

# Electrophotographic properties and ultraviolet light fatigue of dual-layered photoreceptors incorporating phthalocyanine and hole transport polymers

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Dual-layered photoreceptors incorporating  $\tau$ -form metal-free phthalocyanine ( $\tau$ -H<sub>2</sub>Pc) for charge generation material and poly(methylphenylsilylene) (PMPS) for charge transport material (CTM) have been studied concerning their electric properties especially in the electrophotographic characteristics. The photoreceptor using PMPS exhibited high sensitivity; however, the fatigue due to ultraviolet (UV) light was observed. We compared them with well-known poly(N-vinylcarbazole) for CTM based on surface potentials, sensitivities, hole carrier mobilities, and conductivities. As a result of Gel permeation chromatography, Fourier transform infrared and x-ray photoelectron spectroscopy spectra before and after UV light irradiation, the PMPS was cleaved into lower molecular weight products and polymerized, which included cross-linking.

## I. INTRODUCTION

Polysilylenes with aliphatic or aromatic side groups and consisting of a Si backbone are currently being investigated as charge transport materials (CTMs) of photoreceptors in electrophotographic fields.<sup>1-4</sup> In these polymers, the  $\sigma$ -bonded main chain is made up Si atoms, and many of their properties are different when compared to analogous carbon-based polymers such as poly(N-vinylcarbazole) (PVK), which have  $\pi$ -conjugated systems. Hole carrier mobilities of some polysilylenes were measured using the time-of-flight (TOF) technique.<sup>5-10</sup> Hole transport in polysilylenes were initially considered to proceed through  $\sigma$  conjugation in the Si backbone chains. Abkowitz *et al.*, however, described that the microscopic transport process of polysilylenes is hopping between the backbone-derived localized state, which can be associated with a domain-like suborganization of the Si backbone.<sup>2</sup> On the contrary, the hole carriers in PVK have completely dominated the overlapping state of the carbazole group.<sup>11-13</sup>

Polysilylenes have an intense ultraviolet (UV) absorption band, and act as radiation-sensitive polymers.<sup>14-17</sup> These primary photoproducts react via H abstraction, cross-linking, and oxidation to give silanol terminated polymers and cyclosiloxanes.<sup>18</sup> By taking advantage of these phenomena, for example, the electrophotographic multiduplication process using polysilylenes based on UV photodecomposition was developed by Yokoyama *et al.*<sup>19</sup>

In this paper, the dual-layered photoreceptors using  $\tau$ -form metal-free phthalocyanine ( $\tau$ -H<sub>2</sub>Pc) for charge generation material (CGM) and poly(methylphenylsilylene) (PMPS) for charge transport material were investigated as to their electrophotographic and UV light fatigue properties. In addition, we compared them with well-

known PVK for sensitivities, surface potentials and residual potentials for practical use in laser beam printers (LBPs) which has a diode laser for its light source. Additionally, the light fatigues for UV light under the conditions of atmosphere and vacuum have been investigated.

## II. EXPERIMENTAL SECTION

### A. Materials

The  $\tau$ -H<sub>2</sub>Pc used for CGM was obtained from previously described methods.<sup>20</sup> The PMPS was synthesized as follows. Molten Na (40 wt% Na powder in 12 ml toluene) and 100-ml toluene solution were added to a flask containing nitrogen. After momentary stirring, the dichloromethylphenylsilane (15 ml) was added dropwise for 30 minutes, and was continuously stirred at 110 °C for 3 hours. After purification of the slurry, 1.3 g of PMPS was obtained. The PMPS dissolved in tetrahydrofuran (THF) was poured into 2-propylalcohol for recrystallization, and then washed with alcohol. The PVK was obtained from Takasago Perfumery Corporation and used without further purification.

### B. Fabrication of photoreceptors

Materials used in this study for the charge generation material (CGM) and conductive polymers for the charge transport layer (CTL) are shown in Fig. 1. Electrophotographic measurements were obtained from photoreceptor devices on Al substrate. A dual-layered photoreceptor is constructed with a thin charge generation layer (CGL) contiguous with a CTL. The substrate is used a 100- $\mu$ m aluminum plate. The CGL consists of 50 wt%  $\tau$ -H<sub>2</sub>Pc dispersed with poly(vinyl butyral) resin in THF, with a thickness of 0.3  $\mu$ m. The CTL was composed of conductive

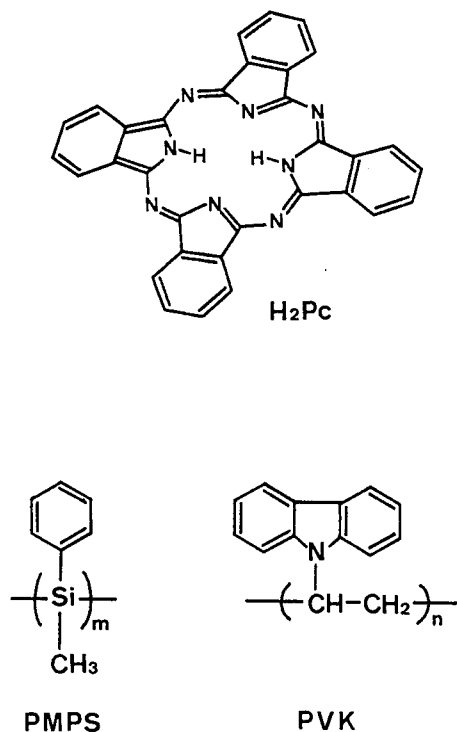


FIG. 1. Structures of  $\tau$ -H<sub>2</sub>Pc and hole carrier transport polymers.

polymers, which are PMPS or PVK, prepared by dissolving in toluene and methylene dichloride, respectively, and coating onto the CGL at a thickness of 10~20  $\mu\text{m}$ . Ionization potential(Ip) was measured by a Riken-Keiki AC-1 photoelectron emission spectrometer in air at room temperature.

### C. Electrophotographic measurements

Electrophotographic measurements were made by a Kawaguchi Electric EPA-8100 Electrophotographic Paper analyzer, using a halogen-lamp light source. The wavelength was selected by interference filters. Photoinduced discharge(PID) curves were measured in terms of surface potential versus time. The measurements were run so that there was a charge, and charging process with a 2-s dark decay period and a 3-s light exposure period.  $V_0$  is the initial dark potential before the light irradiation. The values of  $V_0$  were adjusted by control of the applied corona charge. The residual potential ( $VR_3$ ) is a surface potential after 3-s exposure. The surface potential was measured by an electrostatic voltmeter at various exposures. A half-decay exposure sensitivity( $E_{1/2}$ ) is the exposure for surface potential to a half-decay exposure.

### D. Light fatigue measurements

To measure the light fatigues of polymers with electrophotographic properties, UV light was irradiated from the surface side of the photoreceptor. The light was adjusted through the UV light irradiation filter (Toshiba Glass; UV-D33S) from the Xe-lamp. The light intensities were

0.3 or 3  $\text{mW}/\text{cm}^2$ . The irradiation period at 3  $\text{mW}/\text{cm}^2$  for measuring the molecular weight distribution and ir spectra was one hour.

### E. Hole carrier mobility and conductivity measurements

The sample cells for hole carrier mobility measurements consisted of the PVK or PMPS thin films of approximately 10  $\mu\text{m}$  on NESA glass. The thin films were cast from PVK in methylene dichloride or PMPS in toluene. A semitransparent Au electrode was vacuum deposited on the film surface to form a sandwich-type cell. Hole carrier mobilities of the charge transport polymers were measured by the TOF technique using a N<sub>2</sub> laser pulse(5 ns of pulse duration at 337 nm) irradiated on a positively biased NESA glass under  $10^{-3}$  Torr at  $E = 2 \times 10^3 \sim 5 \times 10^5$  V/cm.

The conducting variations of polymers were measured by the same sandwich-type cells used in TOF measurements. Dark-( $\sigma_d$ ) and photoconductivities( $\sigma_{ph}$ ) of the films can be calculated by the following equation.

$$\sigma = 1/\rho = d \cdot I/S \cdot V,$$

where  $\sigma$  is the conductivity(S/cm),  $\rho$  the resistivity,  $d$  the thickness of the film(cm),  $I$  the current(A),  $S$  the area of the electrode ( $\text{cm}^2$ ), and  $V$  the applied voltage (V). The current was measured using a Keithley 617 electrometer.

### F. Analytical measurements

Electronic absorption spectra were measured on a Shimadzu UV-2100S spectrometer, using thin films of pigment dispersed in poly(vinylbutyral) or conductive polymers. Molecular weight distributions of samples dissolved in THF were detected by a GPC technique with a RI detector. The 0.2 wt% sample solution was injected into the equipment at a constant rate (1.0 ml/min). IR spectra were measured on a JEOL Fourier Transform Infrared(FT-IR) Spectrometer JIR-100. X-ray photoelectron spectra(XPS) were measured using the Perkin-Elmer PHI-5400 ESCA system with an MgK $\alpha$  x-ray target.

## III. RESULTS

### A. Electrophotographic characteristics

The electronic absorption spectra of solid thin films of conductive polymers are shown in Fig. 2. The absorption peaks of PMPS are observed at 300 and 345 nm, which are assigned to the  $\sigma$ - $\sigma^*$  transition of carbons and Si-Si main chains, respectively. The PVK peaks are 308, 339 and 353 nm, and assigned to the  $\sigma$ - $\sigma^*$  transition of carbons.

Spectral dependences of electrophotographic sensitivities of the photoreceptors from 450 to 850 nm, and electronic absorption spectrum of CGL are shown in Fig. 3. The spectral responses are dependent on the absorption spectrum of CGL. Figure 4 shows the PID curves of surface potentials with photoreceptors at 780 nm. Especially, the photoreceptor using PMPS for CTL exhibits high sensitivity, that is, the half-decay sensitivity( $E_{1/2}$ ) is over 0.50

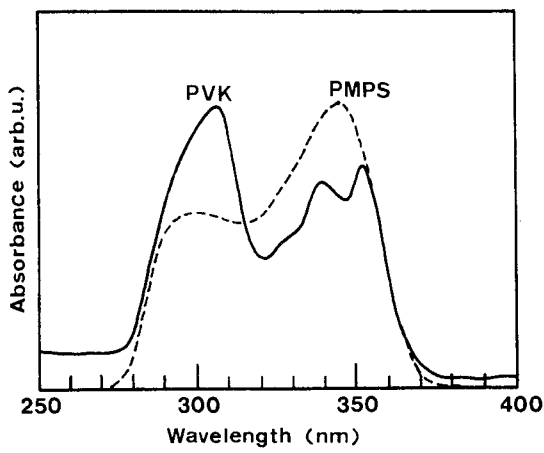


FIG. 2. Electronic absorption spectra of thin films of PMPS and PVK.

$\mu\text{J}/\text{cm}^2$  at a wavelength of 600~800 nm. The maximum sensitivity is measured at 800 nm, and its sensitivity is  $0.28 \mu\text{J}/\text{cm}^2$ . On the contrary, the photoreceptor using PVK for CTL exhibits  $E_{1/2} = 0.42 \mu\text{J}/\text{cm}^2$  at 800 nm. The initial PID curves in Fig. 4 also exhibit the superiority of PMPS. The residual potential of PMPS is approximately  $-30 \text{ V}$ , which is lower than that of PVK. Both photoreceptors, however, are suitable for LBPs equipped with a laser diode. The sensitivities would be affected by the differences in  $I_p$  between CGL and CTL, and the hole carrier mobilities in CTL. In practice, the  $I_p$  of CGL, PMPS and PVK films are 5.14, 5.64 and 5.74 eV, respectively.

### B. Variation in surface potential for UV light

The variations in the electrophotographic characteristics of photoreceptors as a function of UV irradiation time under the conditions of atmosphere and vacuum ( $10^{-3}$  Torr) are shown in Figs. 5 and 6. Figure 5 shows the

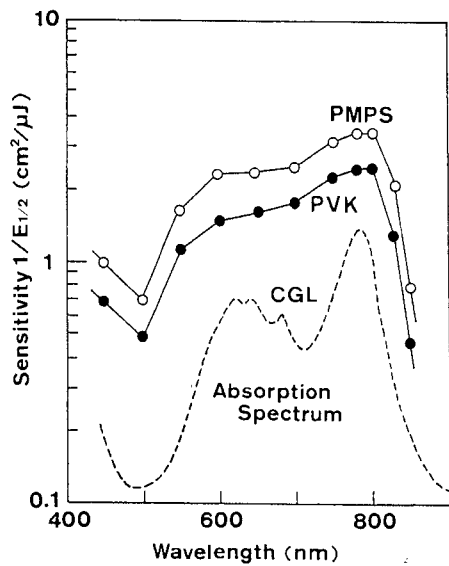


FIG. 3. Spectral sensitivities of photoreceptors and electronic absorption spectra of CGL used  $\tau\text{-H}_2\text{Pc}$ .

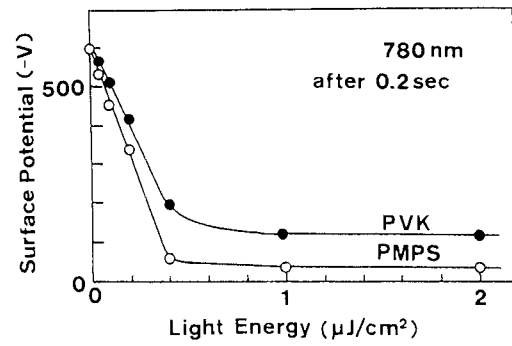


FIG. 4. Photoinduced decay curves of surface potentials with photoreceptors at 780 nm. CGM:  $\tau\text{-H}_2\text{Pc}$ , CTM: PMPS or PVK.

variations in surface potentials ( $V_0$ ). Since these photoreceptors are almost the same thickness, ca.  $15 \mu\text{m}$ , the surface potential of PMPS is higher than that of PVK. In Fig. 5(a), for the case of  $0.3 \text{ mW}/\text{cm}^2$ , the  $V_0$  of both photoreceptors are the same value. Large variations of  $V_0$  can be seen at  $3 \text{ mW}/\text{cm}^2$ , that is, the  $V_0$  of PMPS increases from  $-755 \text{ V}$  to  $-950 \text{ V}$  with increasing UV light irradiation time, and the  $V_0$  of PVK decreased in the initial 5 min

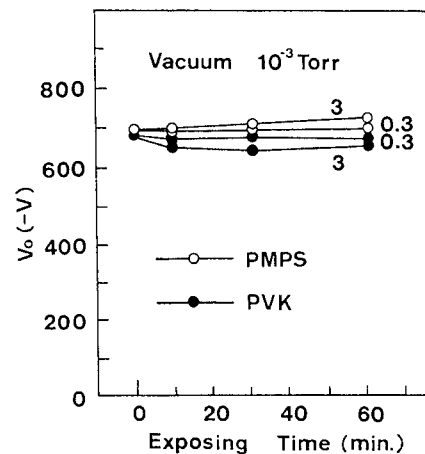
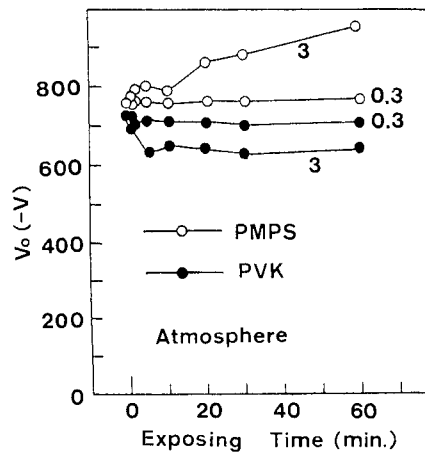


FIG. 5. Surface potentials of UV light irradiated photoreceptors as a function of exposing time. Numerals in the figure represent the light intensities of Xe lamp using UV-D33S filter. (a) atmosphere, (b)  $10^{-3}$  Torr.

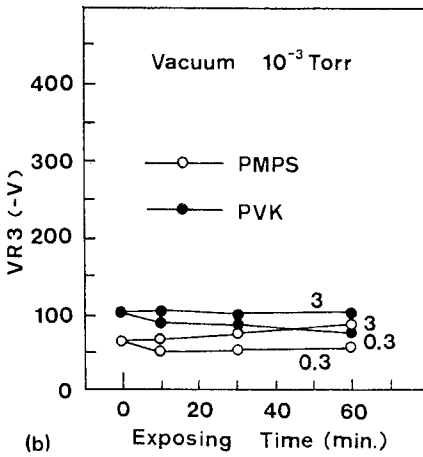
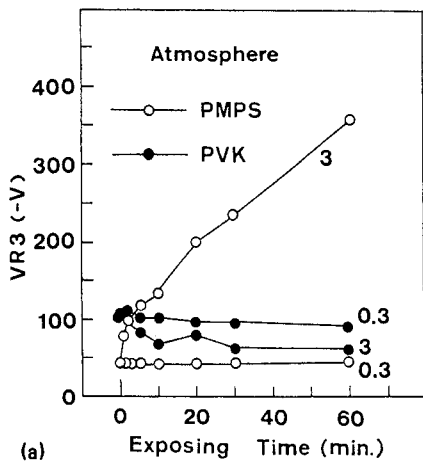


FIG. 6. Residual potentials of UV light irradiated photoreceptors as a function of exposing time.  $VR_3$  is the residual potential at 3 s after exposure. Numerals in the figure represent the light intensities of Xe lamp using UV-D33S filter. (a) atmosphere, (b)  $10^{-3}$  Torr.

from  $-730$  V to  $-635$  V, however, after this initial decrease, the  $V_0$  became constant as was the case of  $0.3$   $\text{mW}/\text{cm}^2$  UV light irradiation. The  $V_0$ s of these photoreceptors would be influenced by atmospheric oxygen at least over  $3$   $\text{mW}/\text{cm}^2$ . On the contrary, the  $V_0$ s of both photoreceptors are practically constant at  $10^{-3}$  Torr. This result also supports the fact that the influences of atmospheric pressure are very large for the surfaces of polymer films. The  $VR_3$  also suggests a large influence by atmospheric pressure. These results support the formation of an insulator in or on the PMPS film. Since the  $3$   $\text{mW}/\text{cm}^2$  UV light produces affects variations, the light intensity of  $3$   $\text{mW}/\text{cm}^2$  is hereinafter used to analyze the influences of polymer films by UV light.

### C. Hole carrier transport

Figure 7 shows the electric field and square root of electric field dependence of the hole carrier mobilities. In Fig. 7(a), the mobilities increase with increasing electric field. The mobilities of PMPS exhibit over  $10^{-4}$   $\text{cm}^2/\text{V s}$ , and these of PVK are  $10^{-6} \sim 10^{-7}$   $\text{cm}^2/\text{V s}$ . In Fig. 7(b), both mobilities exhibit a linear relationship, which show the Poole-Frenkel dependence of the mobility.

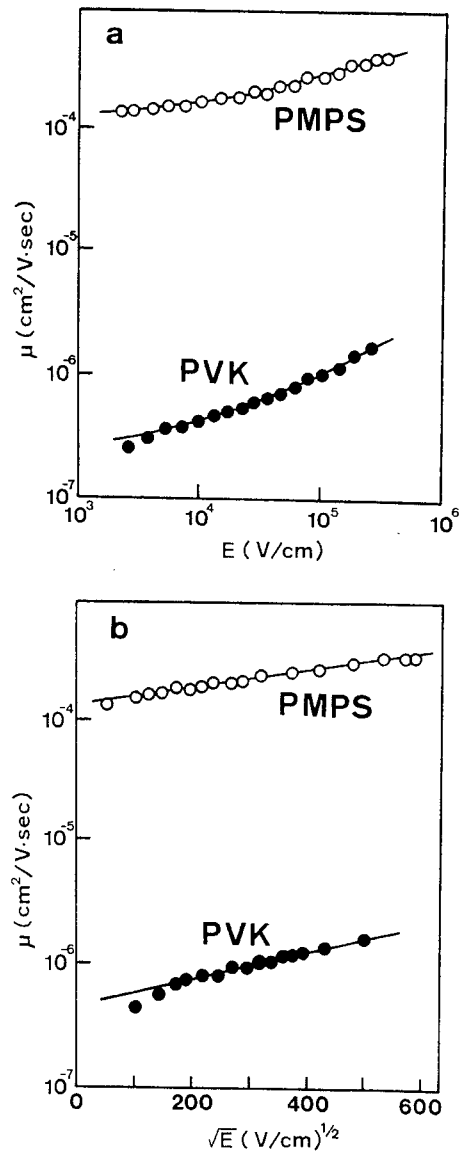


FIG. 7. Electric field dependence of hole carrier mobility of PMPS and PVK.

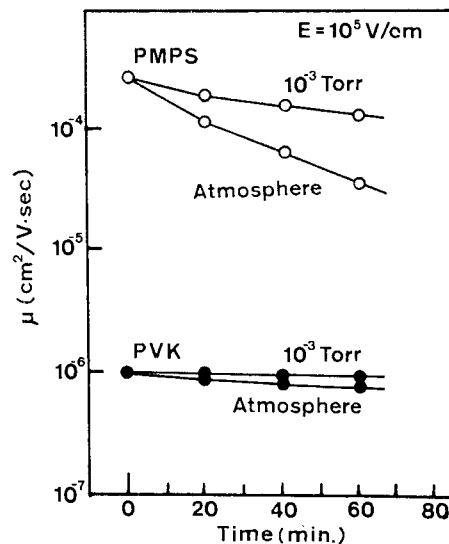


FIG. 8. Variations of hole carrier mobility with PMPS and PVK as a function of UV light irradiating time.

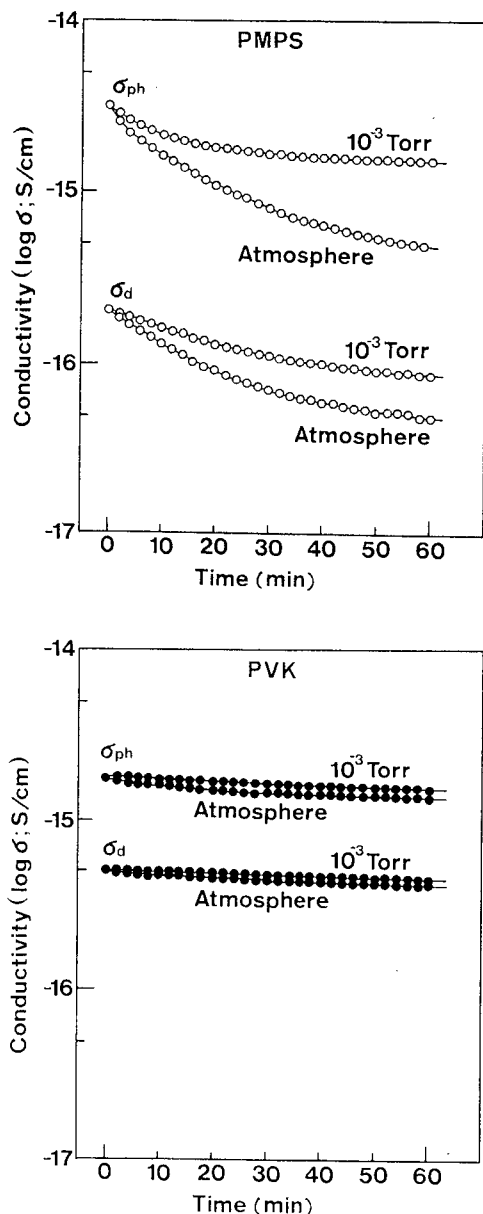


FIG. 9. Variations of conductivity with PMPS and PVK as a function of UV-light irradiating time. Light intensity is  $3 \text{ mW/cm}^2$ .

The hole carrier of polysilylene would be transported through the  $\sigma$  conjugation of the Si-Si backbone. It doesn't have deep traps which result from the chemical structure. On the contrary, since the PVK has structural deep traps, the resulting mobility is rather low compared with that of PMPS.

Figure 8 shows the variations of hole carrier mobility of PMPS and PVK films as a function of UV light irradiation time under the conditions at atmosphere and  $10^{-3}$  Torr, respectively. Hole carrier mobility of PMPS decreases with increasing the UV light irradiation time, especially the mobility at atmospheric pressure decreases approximately an order of magnitude for one hour. Hole carrier mobility of PVK is somewhat constant in this period. This is because PMPS will be influenced by the existence of oxygen in atmosphere.

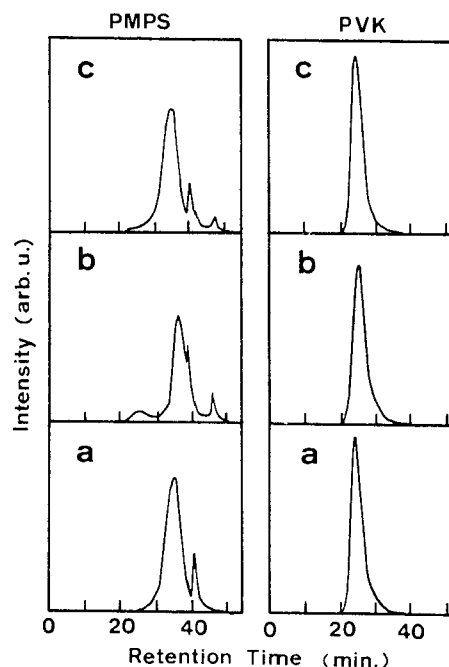


FIG. 10. Molecular weight distribution of before and after UV-light irradiation to photoreceptors of PMPS and PVK. (a) before irradiation, (b) atmosphere, (c)  $10^{-3}$  Torr. Light intensity is  $3 \text{ mW/cm}^2$ .

#### D. Conductivity

The variations of dark- and photoconductivities of PMPS and PVK films under the conditions at atmospheric pressure and  $10^{-3}$  Torr are shown in Fig. 9. Conductivities support the variations in mobilities on PMPS and PVK. In the case of PMPS, the insulated layer is formed from the surface of the film by the UV light irradiation, therefore, the conductivity decreases with increasing the irradiation time. The conductivity of PVK is constant in this period similar to the results of mobility on PVK.

#### E. Molecular weight distribution

Figure 10 and Table I show the molecular weight distributions of PMPS and PVK films under the conditions at atmospheric pressure and  $10^{-3}$  Torr before and after UV light irradiation. The molecular weight distributions of PMPS are varied by the conditions of the UV light irradiation. Typically, the PMPS synthesis produces a mixture of

TABLE I. Molecular weight distributions of PMPS and PVK before and after UV light irradiations. Light intensity is  $3 \text{ mW/cm}^2$ .

CTM	Conditions					
	UV-light	Time (min)	Atmosphere (Torr)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
PMPS	before	0	...	2030	10 200	5.03
	after	60	atmosphere	330	22 000	66.3
	after	60	$10^{-3}$	1820	12 000	9.21
PVK	before	0	...	114 000	516 000	4.55
	after	60	atmosphere	151 000	550 000	4.54
	after	60	$10^{-3}$	123 000	521 000	4.55

products: a cyclic oligomer and a linear polymer. The molecular weight distributions of PMPS used in this study are  $\overline{M}_n = 2030$ ,  $\overline{M}_w = 10\,200$  and  $\overline{M}_w/\overline{M}_n = 5.03$ . After UV light irradiation, the average molecular weight is changed to  $\overline{M}_n = 330$ ,  $\overline{M}_w = 22\,000$  and  $\overline{M}_w/\overline{M}_n = 66.3$  under atmospheric conditions. The PMPS after UV light irradiation has a high molecular weight polymer (3.7%) at a retention time of 24.3 min, and low molecular weight oligomers or degradation products (2.7%) at 44.3 min. From these results, it is presumed that the polymerization and decompositions are produced at the same time by the UV light irradiation under atmospheric conditions. On the contrary, the variations in the average molecular weight under the  $10^{-3}$  Torr are not very large ( $\overline{M}_n = 1820$ ,  $\overline{M}_w = 12\,000$  and  $\overline{M}_w/\overline{M}_n = 9.21$ ) compared with those at atmospheric pressure. PVK is very stable toward UV light based on the results of constant molecular weight distribution before and after UV light irradiation.

### F. FT-IR spectra

Figure 11 shows the FT-IR spectra of PMPS film as a function of UV light irradiation time under atmospheric

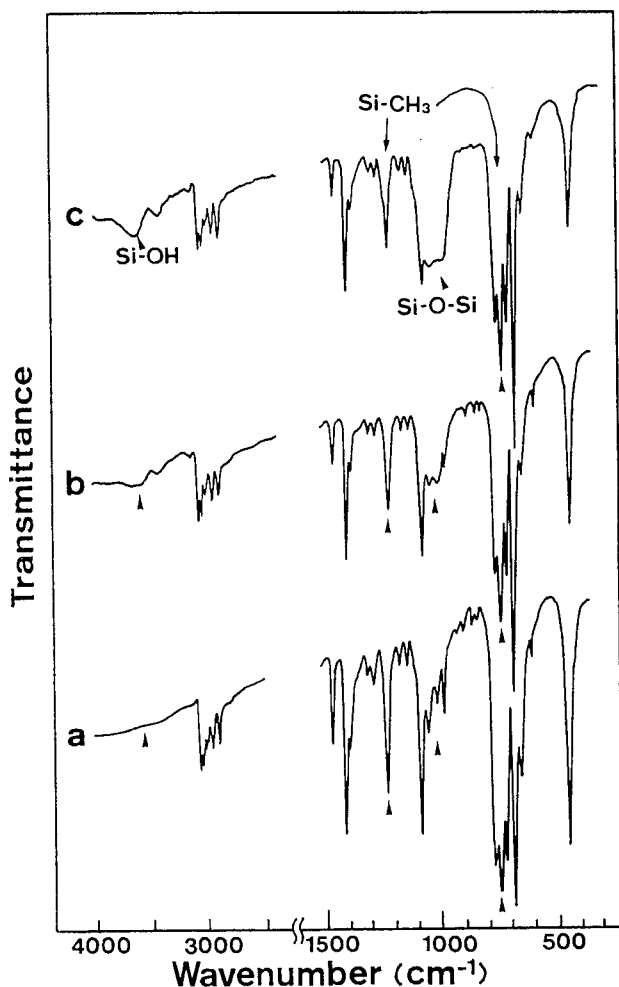


FIG. 11. FT-IR spectra of PMPS irradiated UV-light at  $3\text{ mW/cm}^2$ . (a) before irradiation, (b) 30 min irradiation, (c) 60 min irradiation.

conditions. Before irradiation, the no apparent frequencies of  $\nu$  (Si-OH) and  $\nu$  (Si-O-Si) can be seen in the range of  $3680$  and  $1000\sim 1100\text{ cm}^{-1}$ , respectively. On the contrary, the frequencies assigned to  $\nu$  (Si-OH) and  $\nu$  (Si-O-Si) become larger with increasing irradiating time, which show the formation of Si-OH and Si-O-Si bonds in a PMPS film due to UV light irradiation.

### G. XPS analysis

To extend the study of the electronic structure and surface analysis, XPS has been applied to behavior analysis with PMPS and PVK films. Figure 12 and Table II show the XPS spectra and chemical shifts before and after UV light irradiation of PMPS and PVK films under atmospheric and  $10^{-3}$  Torr conditions. The spectra measured are  $\text{Si}_{2p}$  of PMPS and  $\text{C}_{1s}$  of PVK, respectively. The  $\text{Si}_{2p}$  spectra are measured in the range of  $98\sim 104\text{ eV}$ . As a result of peak separation, the spectra are separated into two or three components, which are assigned to  $\text{Si}_{2p}$  (Si-Si),  $\text{Si}_{2p}$  (Si-OH or Si-OC<sub>2</sub>H<sub>5</sub>) and  $\text{Si}_{2p}$  (Si-O-Si) from the lower binding energy. Before UV light irradiation, 87.5% of the  $\text{Si}_{2p}$  spectrum is assigned to be Si-Si chemical shift at  $100.3\text{ eV}$ , and another chemical shift is assigned to Si-OC<sub>2</sub>H<sub>5</sub> resulting from the end group of the PMPS linear chain. The Si-Si chemical shift is decreased with increasing irradiation time. Instead of the Si-Si chemical shift, the intensities of the shifts resulting from  $\text{Si}_{2p}$  (Si-OH) and  $\text{Si}_{2p}$  (Si-O-Si) increased enormously. After irradiation for 60 min, the ratio of the spectra with  $\text{Si}_{2p}$  (Si-Si),  $\text{Si}_{2p}$  (Si-OH or Si-OC<sub>2</sub>H<sub>5</sub>) and  $\text{Si}_{2p}$  (Si-O-Si) are located at  $100.4\text{ eV}$  (40.1%),  $101.7\text{ eV}$  (50.8%) and  $102.9\text{ eV}$  (9.1%), respectively. Although the increase in spectral strength on  $\text{Si}_{2p}$  (Si-OH or Si-OC<sub>2</sub>H<sub>5</sub>) can be seen under the condition of  $10^{-3}$  Torr, the spectrum of  $\text{Si}_{2p}$  (Si-O-Si) hardly observed until 60 min. This result means that the -OH and -Si-O-Si bonds are formed with assistance of oxygen in the air. On the other hand, the  $\text{C}_{1s}$  spectra are measured in the range of  $282\sim 288\text{ eV}$ . The spectra are separated into two components, which are assigned to the spectra of  $\text{C}_{1s}$  (C-C) and  $\text{C}_{1s}$  (C-N) from the lower binding energy. These spectra are located at approximately  $284.6\text{ eV}$  and  $286.1\text{ eV}$  for various conditions, and the ratio of  $\text{C}_{1s}$  (C-C) and  $\text{C}_{1s}$  (C-N) is also constant for this condition.

### IV. DISCUSSION

The photoreceptor using PMPS for CTL exhibits higher sensitivity than that of PVK. This result suggests the possibility of many trap sites in PVK film. To obtain a dual-layered photoreceptor with a high sensitivity, important characteristics are as follows; (1) use a high carrier generating material in CGL, (2) use the CGM which has a large  $I_p$  and the CTL which has a low  $I_p$  to obtain the high injection efficiency from CGL to CTL, (3) use high carrier drifting material in CTL. Since the CGM used in this study is the same material, the photosensitivity depends on the  $I_p$  and ability of the hole carrier transport. The  $I_p$  value of PMPS is  $0.1\text{ eV}$  smaller than that of PVK, and the hole carrier mobility of PMPS is also superior to

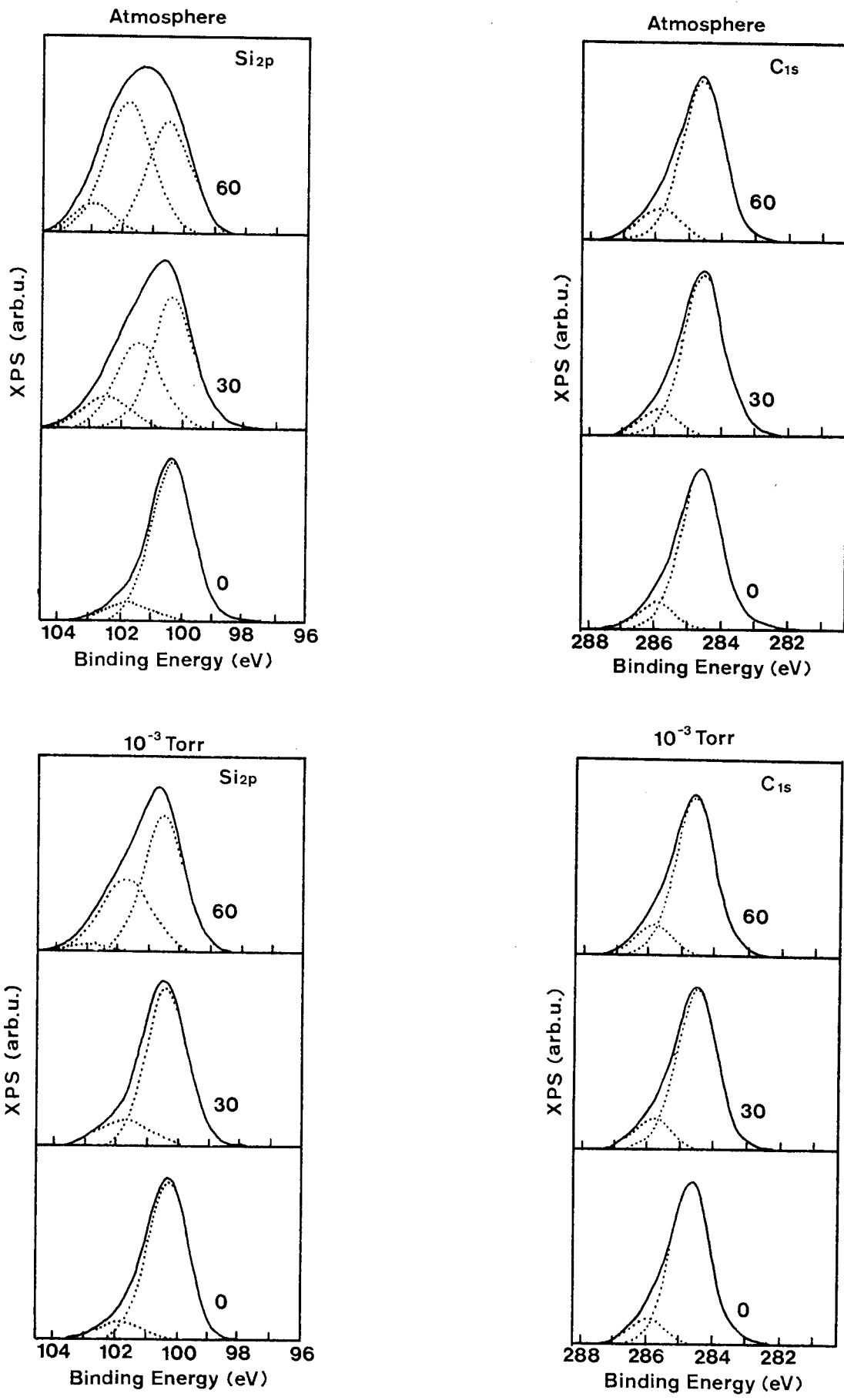


FIG. 12. XPS spectra of PMPS and PVK. Numerals in the figure represent the irradiated time. Light intensity is  $3 \text{ mW/cm}^2$ .

TABLE II. Binding energies of XPS peaks on PMPS and PVK films under the pressure of atmosphere and  $10^{-3}$  Torr. Light intensity is 3 mW/cm<sup>2</sup>.

	Conditions			Si <sub>2p</sub>			
	Lighttime (min)	PR <sup>a</sup>	BE(eV) <sup>b</sup>	ΔBE(eV)	FWHM(eV)	%	
(a) PMPS	OFF	0	AT <sup>c</sup>	100.3	...	1.69	87.5
				101.8	1.5	1.93	12.5
	ON	30	AT	100.3	...	1.73	52.4
				101.4	1.1	1.83	35.0
				102.5	2.2	1.62	12.6
				100.4	...	1.71	40.1
	ON	60	AT	101.7	1.3	1.91	50.8
				102.9	2.5	1.56	9.1
				100.3	...	1.60	82.5
				101.7	1.4	2.17	17.5
	ON	30	10 <sup>-3</sup> Torr	100.3	...	1.65	60.0
				101.6	1.3	1.99	36.9
102.8				2.5	1.73	3.1	
100.3				...	1.65	87.8	
(b) PVK	OFF	0	AT	284.6	...	1.65	87.8
				286.1	1.5	1.43	12.2
	ON	30	AT	284.6	...	1.65	87.9
				286.1	1.5	1.41	12.1
				284.6	...	1.68	84.7
				286.0	1.4	1.63	15.3
	ON	30	10 <sup>-3</sup> Torr	284.6	...	1.62	86.3
				286.0	1.4	1.45	13.7
				284.5	...	1.61	85.5
				285.9	1.4	1.51	14.5

<sup>a</sup>PR suggests the pressure;

<sup>b</sup>BE suggests the binding energy;

<sup>c</sup>AT suggests the atmosphere.

PVK. The large interfacial barriers prevent the carrier injection from CGL to CTL, and carriers would remain near the interfacial zones. Carriers in PVK are transported through the  $\pi$ -conjugated overlapping of the carbazole groups, in which trapping sites would exist by the formation of excimer-type conformation on neighboring carbazole groups.<sup>12</sup> Carriers are captured in deep traps, consequently, a large residual potential can be seen. Carriers in a PMPS polymer chain are mainly transported through the  $\sigma$ -conjugated Si-Si main chain, however, carriers between polymer chains are due to hopping conduction. The formation of trapping sites by steric hindrances only slightly occurs in a PMPS polymer chain. On the contrary, the trap sites are produced by the formation of silanol bonds and the decomposition of the Si-Si main chain. Consequently, the conductivities are reduced due to the formation of insulators after UV light irradiation.

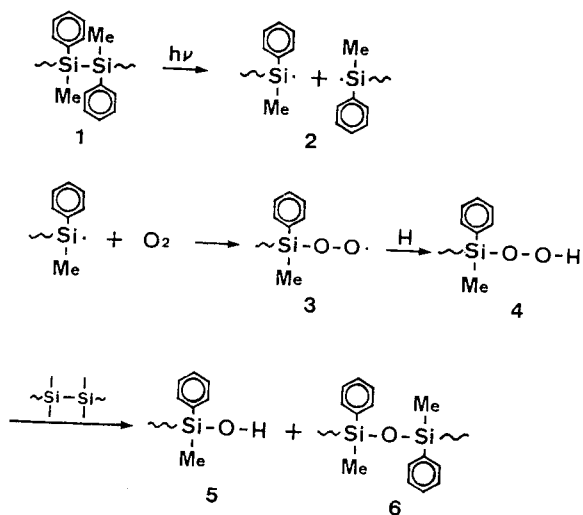
As a result of UV light irradiation,  $V_0$  and  $VR_3$  of the PMPS photoreceptor increased with increasing irradiation time, however, initial light decays in PID curves are invariant. Light decay from saturated potential is a phenomenon in a large electric field, therefore, it is difficult to analyze this initial light decay, because this decay will not reflect the influences of traps and space charge in a film. Light decomposition of the PMPS main chain tends to decrease the carriers through the valence band of  $\sigma$ -bond, and hopping transport carriers will increase among the PMPS chains.

It is confirmed that the polymerization and decomposition in a PMPS film occurred at the same time by UV

light irradiation. This is because the activated terminal groups of the polymer chain act to produce polymerization and decomposition of Si-Si main chain. These results are explained by the GPC analysis. Since the bonding energies ( $E^0$ ) of Si-Si, Si-O and C-C are 224, 622 and 590 kJ/mol, respectively, it can be explained that the C-C bond is stable and Si-O bond is stronger than the Si-Si bond. Hole carrier mobilities of PMPS becomes slow due to UV light irradiation. It is presumed that the carrier mobilities in a PMPS chain are not changed, however, the decomposition of the Si-Si main chain produces many lower molecular weight chains, and insulation becomes large. These results can be explained by the results of variations and differences in surface potentials of the photoreceptors, mobilities, conductivities, GPC, FT-IR spectra and XPS analysis.

Finally, the decomposition of the PMPS polymer by UV light is presumed to be the precesses such as Scheme I. At first, the cleavage of the activated Si main chain (1) will occur by UV light irradiation, and silyle radicals(2) are produced. Silyle radicals(2) react with the oxygen in air, consequently, peroxide radicals of the silyle groups(3,4) are also produced. These active groups tend to react with other Si main chains, and silanol(5), which has a small molecular weight, is produced. At the same time, siloxane(6) is produced by the polymerization with silyle radicals and active oxygens. The possibility of cross-linkage with silyle radicals and paraposition of phenyl groups is also considered. This estimation is proved by the results of IR and XPS spectra, that is, increasing absorbances and spectra assigned Si-O-Si and Si-OH bonds by UV light





The cleavage mechanism of PMPS for UV light.

irradiation show the formation of these bonds in films. Hole carrier mobilities in PMPS films are influenced by state of the polymer chain, and trapping sites resulting from the formation of insulators would increase, and hence the electrophotographic characteristics of photoreceptor using PMPS, especially surface potential and residual potential, are reduced by UV light irradiation. On the contrary, the characteristics that of PVK are only slightly influenced by UV light irradiation. This is because the C-C main chain in PVK is stable toward UV light, and the hole carriers are transported through overlapping of the carbazole groups.

## V. CONCLUSION

We have studied the PMPS as CTM for the purpose of applying it to dual-layered electrophotographic photoreceptors. Light fatigues for UV light irradiation have also been investigated and compared to a typical photoconductive polymer (PVK) using various analyses. Conclusions results in this study are summarized as follows:

(1) Photoreceptor using  $\tau$ -H<sub>2</sub>Pc dispersed in CGL and

PMPS for CTL exhibited high sensitivity of  $E_{1/2} = 0.28 \mu\text{J}/\text{cm}^2$  at 800 nm.

(2) Light fatigue of PMPS photoreceptor was measured by the irradiation of UV light at 330 nm, on the contrary, the PVK photoreceptor exhibited constant properties.

(3) Light fatigue can be considered to be due to the decomposition and polymerization of PMPS based on the analysis of GPC, FT-IR and XPS spectra.

(4) Formation of insulators in PMPS film was presumed by variations in surface potentials of photoreceptors, mobility and conductivity.

(5) As a result of UV light irradiation to PMPS film, Si-Si main chain was produced Si-O-Si and Si-OH bonds in the existence of oxygen.

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