Analysis of Photogeneration in Organic Photoconductors Based on Azo Pigments and Hydrazone Compounds Using Thermally Stimulated Current

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Abstract

The thermally stimulated currents (TSCs) technique were applied to investigate layered organic photoconductors (OPCs) based on azo pigments and hydrazone compounds. The amount of collected carriers was measured with TSC and discussed in terms of carrier generation mechanism. Temperature and/or electric field dependence of generation, recombination and separation processes of ion-pairs were analyzed by using the layered organic photoconductors using the symmetrical and unsymmetrical azo pigments and hydrazones. The sensitivity of OPC sample was mainly determined by the process of initial ion-pair (or charge transfer state) formation. The difference caused by materials is discussed.

Introduction

We have been using a thermally stimulated current (TSC) technique[1-3] for the studies on carrier generation of OPCs using azo pigments, which shows good generation efficiencies even with light illumination at very low temperature. Using this technique, we observed that the carrier generation efficiency of OPCs using an azo pigment showed very small dependence on temperature and electric field at low temperature (<160K). [3-4] We interpreted the TSC results by using the following model illustrated in Fig.1. The excited state (or exciton) of the azo molecule is first formed by light absorption, migrates, and then an initial ion-pair (charge transfer states) is formed at the surface of the azo pigment particle.[5] Then the ion-pairs separate into free carriers or disappear by recombination, which requires thermal activation. Since thermally activated processes are suppressed at sufficiently low temperature, we could distinguish thermal processes (separation and recombination of ion-pairs) from non-thermal processes (from photon absorption to generation of ion-pairs) and investigate separately by using the TSC technique. In this paper, we report results of this analysis on the OPC samples using symmetrical and unsymmetrical azo pigments and hydrazone compounds.

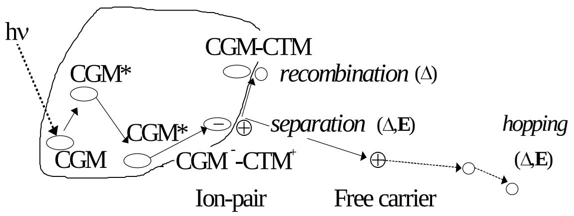


*Figure 1. A schematic illustration of carrier generation mechanism in azo-hydrazone layered OPC. Δ is thermal energy, and **E** is the applied electric field in this figure.*

In the measurements mentioned above, separation and recombination of ion-pairs during the TSC measurements are important processes. We have not fully analyzed the process but we only discussed the overall results. In this paper, we analyzed the process in detail using a simple rate equation model with Arrhenius-type rate constants. We discuss the relation between the rates of separation and recombination.

Experimental

Molecular structures of the azo pigments and the two hydrazone carrier transport molecules (CTMs) used in this work are shown in Fig. 2.

The CGL contains 50wt% bisazo CGM dispersed in poly(vinylbutyral). The CTL is a 50wt% solid solution of a hydrazone (CTM1 or CTM2) in bisphenol A polycarbonate. The CGL and the CTL were coated successively on an aluminized PET film and then semi-transparent aluminum was deposited in vacuum. It formed a sandwich-type electrode structure. The samples were 16-20μm in thickness.

The drift mobility and the oxidation potential of each CTM are shown in Table1. The photoconductive sensitivity of each azo-hydrazone layered OPC sample is shown in Table 2. The OPC sample using CGM2 showed better photoconductive sensitivity than that of the sample using CGM1, when the same CTM was used. The CGM2/CTM2 is the best combination in terms of photoconductive sensitivity of all the OPC samples used in this work.

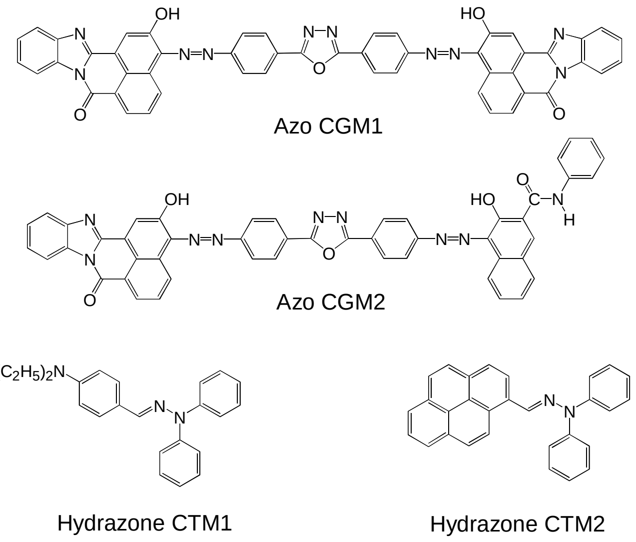


Figure 2. Two azo type pigments and two hydrazone type carrier transport molecules used in this work.

Table 1 Oxidation Potential and Drift Mobility of Each CTM in Bisphenol A Polycarbonate (50wt%).

	Oxidation Potential (V vs. SCE)	Drift mobility a) ($cm^2/(Vs)$)
CTM1	0.52	1.55×10^{-6}
CTM2	0.92	8.51×10^{-6}

a) 307 kV/cm, 25 °C

Table 2 Photoconductive Sensitivity of Each Layered OPC Sample (50wt%).

	Photoconductive sensitivity a) ($cm^2/\mu J$)
CGM1/CTM1	2.3
CGM1/CTM2	4.0
CGM2/CTM1	3.3
CGM2/CTM2	4.8

a) half-decay exposure from 700V, by monochromated light(525nm)

The experimental setup of the TSC measurement was reported previously. [4]

We investigated the electric field dependence of the non-thermal processes (irradiation to ion-pair formation) by applying the electric field stepwise. An electric field F_i was applied until the sample was illuminated and then the electric field was adjusted to F_c to collect carriers. We measured the TSCs by changing the irradiation temperature from 100K to 180K and changing the Fi from 0 kV/cm to 150kV/cm. The F_c was 50kV/cm in all measurements.

We also investigated the collection field F_c dependence. The TSCs were measured with irradiation near 120K under various collection fields from 10kV/cm to 200kV/cm and the applied electric field was kept constant through the measurement (F_i=F_c).

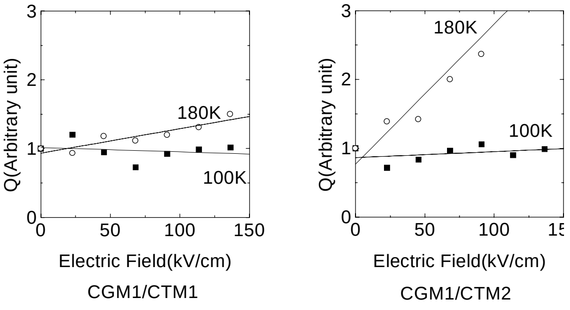
Results and Discussions

Fig. 3 and 4 show the irradiation electric field(F_i) dependence of the generation efficiency for irradiation temperatures of 100K and 180K. The normalized amount of collected carriers is shown in these figures. In each sample, little or no electric field dependence is seen with 100K irradiation while clearer electric field dependence is observed with 180K irradiation.[4] We interpreted this with the partial mobility of the carrier at 180K. The same trend was observed also in the case of CGM2.

From the comparison of Fig.3 and Fig. 4, one can observe the differences related to the CGMs. At 100K, the generation efficiencies are independent of the irradiation electric field F_i irrespective of CGMs. At 180K, the generation efficiencies of CGM1 show steeper dependence than that of CGM2 for the two CTMs.

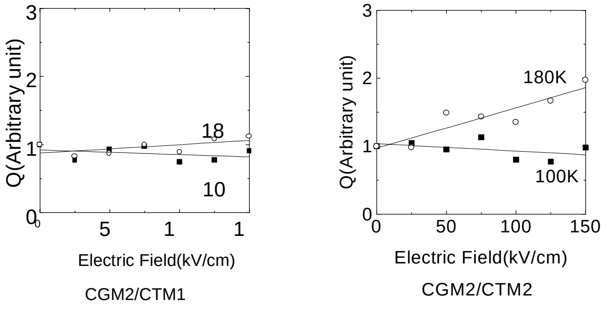
There could be two possible explanations for these differences. One is the electron transport in the CGM particles. If carriers are more mobile in CGM1 than in CGM2 at 180K, one may expect steeper dependence for CGM1. The other is the difference of ion-pair separation/recombination processes during collecting carriers by raising temperature. If the rate of initial ion-pair recombination in the CGM2-based OPCs is smaller than that in the CGM1-based OPCs, more gradual dependence is expected for CGM2, because free carriers are effectively generated irrelevant to the initial separation of the ion-pairs. The second possibility is considered to be more probable, because the electron transport in the azo pigment seemed not to be efficient. The small recombination rate of CGM2 is consistent with the fact that the electric field dependence of the OPC using CGM2 was observed to be smaller than that using CGM1. [6]

The F_c dependence of the generation efficiency is shown in Fig. 5. The collected charge should show saturation because the number of the initially generated ion-pairs limits the amount of collected carriers when the recombination rate becomes negligible against the separation rate. There are two quantities that characterize the saturation behavior, that is, the saturation charge (Q_{sat}) and the electric field strength at which the saturation starts (E_{sat}).



CGM1/CTM1 CGM1/CTM2

Figure 3. The irradiation electric field dependence of the amount of collected carriers at each irradiation temperature for CGM1/CTM1 and CGM1/CTM2.



CGM2/CTM1

CGM2/CTM2

Figure 4. The irradiation electric field dependence of the amount of collected carriers at each irradiation temperature for CGM2/CTM1 and CGM2/CTM2.

E_{sat} should be the electric field where the recombination rate becomes negligible against the separation rate. The small E_{sat} of both OPCs using CTM1 implies that the recombination rate of these OPCs is smaller than other OPCs using CTM2.

Q_{sat} should correspond to the number of ion-pairs generated by irradiation. From comparison between the two samples using the same CTM, Q_{sat} of the sample with the CGM2 is much larger than that of the sample using the CGM1. This fact suggests that the unsymmetrical azo pigment CGM2 has larger initial ion-pairs generation efficiency than the symmetrical azo pigment CGM1.

Q_{sat} of samples using CTM1 shows much smaller value than that of the samples using CTM2 from comparison between the samples using the same CGM. From the above discussion, we conclude that the difference in photogeneration sensitivities of the azo-hydrazone layered samples should mainly come from the generation efficiencies of the ion-pairs or charge transfer between the hydrazone molecule and the azo molecule.

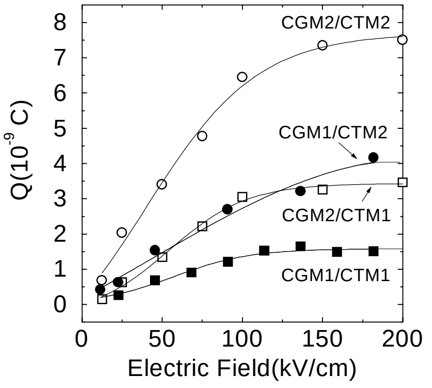


Figure 5. The Fc dependences of collected carriers(Q) with 120K irradiation.

The recombination can be characterized with the transient photocurrent measurements using delayed collection field measurements. We observed that the recombination is especially long in the photoconductor using CGM2 and CTM2. These results also support the discussion mentioned above

Simulation

So far, we used the TSC technique to study the ion-pair separation and recombination processes. However, it is not very clear what is happening during the measurement. We do not know what determines the transition temperature and how the carrier collection process affects the result. To examine the carrier generation processes in the TSC technique more quantitatively, we perform simulation using the following model. Both separation and recombination are thermally activated process and the rate constants of these processes are expressed in Arrhenius-type equations.

$$k^s = k_0^s \exp\left(-\frac{E_a^s}{k_B T}\right), k^r = k_0^r \exp\left(-\frac{E_a^r}{k_B T}\right) \quad (1)$$

where k_s and k_r are the rates of recombination and separation of initial ion pairs, k_B is the Boltzmann constant, T is temperature, and

$$E_a^s \text{ and } E_a^r$$

are the activation energies. Main features of the measurements are described with these parameters. The effect of the electric field should be incorporated into the rate of separation, probably into the activation energy. Here, we have not considered the electric field dependence implicitly.

Then free carriers are produced according to the ratio of the rates of separation and recombination.

$$\begin{aligned} \frac{dC}{dt} &= k^s P \\ \frac{dP}{dt} &= -\left(k^s + k^r\right)P \\ T &= T_0 + \beta t \end{aligned} \quad (2)$$

where C and P stand for the populations of free carriers and initial ion-pairs, respectively, T_0 is the illumination temperature and β is the heating rate. The initial condition is $P(0)=P_0$, $C(0)=0$, where P_0 is the initial concentration of the initial ion pairs.

At very low temperature like 100 K, the two processes actually do not proceed at all. We solved the differential equations (2) numerically with the Runge-Kutta method using a variable step[7], because the appropriate step remarkably changes as the temperature changes in such a wide range in the TSC measurements.

The simulated results were fitted to the observed results[3] of generated charge with wide temperature range irradiation. From the simulation, we found that there are three independent values determined from the observation. First is the transition temperature where the generation efficiency become independent of temperature (~160K).

Second is the slope of the generation efficiency above the transition temperature. Third is the absolute efficiency of carrier separation. From Fig. 5, the carrier separation efficiency at the standard electric field of 50 kV/cm seems to be about 0.3 for all the samples with 120K irradiation if we assume that it becomes 1 (Q_{sat}) under strong electric field. From these three values, all the four parameters

$$(k_0^r,\ k_0^s,\ E_a^r,\ E_a^s)$$

are not determined.

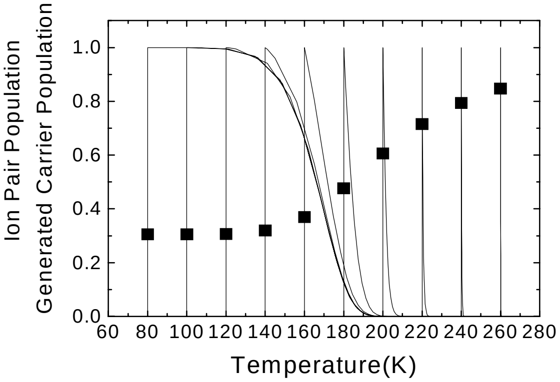


Figure 6. Behavior of ion pair population(solid line) and the amount of collected carriers(square symbol) with irradiation 80K-260K. Populations are normalized to P_0.

$$k_0^r=2.7\text{x}10^6 s^{-1},\ k_0^s=5.9\text{x}10^3 s^{-1},\ E_a^r=0.25eV,\ E_a^s=0.15eV.$$

In Fig. 6, results of the simulation are shown for a set of parameters that give a good fit to the observed data. It shows the decays of the ion-pair population during the heating process after generated from 80K to 260K and the amount of free carriers generated. From ~120K the ion-pair starts to decrease and free carriers are generated. Clear transition temperature is seen around 160K and observed results are well reproduced.

The Onsager's model has been successfully applied to the carrier generation processes of amorphous semiconductors. If the temperature dependence of the diffusion constant is taken into account explicitly, this model could be used. At low temperature, diffusion of the charge is negligible. As the temperature is raised, the charge becomes mobile gradually and separation and recombination take place. The result should be similar to our model.

Conclusion

We observed TSC with CGM excitation to generate carriers and demonstrated the usefulness of the TSC to the application of studies of photogeneration in layered organic photoconductors. Combination of two azo pigments and two hydrazones are studied and discussed. A model for analysis of this measurement is proposed.

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Biography

Takayuki Shoda joined Mitsubishi Chemical Corporation in 1989, after receiving Ph.D degree in quantum chemistry from the University of Hokkaido in 1989. Dr. Shoda worked at the University of Louisville as a postdoctoral fellow from 1993 to 1994. Now, he investigates on organic photoconductor using both computational chemistry and measurements.

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