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Photoconductivity of Donor-Loaded Polyimides

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ABSTRACT: The addition of electron donors to Kapton polyimide film results in an enhancement of photocurrent by as much as 5 orders of magnitude as compared to the virgin polymer. The mechanism of the enhancement is the result of radiation absorption by the 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. This species undergoes rapid back electron transfer, and the geminate recombination process is examined through an Onsager model analysis.

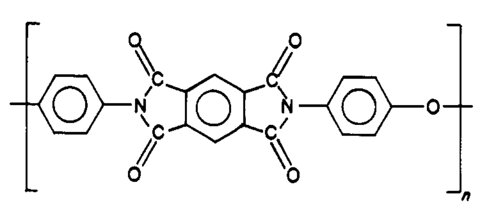
The photoconductivity of Kapton polyimide film has been noted in the literature in recent years.[1-6] UV,[4] X-ray,[5,6] and visible radiation[1-3] have been utilized as excitation sources. Although polyimides are well-known for their high thermal stability, solvent insensitivity, and good dielectric characteristics, the low quantum yield of photocurrent generation has limited the utility of these materials as photoconductors. In this paper, a new class of films with enhanced photoconductive properties is presented, namely electron-donor-loaded polyimide films. These films are characterized by higher photocurrent gains achieved without significantly sacrificing other positive features of polyimides.

Sensitization of photoconductivity in electron-donating polymers by the addition of electron acceptors has been widely reported, with most of the focus on poly(*N*-vinylcarbazole) (PVK).[7,8] Little work has appeared in the literature concerning electron-accepting polymers and electron-donor additives. Kapton polyimide film falls into the class of electron-accepting polymers, by virtue of the pyromellitimide group in the polymer backbone.

The process of photoconductivity can be divided into three individual steps: (1) the absorption of radiation; (2) the conversion of absorbed radiation into charge carriers; (3) the transport of free charge carriers throughout the bulk of the material to create a current flow in the external circuit. This paper reports on the first two steps in the mechanism of photoconductivity of electron-donor-loaded Kapton polyimide film. Carrier transport will be addressed in a future publication.

Experimental Section

Kapton polyimide films of various thicknesses are commercially available from Du Pont. These films are largely composed of oxydianiline pyromellitic acid polyimide (PMDA–ODA), the structure of which is shown below. PMDA–ODA films produced in the laboratory were generated by starting from the poly(amic acid) solution in *N,N*-dimethylacetamide (DMAC). Thus, a 12% solution of the poly(amic acid) was spin-coated onto conductive indium tin oxide coated glass (Kaufman Glass) at 2000 rpm for 1 min. Heating of the films at 90 °C for 10 min followed by immersion in a one-to-one solution of pyridine in acetic anhydride resulted in nearly complete imidization.



Electron donors were obtained from Aldrich Chemical Co. and were purified by standard techniques.

Steady-state DC photoconductivity was measured in the sandwich configuration, using an electrode arrangement consisting of a guard ring to prevent the measurement of surface charge leakage, a back electrode of silver paint, and a front electrode of conductive glass (Kaufman Glass). Current measurement was made through a picoammeter (Keithley 616) after application of a potential across the sample. Illumination was afforded by monochromatized radiation from a quartz–iodide lamp.

Photoinduced discharge measurements were made by passing the grounded film samples under a 1-mil tungsten corona wire and monitoring the change in surface potential as a function of 480-nm illumination time with an electrostatic voltmeter (Monroe Electronics). Photocurrent yield, ϕ, is obtained through the analysis $\phi = (C/eIA)(\mathrm{d}V/\mathrm{d}t_0)$, where C, I, A, and e are the capacitance of the film, the incident photon flux, the absorbance of the sample at the appropriate wavelength, and the electron unit of charge, respectively, and $\mathrm{d}V/\mathrm{d}t_0$ represents the measured initial slope of the voltage vs. time discharge plot.

Transient spectroscopy was performed on a Nd^{+3}:YAG laser flash photolysis apparatus with frequency doubling and tripling

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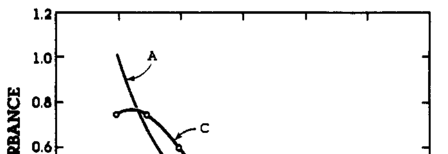


Figure 1. (A) Raw absorption spectrum of 0.3-mil DMA-loaded Kapton polyimide film. (B) Difference spectrum of intrinsic Kapton absorption subtracted from spectrum A, revealing the charge-transfer absorption. (C) Photocurrent action spectrum of 0.3-mil DMA-loaded Kapton polyimide film.

Table I

donor	CT λ_{max}, nm
N,*N*-dimethylaniline (DMA)	460
tetrathiafulvalene (TTF)	600
N,*N*,*N*′,*N*′-tetramethyl-1,4-phenylenediamine	580, 630
2,3-dimethylindole (DMI)	460, 500

to provide excitation at 355 nm and a 35-ps time resolution. Continuum was obtained by focusing the IR beam through H_2O/D_2O, and detection was achieved with an ISIT Vidicon tube and PAR Model 1216, 1215 detection system.

N,*N*′-di-*n*-pentylpyromellitic diimide (I) was synthesized by the method of Verhoeven[9] using distilled *n*-amylamine (Aldrich) and doubly sublimed pyromellitic dianhydride (Aldrich).

Results and Discussion

Addition of electron donors to Kapton polyimide film was carried out by taking advantage of the swelling phenomenon that the polymer undergoes in methylene chloride. Solvent-mediated diffusion of the electron donor through the bulk of the film was accompanied by a certain amount of absorption of the donor into the polymeric matrix; the extent of donor addition was dependent upon the composition of the molecule and the thickness of the film. The addition of certain electron donors to the films resulted in a marked change in the color of the material, as shown in Figure 1. In this figure, the absorption spectrum of *N*,*N*-dimethylaniline (DMA)-loaded polyimide is shown as A. The difference spectrum obtained by subtraction of the intrinsic visible absorption of polyimide from that of the donor-loaded material is shown as B. The maximum in B at 460 nm is assigned as a charge-transfer transition. Other donors generate charge-transfer complexes in Kapton polyimide film with maxima as shown in Table I.

While there has been a fair quantity of work investigating the complex formation between pyromellitic dianhydride and electron donors,[10] little is known about the complexes of pyromellitimides.[11]

The nature of the charge-transfer complex was investigated through the use of model systems, in particular by assuming that the imide unit was responsible for the acceptor characteristics of the polymer, and thus synthesizing a low molecular weight, soluble analogue of this species (**I**). In methylene chloride solution, **I** displayed an absorption spectrum with maxima of 315 and 306 nm, while the addition of electron donors to the solution, e.g., *N*,*N*-dimethylaniline (DMA), resulted in a change in the absorption spectrum through the addition of a broad transition with a maximum at 468 nm. A Job analysis for **I** and DMA in methylene chloride demonstrated that the complex is one-to-one, and Benesi–Hildebrand[12] analysis revealed that the complex is weak, with K_{eq} of 0.54 L/mol^{-1}.

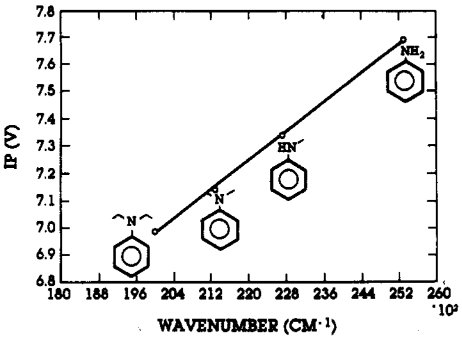


Figure 2. Ionization potential of electron donor vs. transition energy of charge-transfer transition for I and the donor in methylene chloride.

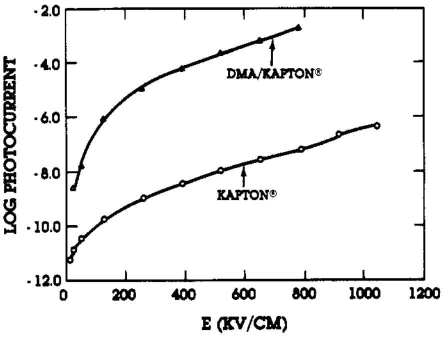


Figure 3. Photocurrent response (A/cm^2) as a function of applied field for 0.3-mil Kapton and 0.3-mil DMA/Kapton. Illumination is carried out at 480 nm.

That the complex is charge transfer in nature was made evident by the linear dependence of ionization potential (I_p) of the electron donor with the energy (E) of the complex optical transition in methylene chloride. Mulliken charge-transfer theory[13] has been shown, with appropriate approximations,[14] to lead to expressions relating E with I_p for a series of related electron donors with the form

$$h\nu_{ct} = aI_p + b$$

Such a correlation was observed for **I** in methylene chloride using the aniline series as the electron donors (Figure 2). X-ray analysis of crystals of **I** and TTF grown from methanol provided further support for the concept of charge-transfer complex formation between the electron donor and **I**. These crystals were composed of alternating stacks of TTF and **I** with a donor–accepter spacing of 3.6 Å,[15a] in good agreement with other organic charge-transfer crystal intermolecular spacings.[16] The similarity of the charge-transfer absorptions of **I** and electron donors in solution with the visible transitions of the polyimide film and added electron donors suggests that this low-energy transition in the polymer is charge transfer in character.

The photoconductivity of Kapton polyimide films is well-known,[1–6] although the yield of photocurrent is quite low in the visible region of the spectrum. The addition of electron donors increased the photocurrent generation by as much as 5 orders of magnitude in the applied field range of 10^5–10^6 V/cm (Figure 3). The photoresponse as a function of applied electric field is displayed for both 0.3-mil Kapton polyimide film and 0.3-mil polyimide film loaded with 7.6% by weight of DMA, with the sample in the sandwich arrangement and illumination at 480 nm. At all applied fields, the presence of the electron donor resulted in an enhancement of photocurrent in the polyimide.

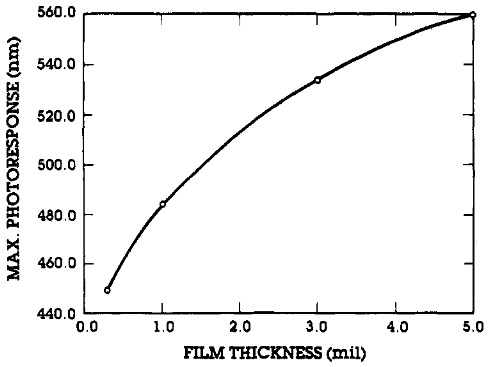


Figure 4. Thickness dependence of DMA/Kapton photoresponse action spectrum.

The action spectrum for a 0.3-mil film of Kapton polyimide loaded with 7.6% by weight DMA (Figure 1C) shows that the photocurrent maximum is approximately 460 nm. This value corresponds to the absorption maximum of the charge-transfer complex discussed above. The correspondence of maxima indicates that the charge-transfer complex is responsible for the generation of charge carriers in these systems.

The photoresponse of the films is thickness dependent (Figure 4), demonstrating that as the thickness of the film increases, there is a concomitant increase in the absorption maximum for photoresponse. Such a correlation suggests that the photoresponse of the donor-loaded films is a bulk response; in particular, the photoresponse behavior follows the model developed by Thommes and Webers[15b] for base response. In this model, the maximum response is obtained with minimum exposure when actinic energy in the base volume element is maximized, from which it follows that

$$E = I_0 \exp(-\mu c d)$$

where E is the energy density absorbed per unit time by the base element of thickness d, μ and c are the absorption coefficient and the molar concentration, respectively, and I_0 is the incident radiation intensity. This function is a maximum when $\mu c d = 1$; therefore maximum photoresponse is obtained when OD = 0.43. Careful examination of Figure 1 demonstrates this to be the case for DMA/Kapton, taking into account the action of the nonphotoactive species, the polymer itself, as an actinic filter. Thus the maximum photoresponse is obtained at the maximum of the charge-transfer absorption for 0.3-mil films, with OD = 0.40 for the charge-transfer transition.

Base element photoresponse is normally associated with processes such as photoresist imaging, in which it is critical for cross-linking to occur throughout the bulk of the material for proper device functioning. In photoconductive systems where electrode effects are minimal, the mechanistic requirements for base element irradiation are not evident. It is hypothesized that this phenomenon results from the presence of trapping sites within the polymer. Irradiation with strongly absorbed light creates a high density of trapped charge in a region of the film close to the surface. A reduction of the field in the illuminated region of the film follows, thus reducing significantly the quantum efficiency of charge generation in the illuminated section (vide infra). The effect can be observed directly by examining the current pulse obtained through irradiation of a PMDA-ODA polyimide film loaded with DMA. At an applied field strength of 1.6 × 10^5 V/cm and irradiation at 420 nm, there is an initial increase in the current, followed by a decay that eventually reaches equilibrium (Figure 5). After termination of illumination, the dark current is reattained. The decay of the initial current is attributed to the trapping of charge in deep traps, resulting in the effect outlined above. Elevated temperatures reduce the magnitude of the current decay, indicating that trapping processes are thermally activated. Increasing the irradiation wavelength attenuates the decay and eventually eliminates it altogether, presumably through an increase in the photon penetration depth. For commercial Kapton polyimide films 0.3–1.0 mil thick, this behavior is observed as predicted above, namely, that the absorption depth of the photons at the wavelength of maximum photocurrent generation is approximately the thickness of the film. At film dimensions greater than 1.0 mil, however, this relationship breaks down. It is assumed that this results from different deep trapping states in the thicker commercial materials. Work is under way in an attempt to understand more fully this phenomenon.

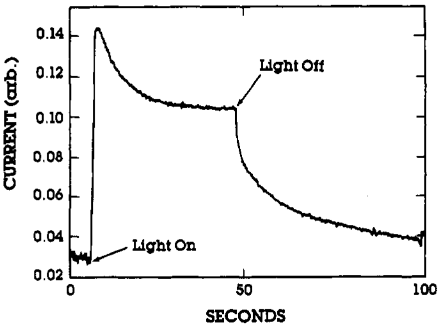


Figure 5. Photocurrent response with time of 420-nm-irradiated DMA-loaded PMDA-ODA under an applied field of 1.6 × 10^5 V/cm.

Charge Carrier Generation. Having demonstrated that photoconductivity is dependent upon excitation of a charge-transfer complex, we envision charge carrier generation as an electron transfer from the donor molecule to the acceptor, resulting in the formation of ground-state contact ion pairs. Such a mechanism has been proposed for poly(*N*-vinylcarbazole) loaded with electron acceptors.[17-20] The validity of the hypothesis is supported by solution-phase flash photolysis experiments by Williams[21] in which it was observed that the radical cation of PVK and the radical anion of dimethyl terephthalate (DMT) were evident within 100 ps following excitation of the polymer and acceptor in a toluene solution. Yokoyama[18] reported that the fluorescence assigned to the exciplex formed between PVK and DMT was quenched by the application of an external electric field; this effect was attributed to field-assisted thermal dissociation of the photogenerated exciplex to form separated ion pairs. We have utilized picosecond absorption flash photolysis to elucidate the mechanism of charge carrier generation in electron-donor-loaded polyimides.

There has been no previous work on the flash photolysis of polyimide films. Thus the study of model systems was appropriate to assist in the assignment of transient phenomena. **I** was utilized as a model for the imide unit in the polymer backbone. Irradiation at 355 nm of a 0.1 M solution of **I** in methylene chloride which was 1 M in DMA resulted in the formation of the transient shown in Figure 6 within 35 ps of excitation. This new species, displaying absorption maxima of 728 and 659 nm, was virtually identical with the radical anion of **I** formed either through wet chemical or electrochemical reduction. Electron transfer from electron donors to excited imides has been previously observed.[22] The lifetime of the **I** donor ion pair was short, and it decayed in a multiexponential fashion (Figure 7A). Although there were insufficient data to deconvolute the individual decay processes, it was possible

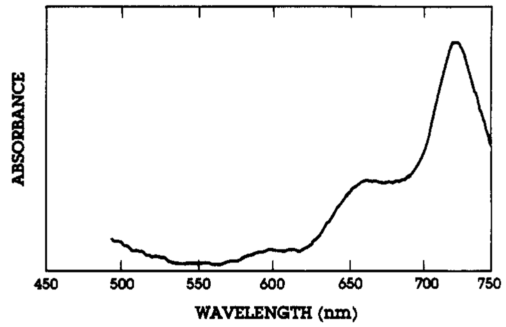


Figure 6. Transient absorption spectrum of **I** 0.1 M in methylene chloride containing 1 M DMA. Spectrum is taken 35 ps following excitation at 355 nm. Transient is identified as the radical anion of **I**.

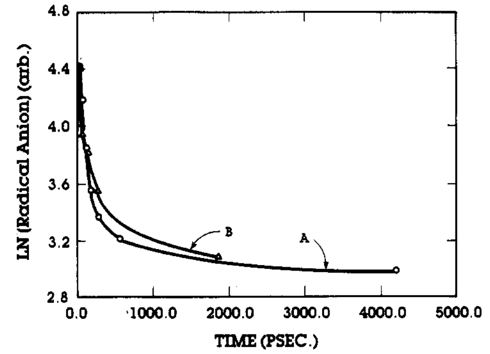


Figure 7. (A) Concentration of **I** radical anion as a function of time after excitation of a solution of **I** in methylene chloride containing DMA. (B) Concentration of radical anion of Kapton polyimide film as a function of time after excitation of a 0.3-mil film loaded with 7.6% DMA.

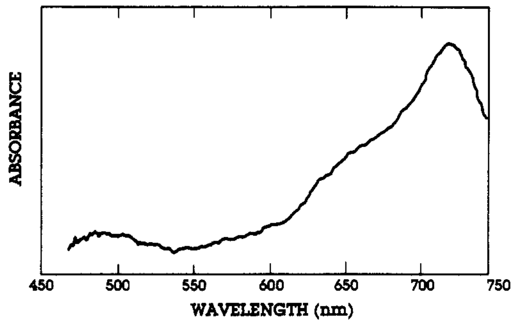


Figure 8. Transient absorption spectrum of the radical anion of Kapton formed 35 ps after excitation of DMA-loaded Kapton polyimide film at 355 nm.

to estimate the lifetime of the initial rapid decay. Analysis of this decay as a unimolecular process yielded a lifetime of 177 ± 35 ps. This rapid decay was attributed to the formation of a singlet ion pair, and thus back electron transfer was a highly favorable and rapid process.[23]

When a 0.3-mil sample of Kapton polyimide film previously soaked in DMA/methylene chloride was placed on a rotating stage in the picosecond spectrometer, a transient was observed within 35 ps of excitation with absorption maxima of 721 and 653 nm (Figure 8). This species was similar to the radical anion of **I** and virtually identical with the radical anion of Kapton polyimide film generated by zintl anion reduction.[24] Thus the transient (Figure 8) was assigned as the radical anion of Kapton polyimide film formed through electron transfer from the donor DMA to the acceptor imide portion of the polymer backbone. In the systems studied in this work, the transient absorption spectrum of the radical cation was outside the interrogation window.

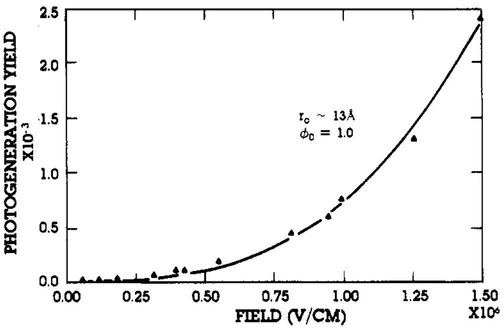


Figure 9. Quantum efficiency of photocurrent generation as a function of applied surface potential for DMA/Kapton under 480-nm irradiation. The data are taken under PID conditions, and the triangles represent the experimental data. The solid line represents the best fit to the Onsager expression with r_0 = 13 Å and ϕ_0 = 1.0.

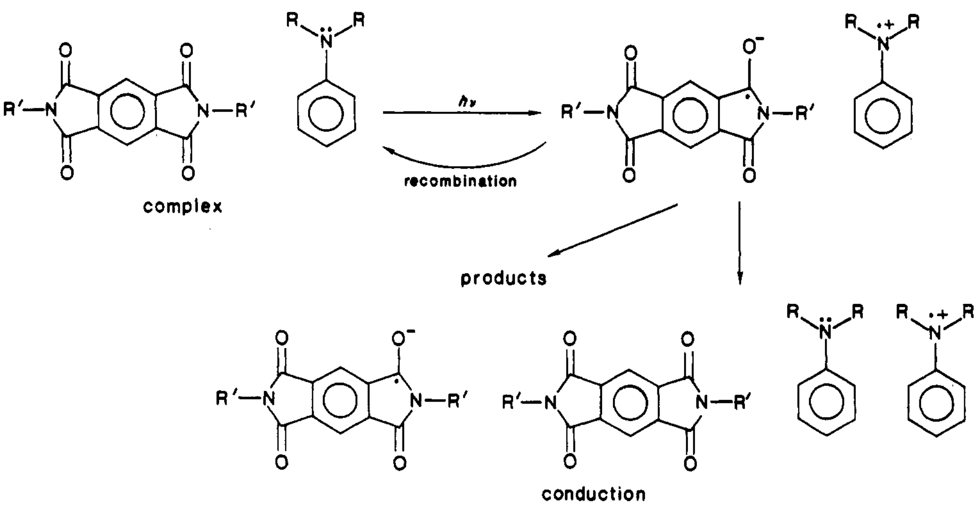
The decay kinetics of the polymer-derived ion pair (Figure 7B) were quite similar to those in Figure 7A, suggesting that similar processes were taking place. The multiexponential decay indicates multiple pathways, yet an initial rapid unimolecular decay with a lifetime of approximately 150 ps may be extracted from the short-time data. This fast decay was attributed to the back electron transfer or geminate recombination process.

The production of ion pairs in the irradiation of donor-loaded Kapton polyimide films is not proof that these species are competent charge carriers; for these ion pairs to be charge carrying species, the concentration of ion pairs must be modified with an applied electric field. Irradiation of DMA/Kapton in an applied field of 10^5 V/cm resulted in the formation of radical ion pairs. At 950 ps following excitation, the concentration of ion pairs was increased by the applied field by 27% over that in the absence of any external field. The effect of the field may be twofold. First, the field may increase the concentration of radical ion by decreasing the extent of geminate recombination, and second, the field may increase the lifetime of the free, separated ion pairs. Both of these effects would result in an increase in the ion pair concentration at 950 ps. Future experimentation is expected to determine the contribution of these two processes to the overall observed effect. More importantly, the observation of a field effect on the concentration of the ion pairs supports the notion that the radical anion of the polyimide and the radical cation of the electron donor function as competent charge carriers in this system. It is not possible at the moment to identify other components that may participate as charge-carrying species, but their presence cannot be ruled out on the basis of the experiments herein reported.

Efficiency of Photocurrent Generation. With a photoinduced discharge (PID) of an applied surface potential, the field effect of photocurrent generation efficiency was measured. The results indicate that with increasing field there was a concomitant increase in the photocurrent gain (Figure 9). As the excitation was into the charge-transfer band of the photoconductor, each photon absorbed by this complex resulted in the formation of a bound electron–hole pair or contact ion pair. The major mode of decay of these species was back electron transfer (vide supra). In order to become free charge carriers, the ions must separate to some distance r_c such that the Coulombic attraction between them is less than kT.

The problem of the escape probability of point charges in a medium of continuous dielectric escaping from their mutual Coulombic attraction in the presence of an external electric field has been dealt with by Onsager.[25] The On-

Scheme I



sager description involves a two-step process, in which initial excitation results in the formation of a bound electron–hole pair, followed by subsequent field-assisted dissociation of this charged species. These processes lead to a description of the quantum efficiency for photocarrier generation

$$\phi(E) = \phi_0 \int f(r_0,\theta,E) g(r_0,\theta)\ d^3r$$

where $f(r_0, \theta, E)$ is the probability that the electron–hole pair will separate from the initial thermalization separation radius of r_0 and a separation vector of θ relative to the applied field E to some large distance where the mutual Coulombic attraction is minimized. The spatial distribution of bound pairs is given by $g(x)$. Recently, the Onsager formalism has been applied to organic photoconductors with limited success.[26-28] Braun[29] has demonstrated that an important internal check for the application validity of the Onsager model for three-dimensional isotropic distribution of charge can be found. In this analysis, it is pointed out that as the applied electric field (E) approaches zero the slope-to-intercept ratio (M) of the gain vs. E plot is a constant, $M \cong 3.1 \times 10^{-5}$ cm/V and that this ratio is independent of the adjustable parameters r_0 and ϕ_0, the initial yield of bound pairs. When such an analysis is applied to the low-field limit for DMA-loaded 0.3-mil Kapton polyimide film irradiated at 480 nm, a roughly linear region of the gain vs. field plot is obtained (Figure 10) and $M = (2.1 \pm 0.7) \times 10^{-5}$ cm/V, in good agreement with the theory after insertion of the material parameters. This correlation suggests applicability of the Onsager analysis to DMA-loaded Kapton polyimide film. Nonetheless, it is recognized that the presence of deep trapping states may effect the absolute value of the initial gain measurements.

Fitting of the field vs. photocurrent gain data to the first three terms of the Onsager expression (Figure 9) gave values for the adjustable parameters of r_0 = 13 Å and ϕ_0 = 1.0. The high value for the initial quantum yield of bound electron–hole pairs was attributed to the fact that radiation was being absorbed into the charge-transfer band and, thus, each photon absorbed resulted in an electron-transfer process. Similarly high values of ϕ_0 were found for PVK/DMT and PVK/1,2,4,5-tetracyanobenzene.[30] The thermalization radius of 13 Å is small, particularly when compared to the 35-Å value calculated for PVK/TNF,[31] but agrees nicely with the theoretical value of r_0 = 15 Å calculated by Rashmi.[32] These data suggest that although the bound ion pair is formed in high yield the small thermalization radius results in a high degree of geminate recombination, or back electron transfer, limiting the photogeneration efficiency.

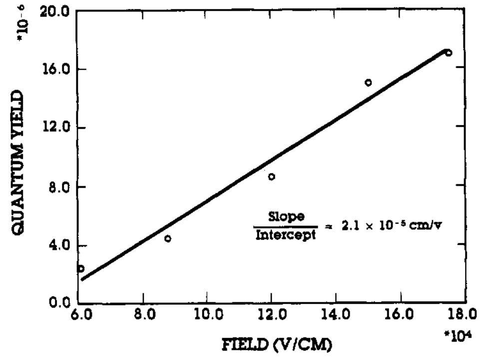


Figure 10. Quantum efficiency of charge generation in DMA/Kapton under 480-nm irradiation as a function of field at the low-field limit. The best fit straight line yields a slope-to-intercept ratio of 2.1×10^{-5} cm/V.

These results lead to a mechanism for the photocurrent generation as shown in Scheme I. Excitation of the sample took place in the visible region of the spectrum through the mediation of a charge-transfer complex formed between the added electron donor and the imide portion of the polymer backbone. Excitation of this complex resulted in rapid and complete electron transfer within 35 ps to yield a singlet-correlated ion pair composed of the radical anion of the polymer and the radical cation of the electron donor. Through a field-assisted hopping process, this contact ion pair underwent separation to form free charge carriers, giving current in the external circuit. Alternatively, the high yield of geminate recombination, as made evident from the small thermalization radius found for DMA-loaded polyimide film, resulted in a regeneration of starting ground-state complex and a reduction in photoefficiency. There was no evidence of further reaction of the polyimide radical anion other than separation or back electron transfer in either flash photolysis or fatigue studies. One of the more interesting aspects of this mechanism is the possibility of modification of the geminate recombination through variation of the donor concentration and composition in the films. Studies are under way to define this variable.

Charge-carrier transport has not been addressed in this work. On the basis of preliminary findings, transport is believed to follow a hopping mechanism, which can be understood in terms of a Scher–Montroll continuous-time random-walk analysis.[33] Such a mechanism has been proposed for carrier mobility in pyrolyzed Kapton polyimide film.[34] More complete investigations of this process are proceeding.

Acknowledgment. I thank Kevin S. Peters of University of Colorado at Boulder for the use of the picosecond flash photolysis apparatus. Many useful discussions were held with R. K. Waring, S. Mazur, and S. Maerov. Sam Tonik and Gloria Worrell were extremely helpful with laboratory assistance.

Registry No. 1·DMA, 107576-77-2; (PMDA-ODA)(SRU)·DMA, 107558-03-2; (PMDA-ODA)(copolymer)·DMA, 107558-07-6; (PMDA-ODA)(SRU)·TTF, 107558-04-3; (PMDA-ODA)(copolymer)·TTF, 107558-08-7; (PMDA-ODA)(SRU)·DMI, 107558-05-4; (PMDA-ODA)(copolymer)·DMI, 107558-10-1; (PMDA-ODA)(SRU)·4-$(CH_3)_2NC_6H_4N(CH_3)_2$, 107558-06-5; (PMDA-ODA)(copolymer)·4-$(CH_3)_2NC_6H_4N(CH_3)_2$, 107558-09-8.

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Electron Transport in Poly(3-vinyl-10-methylphenothiazine) Films

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ABSTRACT: Electrochemical properties of poly(3-vinyl-10-methylphenothiazine) (polyMPT) films spin coated on a Pt electrode were investigated by cyclic voltammetry and chronocoulometry. The polyMPT films showed electrochromism, and the oxidized films remained reddish purple in ambient air under open-circuit conditions for many months. Within the surface coverage range of $\sim 0.6\ \mu\text{mol/cm}^2$, over 90% of all the 10-methylphenothiazine (MPT) residues in the polyMPT films could readily be oxidized by electrolysis, presumably because of efficient self-exchanges of electrons. The apparent diffusion coefficient (D_{ap}) for electron transport through the film was determined by chronocoulometry to be 1.6×10^{-9} and $2.6 \times 10^{-9}\ \text{cm}^2/\text{s}$ for an anodic and a cathodic step, respectively. Copolymers of 3-vinyl-10-methylphenothiazine and methyl methacrylate with various mole fractions of the MPT units (f_{MPT}) were employed to study the dependence of D_{ap} on the concentration of the MPT units in the film, from which electron self-exchange rate constants (k_{ex}) were roughly estimated to be 4.0×10^5 and $5.9 \times 10^5\ \text{M}^{-1}\ \text{s}^{-1}$ for the anodic and cathodic processes, respectively. Absorption spectra of the oxidized polymer films showed a band due to dimer dications of the oxidized MPT units ($(MPT_2)^{2+}$). The intensity of this dimer band decreased with decreasing f_{MPT}. These facts are indicative of a pairwise orientation of the MPT moieties in the oxidized film, which may explain the larger D_{ap} and k_{ex} values for the cathodic process.

Introduction

Recently, an increasing interest has been drawn to redox polymers as a promising electroactive material. A variety of macromolecules with redox functionality has so far been synthesized, and some of them have proven their usefulness for electrode modifications.[1,2] Unlike chemical derivatization of electrode surfaces with low molecular weight functional groups, layers of polymer-modified electrodes can consist of some thousands of monolayers equivalent. In such polymer layers a large number of remote electroactive sites that have virtually no chance to contact the underlying electrode surface can undergo oxidation and reduction by self-exchanges of electrons between neighboring redox sites. The electron-hopping mechanism for this process originally proposed by Kaufman et al.[3,4] is now accepted.

It has been suggested by Murray and co-workers that electron-donating and -accepting redox sites in polymer

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