Organic Photoconductors Using a Novel Charge-Transport Material, 2-[*p*-Di(*p*-tolyl)aminostyryl]-4-methylthiazole

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Organic photoconductors using 2-[*p*-di(*p*-tolyl)aminostyryl]-4-methylthiazole, which is a newly developed material with high hole mobility, as a charge-transport material and τ-type metal-free phthalocyanine as a charge-generation material, have been examined. The photoconductors showed an excellent photoresponse, but had a high residual potential. In order to ascertain the reason for this, the variation of the xerographic gain with the thickness of the charge-transport layer and the electric field was measured. The results suggested that a large energy barrier between 2-[*p*-di(*p*-tolyl)-aminostyryl]-4-methylthiazole and τ-type metal-free phthalocyanine induced a large decrease in the xerographic gain at a low electric field, which caused a high residual potential.

An increasing use of molecularly doped polymers (MDPs) in organic photoconductors (OPCs) and organic light-emitting diodes (OLEDs) has led to much interest in the charge-transport properties of MDPs. The charge-transport properties of the charge-transport layer (CTL), which is an MDP, strongly affect the OPC response times and driving voltage of the OLEDs. The CTL is a homogeneous dispersion of charge-transport materials (CTMs) in host polymers, and it is well known that the CTM molecular structure strongly affects the charge-transport properties. Many researchers have studied the relationships between the molecular structures and their charge-transport properties.[1–6] We also studied the effect of molecular-orbital distributions on the charge-transport properties of MDPs of triphenylamine derivatives, and found that 2-[*p*-di(*p*-tolyl) aminostyryl]-4-methylthiazole (TASMT) has a relatively high hole drift mobility.[7,8] However, it is unclear whether TASMT is a suitable CTM for OPCs, because the electrophotographic properties have not yet been measured. Therefore, we examined the electrophotographic properties of OPCs using TASMT as the CTM. The features of the OPC and the reasons for them are discussed.

Experimental

Figure 1 shows the molecular structures of the charge-generation material (CGMs) and CTMs, and Fig. 2 shows a cross-sectional view of a standard OPC. The CTL is composed of 35 wt% CTM and 65 wt% polycarbonate (General Electric, Lexan 141-111) as a host polymer. A charge-generation layer (CGL), consisting τ-type metal-free phthalocyanine (τ-H_2Pc), is composed of 50 wt% τ-H_2Pc and 50 wt% silicone polymer. A charge-generation layer (CGL) consisting other CGMs shown in Fig. 1 is composed of 60 wt% CGMs and 40 wt% polyester polymer. The electrophotographic properties of the OPC, that is, the initial surface potential (V_0), dark decay ratio (DDR), half decay exposure (E_{50}) and residual potential (V_{r60}), were measured with an apparatus for testing electrostatic recording paper (SP-428, Kawaguchi Electric

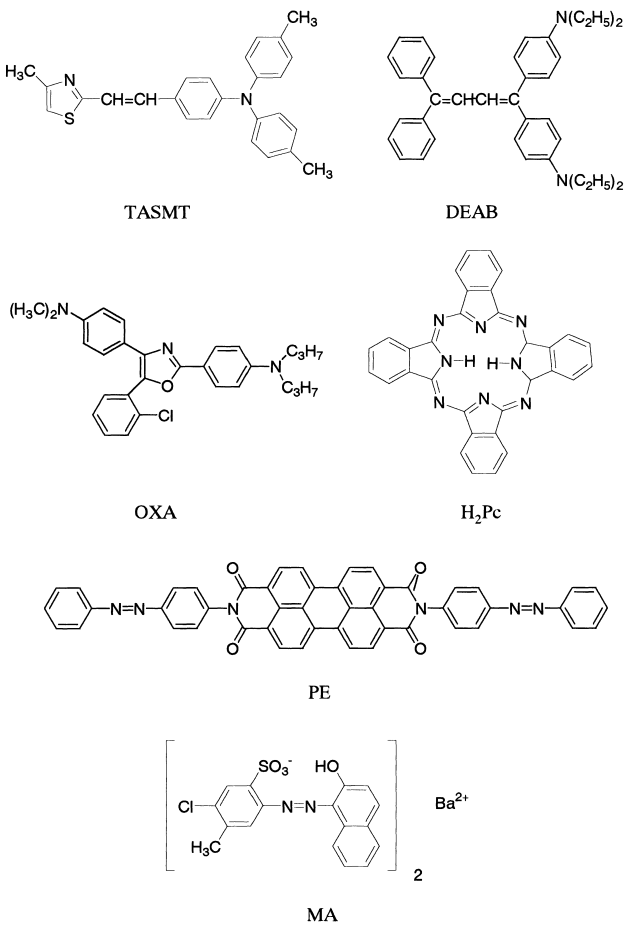

Fig. 1. Molecular structures of the CGM and CTMs used.

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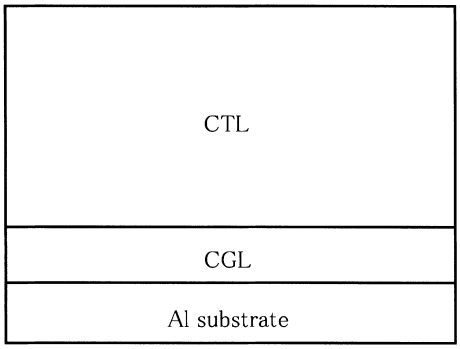

Fig. 2. Cross-sectional view of a conventional OPC as used in this study.

Co.). The measurements were made after a 10 s corona charging of -5 kV (dynamic mode), 30 s standing in the dark and subsequent exposure with a tungsten bulb of 2 lx. The electric potential on the surface of the OPCs was recorded and the voltage at the end of corona charging, which is the initial surface potential (V_0), the voltage at the end of 30 s in the dark (V_{30}), the half-decay exposure (E_{50}) and the voltage at the end of a 60 s exposure, (V_{r60}) were observed. DDR is defined as V_{30}/V_0. The photoresponse and the residual potential at strong exposure (V_r^{sts}) were measured using a high-speed light-decay measurement apparatus (CYNTHIA 30HL, Gentic Co.). In the measurements, OPCs were corona charged until their surface potential reached −700 V. Then, the OPCs were irradiated at the surface potential per thickness of a sample of 45 V/μm with light with a wavelength of 780 nm and a light power of 20 mJ/m^2. The exposure time was 50 ms. The half-decay exposure time of surface potential ($t_{1/2}$) was measured as a parameter of the photoresponse. The residual potential, V_r^{st}, which is defined as a surface potential at certain times after exposure was started, corresponds to the surface potential at the time of the development in actual Laser Beam Printers (LBPs). In order to evaluate the charge-injection properties from several CGMs to CTM, the residual potential at a strong exposure of white light (V_r^{stw}) was measured using an apparatus for testing electrostatic recording paper (SP-428, Kawaguchi Electric Co.). In this measurement, OPCs were corona charged until their surface potential reached −800 V. Then, the OPCs were irradiated at the surface potential per thickness of a sample of 35 V/μm with light of 60 lx with a tungsten bulb. The exposure time was 0.2 s.

Xerographic gains were measured with a high-speed light-decay measurement apparatus (CYNTHIA 30HL, Gentic Co.) according to a pulsed xerographic method.[9] In this method, pulsed light with a wavelength of 780 nm is exposed on the OPCs after corona charging. The intensity of exposure light was chosen in order to suppress the surface potential change by exposure of less than 1/15 of the initial surface potential. The xerographic gain is expressed by $C{\cdot}\Delta V/eN$, where C is the electric capacitance of OPCs; ΔV is the change of the surface potential due to exposure; e is the elementary charge and N is the number of photons of exposure light. The thicknesses of CTL samples for this measurement were about 20 μm.

Results and Discussion

The electrophotographic properties and the half-decay time of the OPCs are given in Table 1. DEAB and OXA were used as references because they are known as CTMs for OPCs, and their mobilities have already been published.[10] DDR and E_{50} of the OPCs with TASMT as CTM are excellent, and almost the same as those with DEAB and OXA. Moreover, $t_{1/2}$ of the OPC with TASMT was shorter than those with DEAB and OXA. This is probably because of the high mobility of TASMT.[7,8] However, V_{r60} of the OPC with TASMT was much higher than V_{r60} of the OPCs with DEAB and OXA.

Table 1. Electrophotographic Properties of the OPCs Using TASMT, OXA and DEAB (35 wt% in the CTLs)

CTMs	V_o/V	DDR/%	E_{50}/lx s	V_{r60}/V	$t_{1/2}$/ms
TASMT	−752	79.7	1.17	−17	14
OXA	−709	75.2	1.15	−1	39.5
DEAB	−709	77.6	1.2	0	14.5

In order to ascertain if this high V_{r60} is a problem for the OPCs used in LBPs, V_r^{sts} of OPCs using TASMT and DEAB were measured. The residual potential, V_r^{sts}, corresponds to the surface potential at the time of the development in actual LBPs. Figure 3 shows the variation of V_r^{sts} with the time after the exposures of OPCs using TASMT and DEAB. Clearly, V_r^{sts} at 0.2 s using TASMT are about 50 V higher than the case with DEAB. This would be a problem for actual OPCs.

Thus, reasons for this behavior were considered. There are two possible reasons. The first is deep traps in the CTL with TASMT. If there are many traps in the CTL, injected holes from the CGL would be caught in them. Therefore, because the surface potential does not drop enough, a high residual potential appears. The second reason is a low injection efficiency from the CGL to the CTL with TASMT. The difference between the ionization potentials (I_ps) of the CGM and CTM strongly affect the hole-injection efficiency. That is, hole injection would be a maximum when the I_ps are almost the same, and a large difference between the I_ps of the CGM and CTM causes a low injection efficiency.[11,12] Because the I_ps of τ-H_2Pc and TASMT were 4.80 eV and 5.25 eV, respectively, the difference is very large, and a low hole injection efficiency would thus result.

The xerographic gains of OPCs using TASMT in CTLs of several thicknesses were measured. If the CTL has deep traps

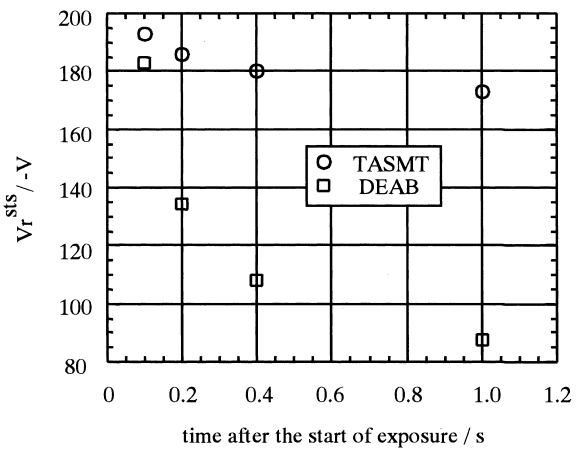

Fig. 3. Variation of V_r^{sts} with the time after the start of exposures of OPCs with TASMT and DEAB.

in it, OPCs with a thick CTL should have many traps.[12] Therefore, the xerographic gains would be low for greater thicknesses of the CTLs. Figure 4 shows that the xerographic gains of OPCs with CTLs of different thickness were almost the same over the whole range of the electric fields. Therefore, there are not significant numbers of deep traps in the CTLs with TASMT. This conclusion is also supported by the result that E_{50} of the OPCs using TASMT and DEAB are almost the same. If there were many deep traps in the CTLs, E_{50} values would decrease, because the decay of the surface potential is slowed by trapping in the CTLs.

Next, xerographic gains of the OPCs using TASMT and DEAB were measured over a range of electric fields. Figure 5 shows the xerographic gains of the OPCs using TASMT and DEAB vs electric field. At a higher electric field than 10 V/μm, the xerographic gains of TASMT and DEAB were almost the same. However, below 10 V/μm, the xerographic gain of TASMT was smaller than that of DEAB. This phenomenon reflects a relatively large difference between the I_ps of CGM and CTM. Even with a large difference between the I_ps of CGM and CTM, holes can be injected from the CGL to CTL because the energy barrier due to the difference of I_ps becomes small at a high electric field. Thus, for a high electric field, large xerographic gains can be obtained even with a large difference of I_ps between CGM and CTM. However, at a low electric field, the energy barrier between CGL and CTL is close to the difference between the I_ps of CGM and CTM. Thus, carrier injection is suppressed, and then xerographic gains drop for a low electric field. This decrease in the xerographic gains for a low electric field has been observed in the case of a large difference of I_ps between CGM and CTM.[13]

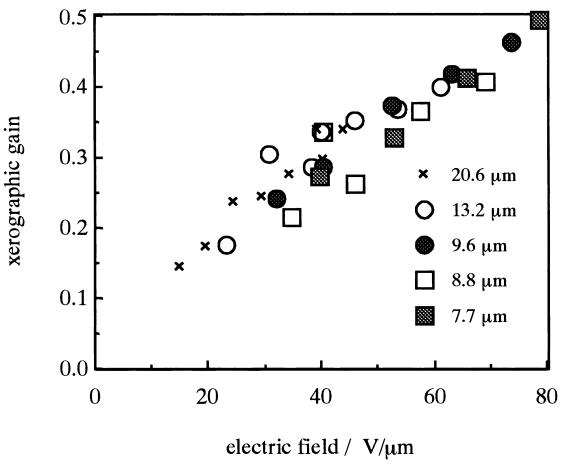

Fig. 4. Xerographic gains of OPCs using TASMT in CTLs of several thicknesses vs electric field.

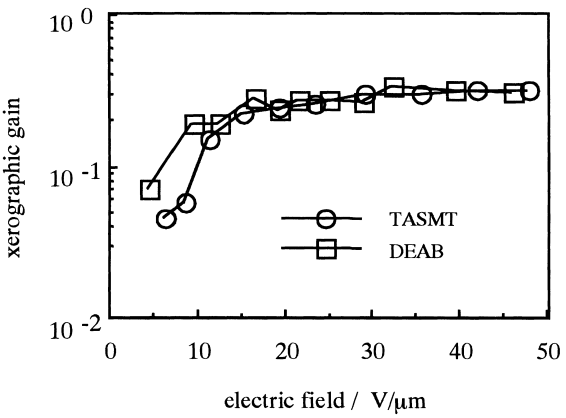

Fig. 5. Xerographic gains of OPCs using TASMT and DEAB vs electric field.

Table 2. I_ps of CGMs and Residual Potential at Strong Exposure of White Light (V_r^{stw}) of the OPCs using τ-H_2Pc, PE and MA as CGMs and DEAB and TASMT as CTMs

CGMs	I_p/eV	V_r^{stw}/V	
		DEAB	TASMT
τ-H_2Pc	4.80	−32	−60
PE	5.35	−36	−22
MA	5.64	−22	−28

I_p of τ-H_2Pc is 4.80 eV and I_ps of TASMT and DEAB are 5.25 eV and 4.76 eV, respectively. Thus, the energy barrier between τ-H_2Pc and TASMT is about 0.45 eV, which is relatively high. On the other hand, there is no energy barrier for holes between τ-H_2Pc and DEAB. Therefore, from the above discussion, the large difference in the I_ps between τ-H_2Pc and TASMT is the reason for the drop in the xerographic gain of TASMT at a low electric field. This drop causes a high residual potential. Therefore, the difference between the I_ps of τ-H_2Pc and TASMT is the reason for the high residual potential.

In order to ascertain this hypothesis, OPCs using some CGMs with I_ps larger than that of TASMT, a perylene compound PE and a monoazo compound MA shown in Fig. 1, and TASMT as CTM were evaluated with OPCs using τ-H_2Pc and TASMT. Since the CGMs have different spectroscopic sensitivities, respectively, the residual potentials at strong exposure of white light (V_r^{stw}) were measured. Table 2 gives the results. The OPC using τ-H_2Pc as CGM and TASMT as CTM showed a high V_r^{stw} value of about 60 V compard with the OPC using DEAB as CTM . On the other hand, OPCs using CGMs of large I_ps , PE and MA, and TASMT as CTM show small V_r^{stw} values, comparable to OPCs with DEAB and τ-H_2Pc. This result confirms the above hypothesis.

Conclusion

The electrophotographic properties of organic photoconductors using TASMT as a charge-transport material (CTM) and τ-H_2Pc as a charge-generation material (CGM) were examined in order to assess the feasibility of TASMT as a CTM. Acceptable properties of the initial surface potential, dark decay ratio and half decay exposure were obtained as well as excellent photoresponse. However, a problem of a high residual potential appeared. In order to ascertain the reason for this, the variation of the xerographic gain with the electric field was measured. It was found that the xerographic gain of TASMT dropped at a low electric field. The results suggested that a large energy gap between τ-H_2Pc and TASMT caused the large decrease of the xerographic gain which, in turn, caused the

high residual potential.

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