, with an initial unimolecular decay of about 150 ps. This short lifetime is most likely the result of rapid recombination of the radical ion pairs due to their close proximity.

Further strong evidence that these ion pairs are the carriers of the photocurrent is provided by picosecond spectroscopy of the Kapton®/DMA system in the presence of an applied electric field. An increase of 27% in ion pair concentration is observed at 950 ps, probably due to increasing the separation and lifetime of the ion pairs.

Onsager has treated theoretically the related, simplified problem of escape probability of point charges in a dielectric medium in the presence of an external electric field.[11] Onsager proposed that the photogeneration efficiency of free carrier formation is described by the following function:

$$\phi(E)=\phi_0\int p(r_0,\delta,E,T)g(r_0,\delta)\mathrm{d}^3r \tag{2}$$

where ϕ_0 is the yield of initially formed ion pairs, $p(x)$ is the probability of separation, $g(x)$ is the initial ion pair distribution (assumed to be isotropic), r_0 is the thermalization radius of the initial bound pairs, δ is the angle the separation vector between the ion pairs forms with the direction of the applied field, E is the magnitude of the applied field, and T is the ambient temperature. This expression assumes a two step process: the first step involves the formation and thermalization of the ion pairs, followed by the second step consisting of field assisted separation. When the present results of photocurrent *vs.* applied electric field are fitted to Onsager's theory, the results are consistent within quantum efficiency of 1 for photocarrier formation and a small "thermalization radius" of 13 Å (Figure 6). These results support the concept that although the bound ion pair is formed very efficiently, the small thermalization radius gives cause to a high degree of geminate recombinations.

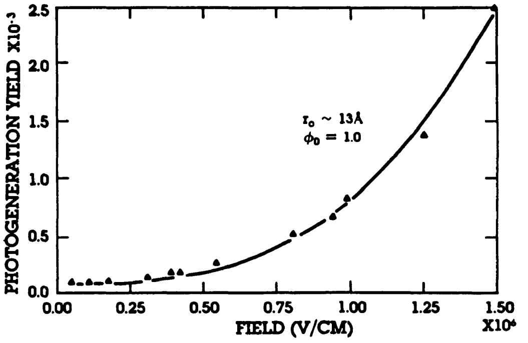


Figure 6. Comparison of Onsager theory (solid line). Equation 2 with photocurrent generation in Kapton®/DMA system, with quantum efficiency, ϕ_0, and thermalization radius, r_0, as shown.

CONCLUSION

In summary, in addition to the many other properties of polyimides described in the introduction of this paper, the work described in this review suggests yet new avenues of potential utility, making use of the electrical and photoelectrical behavior of these polymers.

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