CHEMISTRY LETTERS, pp. 1005-1008, 1989.

Charge Carrier Transport Properties of Organopolysilanes and Their Application to Xerographic Photoreceptor

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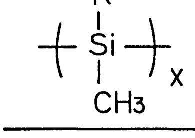
Aiming application of the high hole drift mobility in organopolysilanes, the organopolysilane-based organic layered photoreceptors for electrophotography have been developed with phthalocyanine pigments as a photo-generating material. The photoreceptor combined with titanylphthalocyanine exhibited the high sensitivity of 1.8 $cm^2(\mu J)^{-1}$ at 780 nm and fairly good stability, suggesting the possibility for practical use of organopolysilanes.

Organopolysilanes having a unique structure of the Si backbone and two organic side groups have attracted much attention as a new type of solvent soluble and film-forming amorphous polymers from their potential technological utility. Particularly, the high hole drift mobility as much as $\approx 10^{-4}$ $cm^2V^{-1}s^{-1}$ in organopolysilanes would provide a new class of charge carrier transporting polymeric materials in the field of electrophotography,[1-3] where the high mobility organic materials have been increasingly required for developing high speed and high sensitivity organic photoreceptors. Recently, Stolka et al.[4] showed the possibility of application of an organopolysilane, poly(phenylmethylsilane), to the xerographic photoreceptor combined with selenium as a charge photo-generating material. The genuine organic photoreceptors combined with organic pigments such as phthalocyanines, however, have not been established.

In the present letter, we would like to report some charge carrier transport properties of three typical organopolysilanes necessary for fabricating organic photoreceptors and the first example of organic double-layered photoreceptors

Table 1. Ionization potentials(I_p), hole drift mobilities($\mu_{r.t.}$) and activation energies(E_a) of organopolysilanes

Organoploysilanes		R	I_p	μ r.t.$^{a)}$	E_a
			eV	$cm^2V^{-1}s^{-1}$	eV
 $-\!\!(\mathrm{Si(R)(CH_3)})\!\!-_x$	$(PhMeSi)_x$	C_6H_5	5.62	9.0×10^{-5}	0.28
	$(n\text{-}ProMeSi)_x$	$n\text{-}C_3H_7$	5.77	1.6×10^{-4}	0.15
	$(c\text{-}HexMeSi)_x$	cyclo-C_6H_{11}	5.92	9.2×10^{-5}	0.22

a)Hole drift mobility at room temperature, $F = 1 \times 10^5$ V cm^{-1}.

using high mobility organopolysilanes combined with phthalocyanine pigments as a charge photo-generating material. The photoreceptors constructed showed fairly high sensitivity with the sufficient use of high mobility of organopolysilanes, indicating strong possibility for practical use.

Organopolysilanes selected are poly(phenylmethylsilane); $(PhMeSi)_x$, poly(n-propylmethylsilane); $(n\text{-}ProMeSi)_x$ and poly(cyclohexylmethylsilane); $(c\text{-}HexMeSi)_x$ as shown in Table 1. These polymers were synthesized according to the literature$^{5)}$ and the molecular weights were >5000 as measured by GPC using polystyrene for calibration. The hole drift mobility was measured by the usual time-of-flight (TOF) technique with N_2 gas laser pulse as described elsewhere.$^{6)}$ Ionization potentials were measured by a low energy photo-electron emission analyzer (AC-1, Rikenkeiki Co. Ltd).$^{7,8)}$ Photo-induced surface potential discharge (PID) measurements to estimate the photo-response of the photoreceptors were carried out by an electrostatic paper analyzer EPA-8100 (Kawaguchi Electric Works Co. Ltd.) in static mode using white light (20 lux) or 780 nm monochromatic light (10 μW cm^{-2}).

Figure 1 shows the temperature dependence of the hole drift mobility of the present organopolysilanes under an applied field of 1×10^5 V cm^{-1} in an Arrhenius representation of log μ vs. 1/T. In the vicinity of room temperature all of the organopolysilanes exhibit much higher drift mobility of $\approx 10^{-4}$ cm^{2}V^{-1}s^{-1} compared with that of molecularly dispersed polymeric materials of DEH (N,N-diethylaminophenylhydrazone; DEH : polycarbonate resin = 1:1), for example, which is widely used as a charge carrier transporting material. The mobilities in $(PhMeSi)_x$ and $(c\text{-}HexMeSi)_x$ both having high glass transition of $\approx$ 130 °C show good straight lines with relatively low activation energy of 0.28 and 0.22 eV, respectively, while the mobility of $(n\text{-}ProMeSi)_x$ levels off just above its glass transition of -23 °C and decreases at the temperature region showing thermochromic behavior$^{8,9)}$ just below the melting point of 39 °C. This indicates that the mobility of organopolysilanes is sensitive to the segmental motion and σ conjugation length of Si backbone.$^{6)}$ Interestingly, the carrier transport properties of organopolysilanes, in which charge carrier is considered to be transported through the Si-Si σ conjugation of the backbone chain, are well described by the Gill's empirical expression for the charge hopping conduction.$^{10)}$ This fact suggests that the charge carrier transport even in organopolysilanes is controlled by charge hopping probably through the intrinsic states derived from domain-

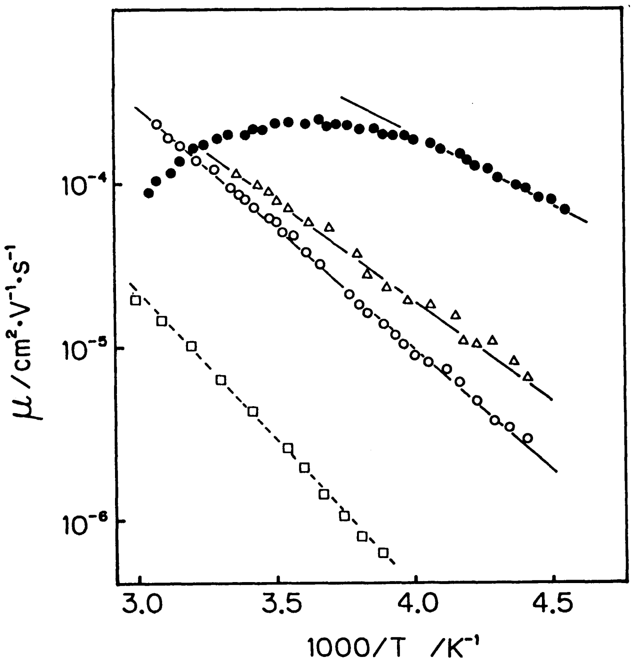
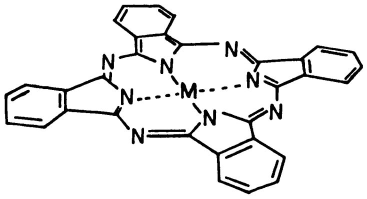


Fig. 1. Temperature dependences of hole drift mobilities of typical three organopolysilanes, (○);$(PhMeSi)_x$, (●); $(n\text{-}ProMeSi)_x$, (△);$(c\text{-}HexMeSi)_x$ at F= 1×10^5 V cm^{-1}, (□);DEH/PC(1:1) at F= 5×10^5 V cm^{-1}.

like segments of the main chain as reported by Abkowitz et al.[2)] and us.[6)] The low activation energy of 0.2-0.3 eV compared with other available amorphous organic solids, is desirable for a charge transport material in the layered photoreceptors. Thus, organopolysilanes have the excellent charge transport properties.

For the effective hole injection in the layered organic photoreceptors consisting of charge generation (CGL) and charge transport (CTL) layers, in general, the lower ionization potential of the material in CTL than that in CGL is required. The present organopolysilanes gave the value of 5.62-5.94 eV depending on the side-group substituents[8)] as shown in Table 1. $(PhMeSi)_x$ capable of interaction between Si backbone σ and side-group π electrons gave lower ionization potential than $(c\text{-}HexMeSi)_x$ and $(n\text{-}ProMeSi)_x$ with only alkyl side-groups. The lower ionization potential of $(n\text{-}ProMeSi)_x$ compared with $(c\text{-}HexMeSi)_x$, although both have alkyl substituents, is considered to be attributed to the difference in the σ conjugation length depending on the Si backbone conformation as discussed in our previous paper.[8)] Therefore, if these organopolysilanes are combined with phthalocyanine pigments (Fig. 2) having ionization potentials of 5.2-5.4 eV as a charge photo-generating material, $(PhMeSi)_x$ with lower ionization potential is suitable for effective hole injection, although it still has small energy barrier to be thermally activated. In this sense, the hole injection from phthalocyanine pigments to organopolysilanes in the layered photoreceptors is of interest.

We have prepared the photoreceptors consisting of a carrier generation layer (CGL: 0.5 μm) of respective phthalocyanines shown in Fig. 2 dispersed in polyvinylbutyral resin with 50 wt% loading on an aluminum substrate and a carrier transport layer (CTL: ≈ 7 μm) of organopolysilanes over-coated by wired-bar technique from toluene solution. Figure 3 shows a typical photo-induced surface voltage decay curve for the combination of titanylphthalocyanine (TiOPc) and $(PhMeSi)_x$ in the negative charge mode. Reflecting the high mobility of organopolysilanes, the photoreceptor showed the excellent photo-response in spite of the energy barrier existed for the hole injection, and the half-decay exposure of 1.4 lux·s obtained is sufficiently of practical use. The combination with metal-free phthalocyanine (H_2Pc) gave slightly poor photo-response of 6.4 lux·s. This depends rather on the charge carrier photo-generating abil-



MPc	I_p /eV
TiOPc	5.38
H_2Pc	5.40

Fig. 2. Phthalocyanine pigments as a charge photo-generating material and their ionization potentials.

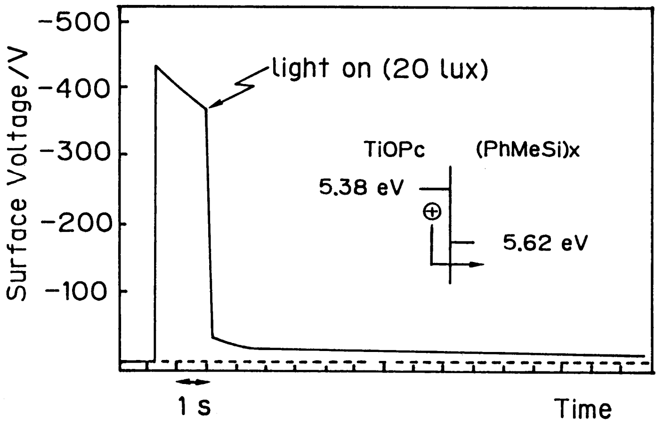


Fig. 3. The photo-induced discharge curve in $(PhMeSi)_x$/TiOPc photoreceptor by irradiation of white light (20 lux). The inset shows the energy barrier due to the difference of the ionization potentials.

Table 2. Half-decay exposures of several organopolysilane-based photoreceptors

MPc	Half-decay exposure /lux·s $(PhMeSi)_x$	$(n\text{-}ProMeSi)_x$	$(c\text{-}HexMeSi)_x$
TiOPc	1.4	1.1	2.1
H_2Pc	6.4	7.2	8.3

ity of TiOPc and H_2Pc. In Table 2 are listed the half-decay exposures for other organopolysilanes. The influence of the energy barrier appeared in residual potentials. The value of -20 – -30 V was observed for $(c\text{-}HexMeSi)_x$ which has large ionization potential of 5.92 eV, i.e., large hole injection energy barrier, while the lower residual potential of -10 – -20 V was obtained for $(PhMeSi)_x$ and $(n\text{-}ProMeSi)_x$ reflecting relatively small energy barriers of 0.2-0.3 eV. There was found to be no need of anxiety about photo-degradation of organopolysilanes due to corona charge in the xerographic process. Thus, from the practical standpoint, the combination of TiOPc and $(PhMeSi)_x$ seems to be most useful, and the photoreceptor exhibited the high sensitivity of 1.8 $cm^2(\mu J)^{-1}$ for monochromatic light of 780 nm, suggesting possibility of practical use as a photoreceptor for laser beam printer. Actually, the printing test using a TiOPc/$(PhMeSi)_x$ layered photoreceptor in a commercially available laser beam printer gave a good quality of the printing images and good stability.

In conclusion, we have demonstrated the first example of organic photoreceptors for electrophotography using organopolysilanes in combination with phthalocyanine pigments as a charge photo-generating material, and showed to be able to make the best use of the high mobility of organopolysilanes for high sensitivity layered organic photoreceptors.

The authors wish to thank Drs. N. Matsumoto and M. Fujino of NTT Basic research Laboratories for their cooperation.

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(Received March 22, 1989)