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Photoconductivity in molecularly doped poly(methylmethacrylate) sandwich cells

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Poly(methyl)methacrylate was made photoconducting by molecular doping and the photoconductivity was investigated using modulated photocurrent technique. Low-temperature current-voltage measurements showed that the transport mechanism was thermally activated hopping. An experimental investigation of the photoconductivity action spectrum along with theoretical calculation enabled an estimation of the diffusion coefficient of the material. The presence of states with a distribution of lifetimes could be understood from the frequency response of the photocurrent. The photocurrent was due to the field-assisted dissociation of these states. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710773]

I. INTRODUCTION

Molecularly doped polymers (MDPs) are amorphous systems with dopants having only weak interactions through van der Waals force, invalidating the application of classical band transport model to them.[1] The charge transport in these systems was subjected to numerous investigations[2–4] and the mechanism of transport was accepted to be hopping through a manifold of localized states whose energetic distribution is Gaussian.[5] The activation energy needed for hopping is a function of electric field and molecular separation.[3] It is considered that the electric field has an effect of lowering the energy required to hop from one localized state to the other.[2]

This article discusses the carrier generation and transport in molecularly doped poly(methylmethacrylate) (PMMA) with aniline (AN) and picric acid (PA) as the dopants. AN is an electron donor while PA is a strong electron acceptor favoring the formation of a charge transfer (CT) complex in the host. Carrier generation through CT complex doping involves the following steps:[6] (1) Excitation of the CT complex by appropriate radiation; (2) charge transfer from a free donor to the excited CT complex; and (3) migration of the carriers through the transport medium.

II. EXPERIMENT

Samples were prepared by drop-casting a 7% solution of the components in spectroscopic grade chloroform onto ITO-coated glass plates. AN (SD Fine Chemicals, India) was purified by distillation and PA (SD Fine Chemicals, India) by twofold recrystallization using ethanol. Concentration of PA was kept low to reduce chances of phase separation and AN was added in excess to make 1:100 mol ratio between the components PA and AN. A drying period of 48 h (at 28 °C) was given for complete solvent removal, and the thickness of the samples was in the range 15–30 μm, measured using a Dektak 6M Stylus profiler. Silver electrodes of area 5×5 mm^2 were vacuum deposited on to the slightly yellow films to get the final sandwiched structure. The samples were labeled S0 (PA-PMMA), S1 (AN-PMMA), S11 (PA: AN-PMMA, 1:1), and S100 (PA: AN-PMMA, 1:100).

Modulated photocurrent detection method using a lock-in-amplifier (Stanford SR830) coupled with a chopper (Stanford SR540) was used for the measurement of the photogenerated voltage across a load resistance connected in series with the sample and a high-voltage dc power supply (Stanford PS350). Spectral dependence of the photocurrent was measured using different excitation wavelengths from a Fluoromax–3 fluorimeter, in which, a 150 W xenon lamp was the source. The samples were irradiated from the ITO side and data normalization was done to compensate the intensity change of the radiation by dividing the data with the intensity distribution of the lamp, obtained using the calibrated photodiode of the fluorimeter. For all other studies, radiation from an Ar$^+$ laser (488 nm, Melles Griot) or from a wavelength selectable He-Cd laser (325 nm/441.6 nm, Kimmon) was used with neutral density filters. Low-temperature

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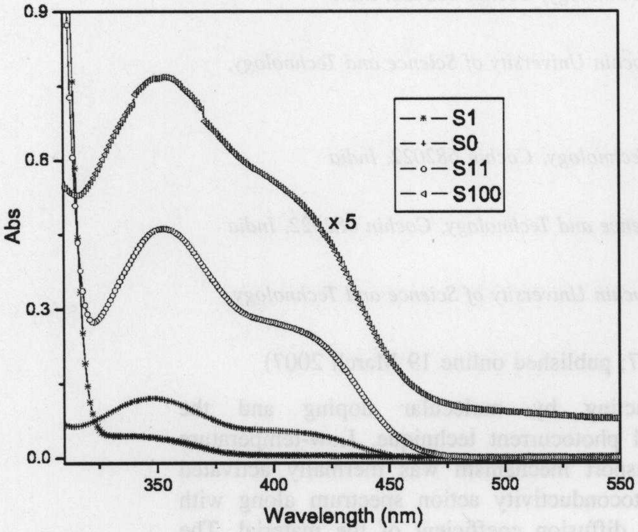

FIG. 1. Absorption spectra of the samples.

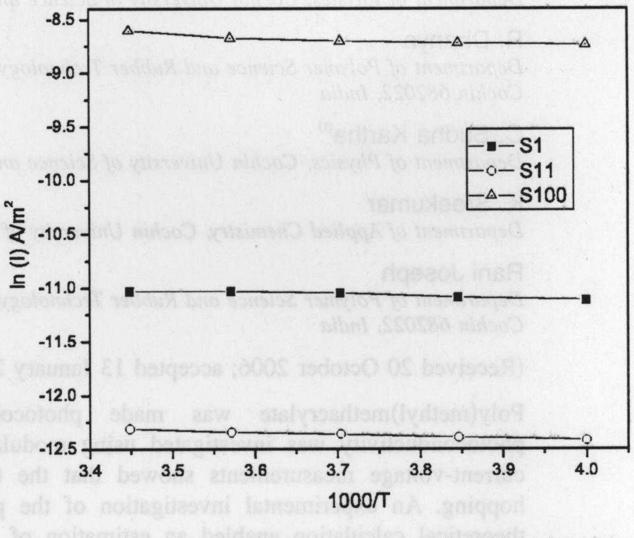

FIG. 2. Arrhenius plots showing the temperature-activated behavior of the samples.

electrical measurements were done in a closed-cycle liquid helium cryostat, equipped with an autotuning temperature controller (LakeShore 321), using a Keithley 236 source-measure unit.

III. RESULTS AND DISCUSSION

The UV-VIS absorption spectra recorded using a Jasco V-570 model spectrophotometer are shown in Fig. 1. The bathochromic and hyperchromic shifts observed in the absorption spectrum of S11 compared to S0 or S1 indicate the formation of a CT complex between AN and PA. This is similar to the CT complex formation in PVK: TNF photoconductive system.[7] The spectra of S11 and S100 were similar but with an increase in absorbance. It is seen that the absorbance has a strong dependence on the concentration of the donor molecules. Due to the strong electrostatic interaction between the donor AN molecules and PA (the acceptor) molecules, multimolecular assembly of AN molecules around PA may be formed similar to a solvent cage, which may contribute to the dependence of absorbance on the concentration of AN. Upon excitation of the CT complex, an electron is transferred from the electron-rich ligand to the electron-poor ligand, thereby initiating charge separation and generation.[8]

Electrical measurements were carried out with ITO biased negative so that the probability of injection of holes could be reduced. Temperature-dependent *I-V* measurements were done on all the samples to study the conduction mechanism in the material. Sample S0 did not show a temperature-activated behavior; instead, the current decreased as the temperature was increased. S11 showed an Arrhenius behavior with activation energy of 0.20 eV. In S1, the activation energy was 0.16 eV. This type of increase in activation energy on complex formation was observed in other systems also.[9] Sample S100 was also similar but the activation energy was slightly increased to 0.22 eV. The Arrhenius plots are shown in Fig. 2.

As thermal activation was involved, the conduction mechanism could be either thermionic emission or hopping conduction.[10] The *I-V* plots were linear ($I \propto V$), ruling out the possibility of thermionic emission where a behavior of the type $I \propto V^{1/2}$ would be observed.[10] So, the dominant conduction mechanism in the material appeared to be temperature-assisted hopping between localized states.

Photocurrent action spectra of the samples S0, S11, and S100 are shown in Fig. 3. In S11, the photocurrent yield was considerably reduced due to the formation of the complex. In sample S100, the spectral photocurrent yield was restored with considerable increase of current in the visible region. There was no photocurrent for S1, small current for S11, and increased current for S100 and S0. The electrical conductivity of S11 sample was less compared to S100 and S1. This may be due to the fact that in S11, the major units were AN:PA complexes, which release lower number of free carriers while S100 and S1 host excess donor-type molecules. The photoaction spectrum of S100 was similar to the absorp-

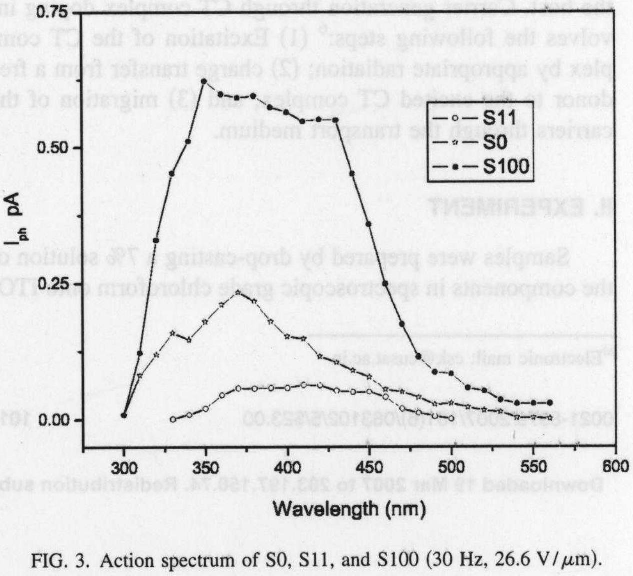

FIG. 3. Action spectrum of S0, S11, and S100 (30 Hz, 26.6 V/μm).

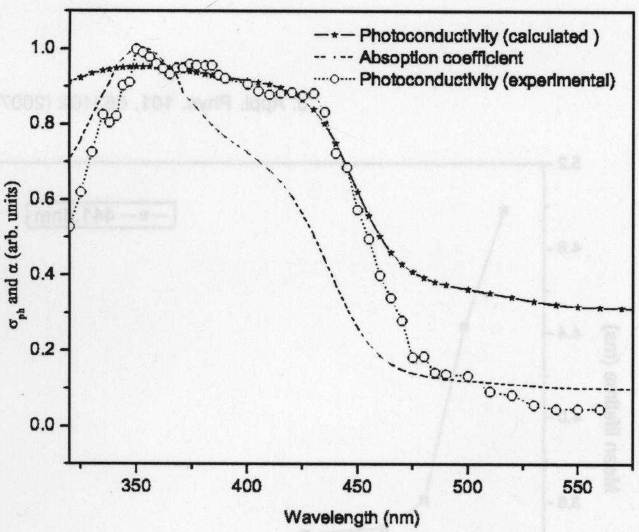

FIG. 4. Photoconductivity action spectra (30 Hz, 26.6 V/μm).

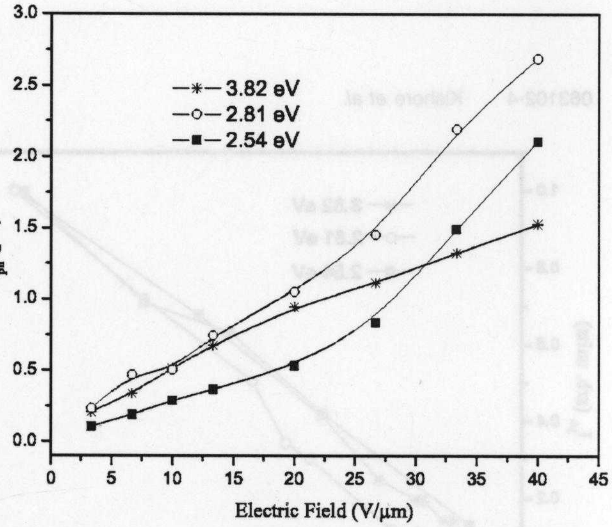

FIG. 5. Photocurrent as a function of applied electric field at different photon energies at 30 Hz.

tion spectrum of S11. These facts show that the generation of carriers in S100 was by the CT units, with excess AN acting as transport units. In S0, the major generation and transport units were acceptor type while in S100, the major units were of donor type. The temperature dependence of S0 and S100 was also opposite, possibly due to the above opposite nature of the transport units.

Sample S100 was subjected to various measurements at room temperature. No thickness dependence was observed for the shape of the spectral response and all samples showed an increase in I_{ph} at the onset of absorption. A theoretical calculation of the photoconductivity spectral response was done using the formulation of Devore,[11] from the measured absorption values. The calculated spectrum is shown in Fig. 4 together with the experimental values and the absorption coefficients.

The theoretical analysis used here was originally formulated to account for the observed decrease in photoconductivity spectral response at high absorption region in a planar photoconductor, taking into account the difference in surface and volume recombination rates. The expression for photoconductivity spectral response is

$$\sigma_{\text{ph}}(\alpha) = \frac{1 - e^{-\alpha t}}{1 + \zeta \coth(\delta/2)} \times \left\{ 1 + \frac{\zeta \delta [\delta \coth(\delta/2) - \alpha t \coth(\alpha t/2)]}{\delta^2 - (\alpha t)^2} \right\}, \tag{1}$$

where α is the absorption coefficient, t is the thickness, ζ is the ratio of surface to volume recombination rates, $\delta = t/(D\tau)^{1/2}$, D is the diffusion constant, and τ is the volume recombination lifetime. Calculation was done assuming the following values for the various parameters: $t = 10^{-3}$ cm, $\tau \approx 3$ ms, the mean lifetime, calculated from the frequency response of the PC,[12] surface recombination velocity $S = 0.001 - 0.1$ cm/s and the diffusion coefficient $D = 10^{-7} - 10^{-1}$ cm^2/s from earlier calculations of D in MDPs.[13,14] These values restricted the calculation parameter δ from 0.058 to 58 and ζ from 0.000 17 to 17. The structure and the presence of a high electric field inside the material justified the selection of small values for S. The theoretical photoconductivity response with $\zeta = 0.0017$ (high volume recombination) and $\delta = 30$ agreed well with the experimental values. Departure from the theoretical prediction at low energies might be due to the presence of nonphotoconductive transitions and/or high dependence of PC on electric field in this region, whereas the experiments were performed with a constant field for the whole spectral range. The increased dependence of photocurrent on electric field for low-energy photons was evident from Fig. 5. The diffusion constant D, which cannot be calculated using Einstein's relation,[14] could be estimated to be $D \approx 3 \times 10^{-7}$ cm^2 s^{-1}.

Photocurrent showed a power-law behavior of the form $I_{\text{ph}} \propto E^{\beta}$ with respect to the electric field (Fig. 5), with the exponent having lower values at higher photon energies. The value of $\beta = 0.78$ for 3.82 eV (325 nm), 1.2 for 2.81 eV (441.6 nm), and 1.8 for 2.54 eV (488 nm) showed the increasing dependence of I_{ph} on electric field for low-energy photons. This could be due to the fact that carriers, which were photogenerated with high-energy photons, required less activation energy as the excess photon energy was carried away with them in the absence of heating and fluorescence effects.

Dependence of the photocurrent (PC) on intensity of illumination and applied electric field was studied at three different photon energies. Intensity dependence was linear and yielded good fits to the power law, $I_{\text{ph}} \propto W^{\gamma}$, with $\gamma = 0.99$ for 3.82 eV, 1.11 for 2.81 eV, and 1.12 for 2.54 eV (Fig. 6).

The maximum value of the light intensity used was 6.3 mW/cm^2. Linearity of photocurrent with light intensity indicated the absence of bimolecular charge carrier recombination and space-charge effects. It also indicated the absence of heating effects.[15]

Photocurrents were measured as a function of chopping frequency in the range 15–650 Hz at different photon ener-

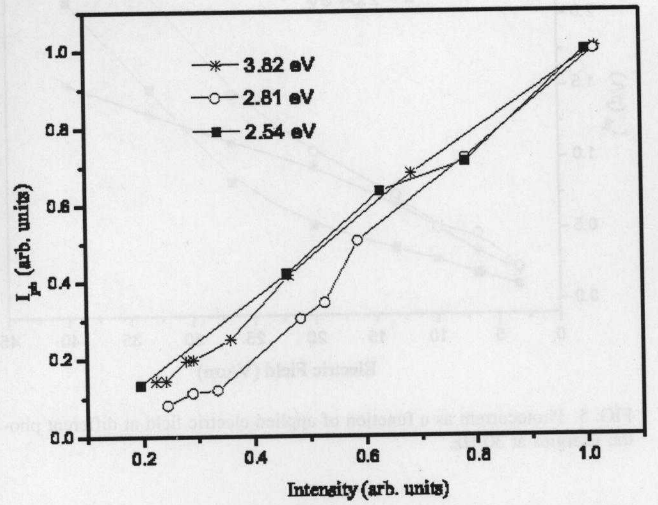

FIG. 6. Intensity dependence of photocurrent at an applied field of 26.6 V/μm, 30 Hz.

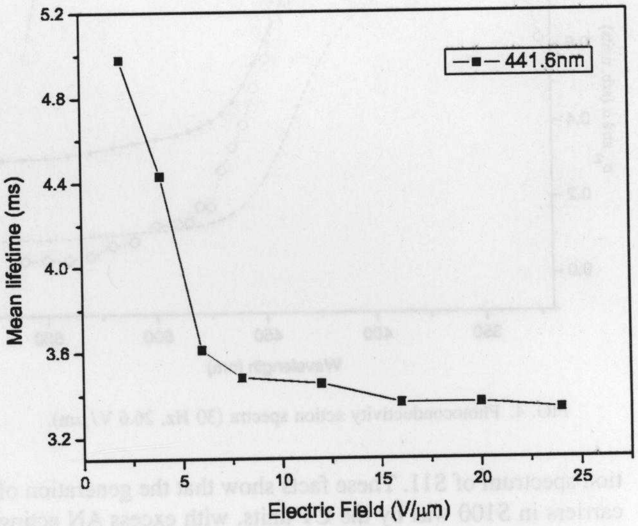

FIG. 8. Dependence of lifetime on the applied electric field.

gies. Graphs with $\log(I_{ph})$ as a function of chopping frequency could be fitted onto linear lines with slopes $m=-0.001$ for 2.54 eV, $m=-0.0016$ for 2.81 eV, and $m=-0.0012$ for 3.82 eV excitations (Fig. 7).

The frequency response of the PC would be proportional to ω^{-1} if there was only a single recombination lifetime involved,[16] and the plot would be a stretched exponential. In the present material, instead of a stretched exponential, a good exponential behavior was observed as shown in Fig. 7. This deviation in frequency dependence from the earlier studies on polymers[17] could be due to the presence of long-lived states with a distribution of lifetimes.[16] As MDPs are highly disordered, a distribution is expected for the energy and lifetime of the states, and the energetic distributions may be calculated from time-of-flight (TOF) transient photocurrents.[5] The similarity in chopping frequency dependence of the PC was due to the similarity in carrier generation at different photon energies. As the activation energy for hopping is dependent on the separation between the molecules,[3] the photocurrent was dependent on the concentration of AN.[18]

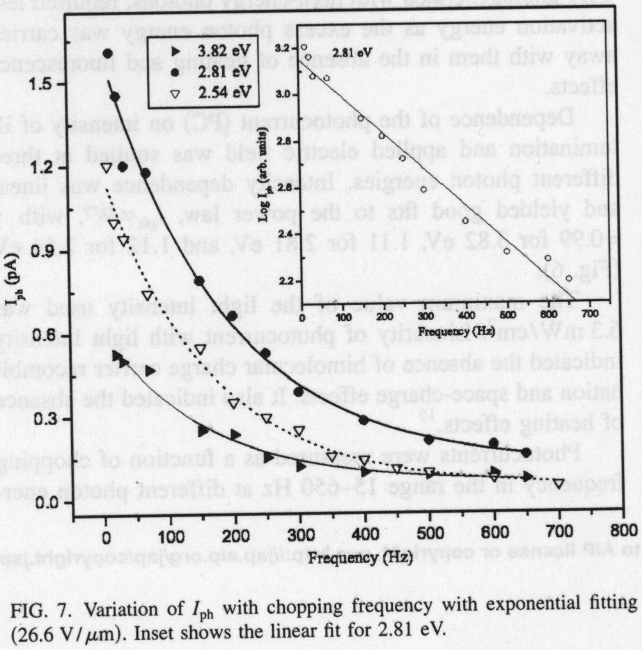

FIG. 7. Variation of I_{ph} with chopping frequency with exponential fitting (26.6 V/μm). Inset shows the linear fit for 2.81 eV.

It was found that the mean lifetime decreased as the field was increased due to the increased rate of dissociation of the long-lived states (Fig. 8). Excited state dissociation to free carriers requires input of energy, as it has to proceed against the Coulombic attraction.[19] This energy can be supplied either by the excess energy of the incoming photon or from the electric field. This was clear from the electric field dependence of the lifetime of excited states and the increased field dependence of the photocurrent yield for low-energy photons. So, the generation of photocurrent can be concluded to be due to the electric field-assisted dissociation of these excited states. Photoinduced absorption measurements can reveal the nature of these excited species in detail.[20]

IV. CONCLUSIONS

Molecularly doped PMMA was found to be a photoconductor having a thermally activated transport behavior. It was found that the formation of a complex shifted the action spectrum to the low-frequency region of the spectrum, and excess donor-type dopant increased the spectral range. A comparison of the experimental action spectrum with the theoretical prediction enabled a rough estimation of the diffusion coefficient of the MDP; however, the verification requires the analysis of TOF signals. The chopping frequency dependence of photocurrent indicated a distribution of lifetimes for the states inside the material, with the lifetime decreasing exponentially with increasing field. It is concluded that generation of photocurrent was due to the field-assisted dissociation of the excited species in the bulk of the material.

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