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Structure−Property Relationships for Photoconduction in Substituted Polyacetylenes

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New photoconductive materials are explored from three groups of polyacetylenes: poly(phenylacetylenes) $-[HC{=}C(C_6H_5\text{-}p\text{-}R)]_n-$, poly(3-thienylacetylenes) $-[HC{=}C(3\text{-}C_4H_2S\text{-}\beta\text{-}R')]_n-$, and poly(1-alkynes) $-\{HC{=}C[(CH_2)_mR'']\}_n-$, where R = CH_3 (**2**), $CO_2(CH_2)_6OCO$-Biph-OC_7H_{15} (Biph = 4,4′-biphenylyl; **3**); R′ = $Si(CH_3)_3$ (**4**), Br (**5**); and R″ = $CO_2(CH_2)_6OCO$-Biph-OC_9H_{19} (m = 2; **6**), 9-carbazolyl (m = 3; **7**) and OCO-Biph-OC_7H_{15} (m = 9; **8**). Photoconduction in the polyacetylenes under illumination of visible light is investigated using photoinduced xerographic discharge technique. In the pure (undoped) state, all the polyacetylenes except **5** show higher photosensitivity than do poly(phenylacetylene) (R = H; **1**), a well-studied photoconducting polyacetylene, and poly(9-vinylcarbazole), the best-known photoconducting vinyl polymer. Among the polyacetylenes, photoconduction performance of the polymers with electron-donating and/or hole-transporting moieties is superior to those with electron-accepting ones. The liquid crystalline polymer **6** exhibits very high photosensitivity, probably due to the formation of crystalline aggregates of its mesogenic pendants induced by the thermal treatment in the photoreceptor preparation process. C_{60} acts as a photoconductivity enhancer when doped to amorphous **3**, but functions as a crystallinity-breaking plasticizer when doped to liquid crystalline **6**, leading to a large decrease in photoconductivity. While **3** shows a low photosensitivity (2.8×10^{-3} lx^{-1} s^{-1}) to a 573 nm light in the undoped state, doping with I_2 and sensitization with crystal violet (CV) dramatically increase its photosensitivity (up to 41.2×10^{-3} lx^{-1} s^{-1}). The CV-sensitized **4** exhibits high photoconductivity in the near-infrared spectral region, which may find technological applications in the digital photoimaging systems.

Introduction

Since its invention by Carlson in the late 1930s,[1] xerography has become a technology of choice for a wide variety of photoelectronic applications. Of the many technologies that have led to the evolution of xerography, photoreceptor materials have played a major role.[2] Today, the development of new materials with novel photoconducting properties still holds the key to the further exploration of new technological applications of the photoimaging process.

A large research effort in the development of efficient polymeric photoreceptor systems has resulted in the accumulation of a wealth of information on the structure−property relationships of photoconducting polymers. Many groups have studied the influence of morphologic structure on the charge carrier mobility in poly(9-vinylcarbazole) (PVK)[2−4] and found that the hole mobility in the crystalline PVK is about 1 order of magnitude higher than that in the amorphous one over a wide range of electrical field strengths. A few groups have investigated photoconduction in polyethylene and observed that an increase in crystallinity is accompanied by an increase in photocurrent.[5] Photosensitivity of polyimides containing thiophenylene moieties remarkably increases with an increase in crystallinity,[6] and the same trend has also been observed in the poly(phenylene sulfide) photoreceptor systems.[7]

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During the course of the exploration of molecular−complex photoreceptor systems, aggregate formation has been found to dramatically boost photosensitivity.[2] For example, when a homogeneous film of 4-(4′-dimethylaminophenyl)-2,6-diphenylthiapyrylium perchlorate, bis(4-diethylamino-2-methylphenyl)phenylmethane, and polycarbonate is exposed to the vapor of dichloromethane ("solvent fuming"), crystalline aggregates form, which lead to a 100-fold increase in photosensitivity over its amorphous counterpart. X-ray diffraction studies of the aggregates reveal that the thiapyrylium dye molecules are arranged in quasi-one-dimensional stacks separated by layers of the polycarbonate molecules. Photogeneration in the aggregate photoreceptor system is believed to occur via singlet excitons, which diffuse to the interface between the aggregate and polymer phases and then dissociate into free electron−hole pairs.[8] The thiapyrylium dye aggregate systems are one of the best commercial photoreceptors developed so far.[9] Because of their high photosensitivity as well as excellent cycling characteristics, single- and dual-layer aggregate photoreceptors have been widely used in the photocopier industry.[2] However, the aggregate formation induced by the "wet" fuming process using the toxic halogenated solvent of dichloromethane is an obvious disadvantage of the thiapyrylium dye photoreceptor system. It is well-known that mesogenic groups in a thermotropic liquid crystal pack in an ordered fashion upon cooling from its molten state.[10] Thermal treatment of a liquid crystal with a low transition temperature thus may be utilized as a simple "dry" process to induce the formation of crystalline aggregates and hence to enhance the efficiency of photoconduction. Such possibility, however, has not been explored.

Conjugated polymers have attracted much interest among scientists and technologists because of their intriguing potential applications in optics and electronics systems. Polyacetylene is a prototypical conjugated polymer and shows high photoconductivity.[11] Unfortunately, however, polyacetylene is intractable and unstable, which makes it difficult, if not impossible, for the polymer to find any practical applications. The extensive synthetic efforts in the past two decades have created a great number of processable and stable polyacetylene derivatives with different substituents ("substituted polyacetylenes"),[12] some of which have been found to possess unique materials properties such as γ-radiolysis susceptibility,[13] optical activity,[14] gas permeability,[15] and liquid pervaporation capacity.[16] The study on photoconductivity of substituted polyacetylenes, however, has been confined to only one group of this family of polymers, that is, poly(phenylacetylene) (PPA) and its derivatives.[17−22] It has been found that doping with acceptor molecules such as iodine (I_2) enhances the photosensitivity of PPA, the optimum of which is obtained for heterogeneous phases with a large interface area. The transition from amorphous to crystalline structure promotes the photosensitivity increase.[3] When an electron-accepting group of trifluoromethyl (CF_3) is chemically introduced to the ortho position of the phenyl ring of PPA, the resultant poly[*o*-(trifluoromethyl)phenylacetylene] shows a low photoconductivity.[20] On the other hand, the incorporation of electron-donating groups into the molecular structure of PPA significantly enhances its photoconductivity. Thus, poly[*o*-(trimethylsilyl)phenylacetylene][20,21] and poly[(2,6-dimethyl-4-*tert*-butyl)phenylacetylene][20] are both excellent photoconductors, with the later (containing multiple donor groups) showing much higher photoconductivity and carrier mobility. Interestingly, however, the PPA containing an acceptor group of iodo (I), i.e., poly(*p*-iodophenylacetylene), exhibits a complex photoconduction pattern: its photogeneration efficiency, compared to that of the PPA parent, is higher at the low electrical field but lower at the high field.[22]

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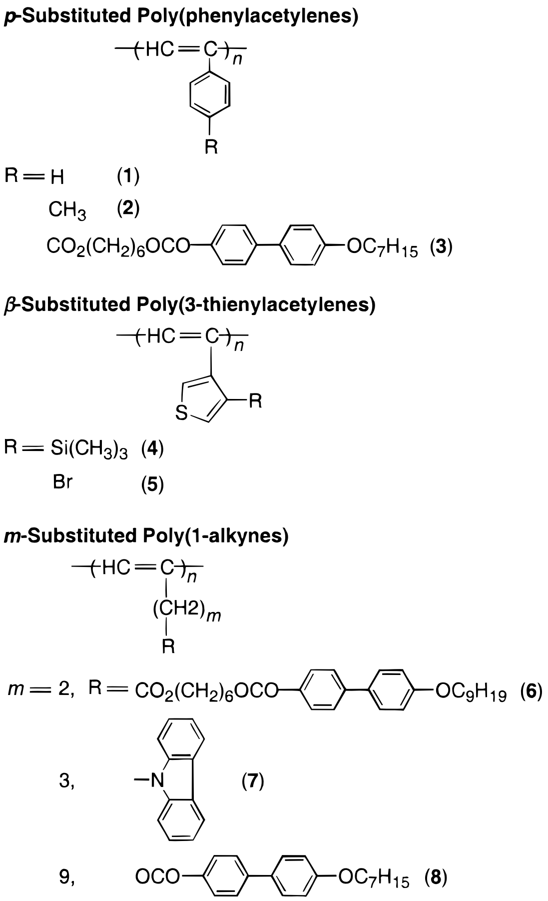
Through the development of robust catalysts, we have recently synthesized a large variety of new functionalized polyacetylenes.[23−30] In our previous studies, we investigated their liquid crystallinity,[23,29a] light emissivity,[23k,24,25a] chirality/helicity,[25] optical nonlinearity,[25a,26] and self-assembling and -organizational properties.[25a,e,27] In this work, we examined photoconductivity of some of the substituted polyacetylenes (Chart 1), with the aims of developing new polyacetylene-based photoreceptor materials and understanding the structure−property relationships in the photoconduction processes. We studied electronic, morphological, and doping/sensitization effects on the photoconductivity of the polyacetylenes and found that thermally induced aggregate formation of liquid crystalline mesogens led to a large increase in the photoconductivity.

Chart 1



Experimental Section

Materials and Instrumentation. All the substituted polyacetylenes used in this study, that is, the *p*-substituted poly(phenylacetylenes) **1**−**3**, the *β*-substituted poly(3-thienylacetylenes) **4** and **5**, and the *m*-substituted poly(1-alkynes) **6**−**8** (cf., Chart 1), were synthesized according to our previously published procedures. The major polymerization conditions and results along with the related references are given in Table 1. PVK was prepared in our laboratories following a published polymerization procedure.[31] 4-(Diethylamino)benzaldehyde 1-(1′-naphthyl)-1-phenylhydrazone (DENPH),[32] polycarbonate (PC), polyamide (PAm), C_{60}, I_2, and CV were all purchased from commercial sources. All the organic solvents used in this study, including tetrahydrofuran (THF), chloroform, 1,2-dichloroethane, carbon tetrachloride, toluene, and dioxane, were of spectroscopic grades and were purified by distillation prior to use.

UV−vis spectra were recorded on a Milton Roy Spectronic 3000 Array spectrophotometer in THF, and fluorescence spectra were measured in chloroform on a SLM Aminco JD-490 spectrofluorometer. Film thickness was evaluated using an Elektko-Physik Minitest 2000 thin film thickness measurement system. Photosensitivity of the photoreceptor systems was measured on a GDT-II photoconductivity measurement device using a 5 W, 24 V incandescent lamp as light source, whose emission is mainly in the visible spectral region (~400−800 nm).[33] The light with monochromatic wavelength of 500, 573, 601, or 762 nm was isolated from the lamp using optical filters.

Photoreceptor Preparation. The photoreceptors based on the undoped and doped/sensitized substituted polyacetylenes with single- and dual-layer configurations were constructed (Chart 2; for illustration only, layer thicknesses not in exact proportion to those actually used in this study).

A single-layer photoreceptor based on an undoped polyacetylene was prepared by coating a 1,2-dichloroethane solution of a substituted polyacetylene, DENPH, and PC (3:40:40 by weight)[34] onto an electrically grounded aluminum substrate. The thickness of the resultant film was 20−30 μm. The aluminum plate had been precoated with a 1 μm thick interface layer of PAm. The photoreceptor dried at room temperature was further heated at 353 K in an oven for several hours to remove the residual solvent. In the photoreceptor system, the polyacetylene functions as a charge generation

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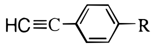
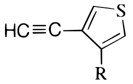
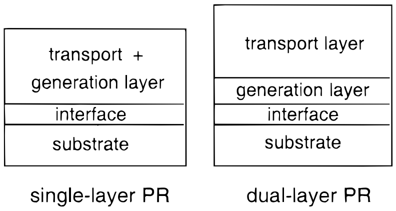
(34) We fabricated the single-layer photoreceptors with different ratios of polyacetylene, DENPH, and PC, and found that the photosensitivity was the highest when the ratio was 3:40:40 by weight.

Table 1. Preparation of Substituted Polyacetylenes[a]

no.	monomer	$[M]_o$ (M)	catalyst	solvent	[cat.] (mM)	temp (°C)	yield (%)	M_w[b]	M_w/M_n[b]	ref
										
1	R = H	0.85	Rh(cod)(tos)(H_2O)	THF	1.8	rt	70.3	225400	6.8	28b
2	CH_3	0.79	Rh(nbd)(tos)(H_2O)	H_2O	1.0	rt	31.5	17500	2.8	29b
3	$CO_2(CH_2)_6OCO$-Biph-OC_7H_{15}	0.20	$[Rh(cod)Cl]_2$	THF/Et_3N	20.0	rt	85.7	385400	4.6	23e
										
4	R = $Si(CH_3)_3$	1.20	$MoCl_5$	toluene	24.0	80	68.1	133400	3.0	28d, e
5	Br	1.20	$MoCl_5$–Ph_3BiH	toluene	24.0	rt	100	48400	5.6	28d, e
	HC≡CR									
6	R = $(CH_2)_2CO_2(CH_2)_6OCO$-Biph-OC_9H_{19}	0.20	$W(mes)(CO)_4$	CCl_4	20.0	60	56.0	4600	1.5	23h
7	$(CH_2)_3$-Cz	0.50	WCl_6–Ph_4Sn	toluene	20.0	rt	70.9	61200	4.9	28f, g
8	$(CH_2)_9OCO$-Biph-OC_7H_{15}	0.20	WCl_6–Ph_4Sn	dioxane	20.0	60	82.2	41200	2.2	23j

[a] All polymerization reactions were carried out under nitrogen for 24 h. Abbreviation: Biph = 4,4′-biphenylyl, Cz = 9-carbazolyl, cod = 1,5-cyclooctadiene, tos = *p*-toluenesulfonate, nbd = 2,5-norborndiene, mes = mesitylene, rt = room temperature. [b] Estimated by GPC in THF on the basis of a polystyrene calibration.

Chart 2. Photoreceptor (PR) Configuration



material and DENPH serves as a charge transport material (while PC is the most widely used polymer matrix in photoreceptor systems[2,3]). For comparison, a single-layer photoreceptor containing PVK, DENPH, and PC in the same weight ratio (i.e., 3:40:40) was also prepared.

A single-layer photoreceptor consisting of a doped or sensitized substituted polyacetylene was prepared in the similar fashion with the addition of a dopant or sensitizer. A 1,2-dichloroethane solution of a substituted polyacetylene with a known amount of dopant or sensitizer (C_{60}, I_2, or CV) was added to a DENPH and PC solution in the same solvent. The ratio of polyacetylene, DENPH, and PC was fixed at 3:40:40 by weight. The solution was coated onto a PAm-precoated aluminum substrate and the resultant film was then thoroughly dried.

A dual-layer photoreceptor was prepared by coating an interface layer of PAm (1 μm in thickness), a charge generation layer of an undoped or doped/sensitized polyacetylene (0.5 μm), and a charge transport layer of DENPH/PC (1:1 by weight; 25 μm) in sequence.

Photoconductivity Measurement. Photoconductivity of the polyacetylene photoreceptors was evaluated using the standard photoinduced discharge technique, which is the basis of the xerographic process in the photocopying systems.[9,35] The photoreceptor was first negatively corona-charged to a surface potential V_o and then kept in the dark for 3 s. Upon exposure to a light of intensity I, the electron−hole pairs form. A fraction of the pairs separate and migrate to the free surface and substrate electrode. The surface charge is thus dissipated by neutralization. From the photoinduced discharge curve illustrated in Figure 1, the following photoconduction parameters can be readily obtained: dark decay [R_d; in our particular case, $R_d = (V_o - V_i)/3$, where V_i is the surface potential right before illumination], percentage of potential discharge in 1 s $\{\Delta V_1 = [(V_i - V_1)/V_i] \times 100\%$, where V_1 is the surface potential after 1 s exposure$\}$, time from V_i to its half value under exposure ($t_{1/2}$), residual surface charge potential (V_r), and half-discharge exposure energy ($E_{1/2} = t_{1/2} \times I$). Photosensitivity ($S$) is defined as the reciprocal of the half-discharge exposure energy ($S = 1/E_{1/2}$). As can be seen from Figure 1, under identical initial surface charge (V_o) and illumination intensity (I), a good photoreceptor has small R_d, $t_{1/2}$, and V_r values and hence high ΔV_1 and S values.

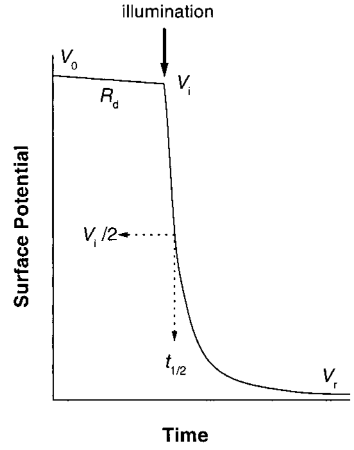


Figure 1. A typical photoinduced xerographic discharge curve, where V_o is initial surface charge potential, R_d is dark decay, V_i is surface potential at illumination, $t_{1/2}$ is half-discharge time, and V_r is residual surface charge potential.

Results and Discussion

Photoconductivity of Pure (Undoped) Polyacetylenes. Xerographic photoreceptors are usually constructed in a dual-layer configuration, composed of two separate layers of charge-generation and -transport layers (cf., Chart 2). Although the dual-layer configuration offers many advantages including minimal bulk trapping, low thermal generation rate, and long process lifetime, it suffers from the problems such as added cost and manufacturing complexity.[2] In our system, because the charge generation materials of the substituted polyacetylenes have the solubility similar to that of the materials in the charge transport layer (i.e., DENPH and PC), we had difficulty in manufacturing the dual-layer photoreceptors with good quality. We nevertheless managed to construct the polyacetylene photoreceptors of dual-layer configuration but found that their performance was poorer than their single-layer counterparts, which can be manufactured with ease. For example, the photosensitivity of a single-layer photoreceptor of **3** doped with ~44 wt % CV ($S = 41.2 \times 10^{-3}$ lx^{-1} s^{-1}) is

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(35) Renensburger, P. J. *J. Photochem. Photobiol.* **1968**, *8*, 429 (b) Chen, I.; Mort, J. *J. Appl. Phys.* **1972**, *43*, 1164.

Table 2. Photoconductivity of Substituted Polyacetylenes[a]

no.	polymer	V_o (V)	R_d (V s^{-1})	ΔV_1 (%)	$t_{1/2}$ (s)	V_r (V)	S (10^{-3} lx^{-1} s^{-1})
			Poly(phenylacetylenes)				
1	**1**	781	10	13	6.313	292	2.64
2	**2**	816	12	16	4.438	203	3.76
3	**3**	808	10	14	5.813	282	2.80
			Poly(3-thienylacetylenes)				
4	**4**	736	19	28	2.375	154	6.99
5	**5**	707	13	7	>10	339	<1.67
			Poly(1-alkynes)				
6	**6**	707	20	40	1.438	98	11.63
7	**7**	696	18	35	1.750	106	9.52
8	**8**	656	18	22	3.063	117	5.43
			Poly(9-vinylcarbazole) (PVK)[b]				
9	PVK	700	9	8	8.625	342	1.93

[a] Photoreceptors of single-layer configuration were exposed to a 573 nm light with an intensity of 60 lx. Abbreviation: V_o = initial surface charge potential, R_d = dark decay, ΔV_1 = percentage of potential discharge after 1 s of exposure, $t_{1/2}$ = half-discharge time, V_r = residual surface charge potential, S = photosensitivity. [b] For the purpose of comparison.

much higher than that of a dual-layer one (26.7×10^{-3} lx^{-1} s^{-1}) under the same composition and illumination (573 nm, 60 lx) conditions. Thus, in this study, we used the single-layer configuration to investigate the photoconduction in the polyacetylene-based photoreceptor systems.

The photoconductivity of single-layer photoreceptors of the undoped polyacetylenes along with that of PVK exposed to a visible light of 573 nm is summarized in Table 2. The photoreceptor of PPA (**1**) can be readily negatively charged to a surface potential of 781 V, which slightly decreases to 751 V in 3 s (V_i) in the dark, giving a low dark decay (R_d) of 10 V s^{-1} (Table 2, no. 1). After exposure to the visible light of 60 lx for 1 s, V_i decreases to 653 V, achieving a 13% potential discharge (ΔV_1). The surface potential drops to its half value in ~6 s ($t_{1/2}$). The residual charge potential (V_r) left on the photoreceptor surface is 292 V and the photosensitivity (S) of **1** is estimated to be 2.64×10^{-3} lx^{-1} s^{-1}. When an electron-donating group of methyl (CH_3; $\sigma_p = -0.14^{36}$) is introduced to the para position of the phenyl ring (**2**), the R_d and ΔV_1 values do not change much. The $t_{1/2}$ and V_r values, however, decrease, and as a result, the S value increases. When an electron-accepting group of ester (CO_2R; $\sigma_p = +0.44^{36}$) is introduced (**3**), the photosensitivity of the photoreceptor slightly increases. This is different from the previous observation by other research group (incorporation of an acceptor group leading to a decrease in photosensitivity[20]). It is known that **3** is liquid crystalline and its melting transition temperature is quite high (409 K).[23e] The high rigidity of the PPA backbone distorts the packing arrangements of the liquid crystalline mesogens, but there might still be some small fraction of the mesogenic groups that have aggregated. The competition between the constructive (aggregation) and destructive (electron-withdrawing) effects may have resulted in the observed slight increase in the photosensitivity.

The electronic effects of donor and acceptor groups are clearly observed in the photoreceptors of two poly(3-thienylacetylenes), neither of which are liquid crystalline.[28d,e,29b] The poly(3-thienylacetylene) with a donor group of trimethylsilyl [$Si(CH_3)_3$] at the β position (**4**) shows a fast ΔV_1 (28%), a short $t_{1/2}$ (~2 s), a low V_r (154 V), and a high S value (~7×10^{-3} lx^{-1} s^{-1}; Table 1, no. 4). In contrast, the polymer with an acceptor group of bromo (Br; **5**) performs poorly as a photoreceptor with its $t_{1/2} > 10$ s, $V_r > V_i/2$, and $S < 1.67 \times 10^{-3}$ lx^{-1} s^{-1}. The photosensitivity of **4** is more than 4.2 times higher than that of **5**. It is thus clear that in the poly(3-thienylacetylene) photoreceptors, the incorporation of a donor group to the molecular structure of the pendant thienyl ring largely increases the photoconductivity. It is known that polysilanes are hole-transporting.[2,37] The trimethylsilyl moiety attached to the thienyl ring in **4** may take part in the charge carrier transport processes, facilitating the movement of the holes toward the surface of the photoreceptor for neutralization. Combination of the electron-donating and hole-transporting effects thus makes **4** an excellent photoconductor.

Because of the electron donating nature of the alkyl spacers directly linked to the polyene backbones, all the three poly(1-alkynes), i.e., **6**, **7**, and **8**, exhibit high photosensitivity. Compared with the above-discussed two groups of polyacetylenes, this group of polyacetylenes are much better photoreceptors. The high photosensitivity of **7** may be due to the synergetic contribution of the electron-donating propyl spacer and the hole-transporting carbazolyl group. The pendant group of **6** is structurally similar to that of **8**, but the photosensitivity of the former is more than 2-fold higher than that of the latter. While both **6** and **8** are liquid crystalline, their melting transition temperatures are different (347 K for **6**[23h] and 357 K for **8**[23j]). When **6** is heated at 353 K in the photoreceptor preparation process (see Experimental Section for details), the fluidity in the molten sample of **6** allows the mesogenic groups to move together to self-align in an ordered s_A phase.[23h] Cooling the liquid crystalline **6** to room-temperature further enhances the ordering of the mesogenic pendants (just like what happens in a recrystallization process), and the crystalline aggregates will boost the photosensitivity of the polymer. On the other hand, at 353 K, **8** is still in the solid, at most semisolid, state. There might be some ordering, but its extent should be quite small. Thus, unlike its liquid crystalline cousin **6** with a lower melting transition temperature, there is no marked aggregation effect observed in the photoreceptor of **8**.

PVK shows excellent photoconductivity in the visible spectral region when it is doped with 2,4,7-trinitrofluorenone.[38,39] Its photosensitivity in the undoped state is, however, rather low (Table 1, no. 9; see also ref 38). Compared to PVK, **6** displays a 6-fold higher photosensitivity in the undoped state, thanks to its conjugated backbone consisting of alternating double bonds. It is generally agreed that for xerographic applications, a photoreceptor should meet the following criteria: (1)

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(36) Exner, O. *Correlation Analysis of Chemical Data*; Plenum Press: New York, 1988.

(37) Stolka, M.; Yuh, H.-J.; McGrane, K.; Pai, D. M. *J. Polym. Sci. Part A: Polym. Sci.* **1987**, *25*, 823.

(38) Goosey, M. In *Specialty Polymers*; Dyson, R. W., Ed.; Chapman and Hall: New York, 1987; Chapter 5.

(39) Regensburger, P. J. *Photochem. Photobiol.* **1968**, *8*, 429. (b) Melz, P. J. *J. Chem. Phys.* **1972**, *57*, 1694. (c) Pai, D. M. *J. Chem. Phys.* **1969**, *50*, 3568. (d) Pfister, G.; Williams, D. J. *J. Chem. Phys.* **1974**, *61*, 2416.

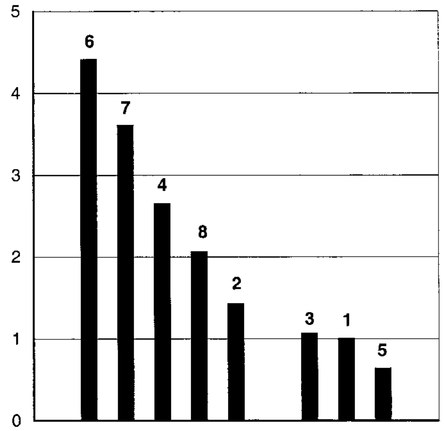

Figure 2. Relative photosensitivity (S) of polyacetylenes with donor (**2**, **4**, **6**, **7**, **8**) and acceptor groups (**1**, **3**, **5**). The bar for **5** is an approximate illustration because its poor photoconductivity prevents its S value from being accurately determined (cf., Table 2).

chargeable to a high surface potential and having a low rate of thermal generation of free carriers, (2) possessing a high sensitivity in the visible and/or near-infrared spectral region, and (3) dissipating the surface charge at a fast rate to a high extent upon exposure to light.[9] The photoreceptor of **6** meets all of these requirements: it can be charged to a high potential, has a low rate of dark discharge, sensitively responds to the visible light, and discharge the surface potential to a very low level. It must be stressed that all of these remarkable characteristics are for the pure polymer in its undoped state. Thus, **6** is an excellent photoreceptor material with great commercial potential.

Figure 2 shows the relative photosensitivity of the substituted polyacetylenes. The comparison clearly separates the polyacetylenes into two categories: one with donor groups (**6**, **7**, **4**, **8**, and **2**) and one with acceptor groups (**3**, **1**, and **5**). Obviously, the former shows higher photosensitivity than the latter. Thus, the donor groups facilitate but the acceptor ones hamper the photoconduction in the polyacetylene photoreceptors. For the liquid crystalline polymers (**3**, **6**, and **8**), the photosensitivity changes according to whether the morphologic and electronic effects are working in a synergistic or antagonistic fashion. When the morphologic effect is opposite to the electronic one, the photosensitivity remains low (**3**). When the two effects are both constructive, it leads to large enhancements in the photosensitivity (**6** and **8**).

Figure 3 shows the photosensitivity spectra of the polyacetylene photoreceptors. In almost the entire spectral region investigated, the photosensitivity of the polymers with donor groups (**6**, **7**, **4**, **8**, and **2**) is consistently higher than that of their counterparts with acceptor groups (**3**, **1**, and **5**). Another noticeable feature is that all the polyacetylenes containing (bi)phenyl rings (**6**, **8**, **2**, **3**, and **1**) exhibit the highest photosensitivity at ~573 nm, whereas all the polymers containing the heterocyclic rings (**7**, **4**, and **5**) show the highest photosensitivity at ~500 nm.

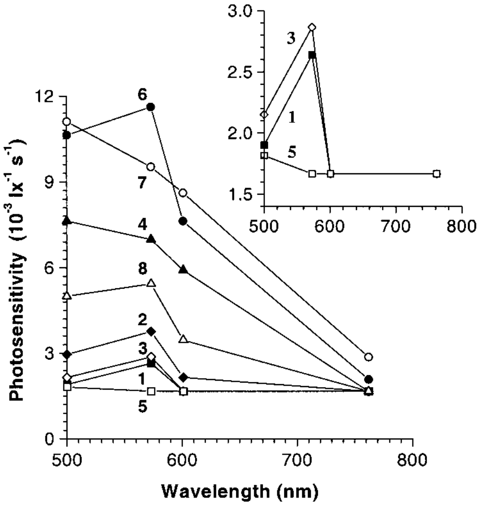

Figure 3. Spectral dependence of photosensitivity of single-layer photoreceptors of substituted polyacetylenes exposed to visible light of 60 lx. The inset shows the enlarged photosensitivity spectra of the polyacetylenes with donor substituents.

Photoconductivity of C_{60}-Doped Polyacetylenes. Enhanced photoconductivity has been observed in the photoreceptors of C_{60}-doped PVK[9] and poly(p-phenylenevinylene) derivatives,[40] which has been interpreted in terms of photoinduced electron transfer from the polymers to C_{60} because photoluminescence of the polymers are remarkably quenched upon doping with C_{60}. We thus tried to boost the photoconductivity of the photoreceptors of the substituted polyacetylenes by C_{60} doping.

In the visible spectral region, the single-layer photoreceptor of pure (undoped) **3** shows a half-discharge time ($t_{1/2}$) of ~1 s, a residual potential (V_r) of 140 V, and a photosensitivity (S) of $\sim 1 \times 10^{-3}$ lx^{-1} s^{-1} (Table 3, no. 1). When doped with a small amount of C_{60} (1.5 wt %), both $t_{1/2}$ and V_r decrease. Thus, in agreement with other groups' observation, doping with C_{60} helps dissipate the charge potential at a fast rate to a lower level. As a result, the S value of the photoreceptor increases by a factor of about 4. When the light with monochromatic wavelength of 500, 573, 601, or 762 nm is used as the illumination source, the photoreceptor shows high photosensitivity at all the wavelengths, with the highest S value (9.52×10^{-3} lx^{-1} s^{-1}) obtained again at 573 nm.

When **6** is doped with C_{60}, however, its photosensitivity drops to about one-third of that of the undoped form in the visible spectral region (Table 3, nos. 7 and 8). The photoconductivity at 601 or 762 nm is so low that its S value cannot be accurately determined. Interestingly, however, when **8** is doped with C_{60}, the increase in the photosensitivity is again observed, although the extent of the enhancement is not as large as that observed in doped **3**.

Figure 4 depicts the effect of C_{60} doping on the photosensitivity of the polyacetylene photoreceptors. Doping **3** with C_{60} leads to a large increase in the photosensitivity to the 573 nm illumination but the doping to **6** results in a pronounced reverse effect. The change in the photosensitivity of **8** upon doping with C_{60} is, however, insignificant.

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(40) Sariciftci, N. S.; Braun, D.; Zhang, C.; Srdanov, V. I.; Heeger, A. J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585. (b) Sariciftci, N. S.; Heeger, A. J. *Inter. J. Mod. Phys. B* **1994**, *8*, 237. (c) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.

Table 3. Photoconductivity of C_{60}-Doped Polyacetylenes (PAs)[a]

no.	PA	C_{60} (wt %)	wavelength (nm)	I (lx)	V_o (V)	R_d (V s^{-1})	ΔV_1 (%)	$t_{1/2}$ (s)	V_r (V)	S (10^{-3} lx^{-1} s^{-1})
1	3	0	visible	800	882	18	48	1.063	140	1.18
2		1.5	visible	800	621	33	77	0.313	82	4.00
3			500	60	562	15	27	2.625	109	6.35
4			573	60	636	18	36	1.750	136	9.52
5			601	60	585	10	18	4.313	148	3.86
6			762	60	554	11	15	5.188	171	3.21
7	6	0	visible	800	750	46	70	0.438	113	2.86
8		1.5	visible	800	492	13	46	1.190	117	1.05
9			500	60	445	6	10	8.000	183	2.08
10			573	60	503	6	10	7.625	203	2.19
11			601	60	503	5	6	>10	285	<1.67
12			762	60	498	5	3	>10	358	<1.67
13	8	0	visible	800	623	62	52	0.875	131	1.43
14		1.5	visible	800	539	34	75	0.375	70	3.33
15			500	60	527	16	22	3.125	97	5.33
16			573	60	589	15	25	2.750	101	6.06
17			601	60	609	15	18	4.063	128	4.10
18			762	60	664	14	7	>10	300	<1.67

[a] Single-layer photoreceptors were exposed to an incandescent lamp, whose emission is mainly in the visible spectral region (~400–800 nm), or to a monochromatic light with wavelength of 500, 573, 601, or 762 nm, which was isolated from the lamp using optical filters. I: exposure intensity. Other abbreviations bear the same meanings as defined in Table 2.

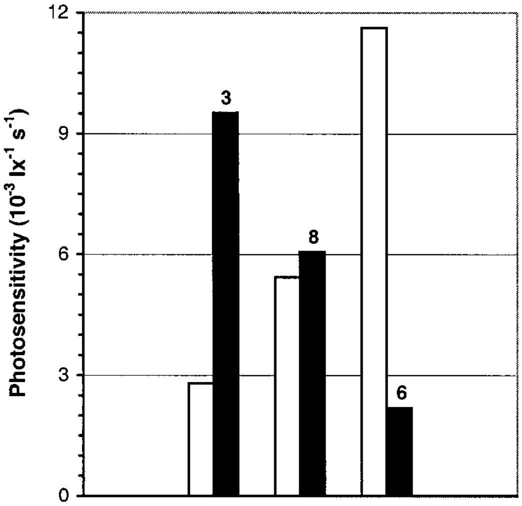

Figure 4. Photosensitivity of single-layer photoreceptors of substituted polyacetylenes **3**, **6**, and **8** to a 573 nm light before (open bar) and after (solid bar) doping with C_{60}.

To get insights into the cause of the doping effects, UV–vis absorption and fluorescence emission spectra of the (un)doped polymers are measured. Not much change, however, is observed in both the absorption and emission spectra before and after doping, implying that the charge-transfer complexes between the polymers and C_{60} may have not formed in the ground states. All the three polyacetylenes (**3**, **8**, and **6**) are liquid crystalline but with different melting transition temperatures. Because of the distorting effect of the rigid PPA backbone, the mesogenic groups in **3** cannot pack well and thus the polymer is predominantly amorphous in the solid state.[23e] The melting transition temperature of **3** is very high, and the thermal treatment at 353 K in the photoreceptor manufacturing process can hardly bring the amorphous film to liquid crystalline state. Fullerene molecules are known to aggregate in amorphous polymer matrixes. The aggregation generates polymer/fullerene heterojunctions, through the interfaces of which, fast photoinduced electron transfer and charge separation occur,[40] which effectively enhances the photoconductivity of the photoreceptor.

The melting transition temperature of **6** is below 353 K and the molten polymer "liquid" may dissolve the C_{60} molecules. Upon cooling, the molecularly dispersed bulky C_{60} cages may act as "impurities" to hamper the packing of the liquid crystal mesogens, leading to a large decrease in the photosensitivity. We have previously found[41] that the giant three-dimensional C_{60} cages (or buckyballs) act as plasticizers in the PC systems, which increases the free volumes between the polymer chains, enhances the local segmental flexibility, and consequently lowers the glass transition temperature of the C_{60}-containing polymers. Edman et al. have observed that C_{60} works as an effective "structure-breaking plasticizer": addition of a very small amount of C_{60} to a mixture of poly(ethylene oxide) and $LiCF_3SO_3$ readily breaks up the crystalline structure of the polymer–salt complexes.[42] It is thus highly likely that the fullerene molecules also destroys the packing arrangements of the mesogenic pendants of **6**.

The temperature of melting transition in **8** is close to that employed in the drying process of the photoreceptor films. Thus, the two antagonistic effects compete in the photoreceptor system: part of the buckyballs may act as the crystallinity-breaking plasticizers while a somewhat larger fraction of the C_{60} molecules may aggregate in the amorphous region of the polymer. The result of the competition is the observed slight increase in the photosensitivity.

Photoconductivity of I_2-Doped and CV-Sensitized Polyacetylenes. As discussed in the Introduction section, doping PPA with I_2 increases its photoconductivity. Polymer **3** is a PPA derivative with a relatively

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(41) Tang, B. Z.; Peng, H.; Leung, S. M.; Au, C. F.; Poon, W. H.; Chen, H.; Wu, X.; Fok, M. W.; Yu, N.-T.; Hiraoka, H.; Song, C.; Fu, J.; Ge, W.; Wong, K. L. G.; Monde, T.; Nemoto, F.; Su, K. C. *Macromolecules* **1998**, *31*, 103. (b) Tang, B. Z.; Leung, S. M.; Peng, H.; Yu, N.-T.; Su, K. C. *Macromolecules* **1997**, *30*, 2848. (c) Tang, B. Z.; Peng, H.; Leung, S. M. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennington, NJ, 1997; Vol. 4, pp 655–667. (d) Tang, B. Z.; Peng, H. In *Recent Advances in Overseas Polymer Science*; He, T., Hu, H., Eds.; Chemical Industry Press: Beijing, 1997; Chapter 10, pp 165–173.

(42) Edman, L.; Ferry, A.; Jacobsson, P. *Macromolecules* **1999**, *32*, 4130.

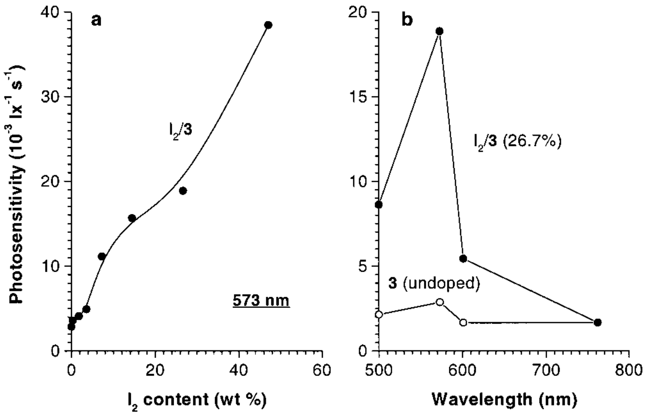

Figure 5. Effects of (a) iodine (I_2) content and (b) illumination wavelength on photosensitivity of single-layer photoreceptors of **3** exposed to visible light of 60 lx.

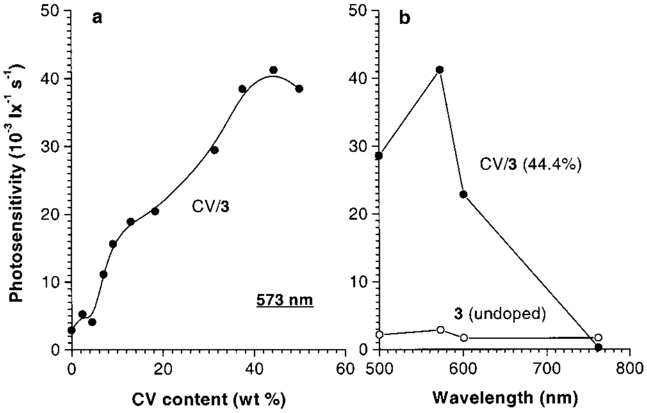

Figure 6. Effects of (a) crystal violet (CV) content and (b) illumination wavelength on photosensitivity of single-layer photoreceptors of **3** exposed to visible light of 60 lx.

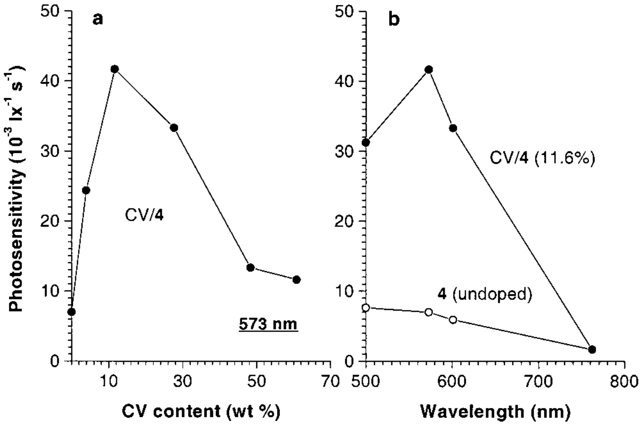

Figure 7. Effects of (a) crystal violet (CV) content and (b) illumination wavelength on photosensitivity of single-layer photoreceptors of **4** exposed to visible light of 60 lx.

low photoconductivity in the undoped state (cf., Table 2) and we thus tried to boost its photosensitivity by I_2 doping. As shown in Figure 5a, the photosensitivity of the photoreceptors of I_2-doped **3** to the 573 nm illumination monotonically increases with the increase in the I_2 content. The increase in the high I_2 content region becomes sharper, possibly because the more efficient iodine aggregation leads to the formation of heterojunctions with larger interface areas. At ~46 wt % I_2 doping, the photosensitivity is as high as $\sim 38 \times 10^{-3}$ lx^{-1} s^{-1}, which is ~14 times higher than that of the undoped parent. The shapes of the photosensitivity spectra of the photoreceptors of the undoped and doped **3** (with 26.7 wt % I_2) are similar, both giving a maximum at 573 nm (Figure 5b). The magnitudes of the photosensitivity of the doped **3** are, however, much higher in most part of the visible spectral region.

We also tried to increase the photoconductivity of **3** by CV sensitization. The photosensitivity of the photoreceptors of the CV-sensitized **3** at 573 nm increases with the CV content, reaching a maximum at ~44 wt % (Figure 6a). Carrier injection into polymers is known to be the main process in dye-sensitized photoconduction.[3b] The enhancement in the photosensitivity of the sensitized **3** thus may involve efficient electron transfer from the donor molecule (CV) to the photoexcited **3**. The photosensitivity spectra of the sensitized and unsensitized **3** again have the similar shapes, with the former locating well above the latter in most of the visible region. At 573 nm, the sensitized **3** shows a photosensitivity ~15 times higher than does the unsensitized one.

Similar results are obtained when **4** is sensitized by CV. However, the photosensitivity of the CV-sensitized **4** at 573 nm reaches its maximum at a much lower CV content (~12 wt %; Figure 7a). The CV-sensitized **4** with this relatively small amount of sensitizer exhibits quite high photoconductivity in the spectral region around 700 nm (Figure 7b). For a material to be useful in digital xerography, its photosensitivity in the red and infrared regions is usually required.[2,9,43] The CV-sensitized **4** with the infrared sensitivity thus may find potential applications in the digital imaging technologies.

Concluding Remarks

In this study, we have investigated photoconduction in the single-layer photoreceptors of substituted polyacetylenes. The nature of the substituents has been found to affect the photosensitivity of the polyacetylene photoreceptors to the visible light illumination: (i) the polymers with donor substituents (**2**, **4**, and **6**−**8**) show higher photosensitivity than do those with acceptor ones (**3** and **5**); (ii) when the donor substituents are simultaneously hole transporting (**4** and **7**), the photosensitivity becomes even higher; and (iii) when the donor substituent is mesogenic and can be packed in an ordered fashion (**6**), the photosensitivity further increases. Thus, incorporation of substituents capable of electron donating, hole transporting, and self-aggregating should lead to the development of excellent photoreceptor materials. Such structure−property relationships will help guide molecular engineering endeavor in designing new functional polyacetylenes with superior photoconduction performance.

We have found that a simple thermal treatment to a liquid crystalline polyacetylene with an appropriate transition temperature (**6**) leads to a large increase in photosensitivity. The formation of the crystalline aggregates induced by the "dry" process is a novel approach, with an obvious advantage of obviating the use of the toxic solvent in the "wet" fuming process in the preparation of conventional photoreceptors of dye ag-

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(43) Chen, I. *J. Imag. Sci. Technol.* **1990**, *34*, 15. (b) Jeyadev, S.; Pai, D. M. *J. Imaging Sci. Technol.* **1996**, *40*, 327.

gregates.[2] Noticing that **6** is both liquid crystalline and photoconductive, it may find attractive applications as a photosensitive element in the liquid crystal spatial light modulating systems.[44]

Heeger and Wudl's groups have observed that the efficient photoinduced electron transfer from the conjugated polymers to fullerene molecules brings about an increase in photoconductivity.[40] In our polyacetylene photoreceptor systems, we have discovered multifaceted doping effects of C_{60}: it functions as either a photoconductivity enhancer or a crystallinity-breaking plasticizer depending on the morphology of the polymers. When the polymer is amorphous, the aggregation of the C_{60} molecules[45] increases its photoconductivity. In the liquid crystalline state, the $\pi-\pi$ interaction of C_{60} with the aromatic rings of the mesogenic groups dissolves the buckyballs. The well-dispersed fullerene molecules may plasticize the polymer chains[41] and break the crystalline packing[42] of the mesogenic groups in the solid state when the photoreceptor film is cooled to room temperature, thus leading to a decrease in the photosensitivity.

We have further demonstrated that doping with I_2 and sensitization with CV can dramatically increase the photoconductivity of the polyacetylene photoreceptors. The CV-sensitized **4** possesses quite high photosensitivity in the near-infrared spectral region; such attribute makes the polymer a promising candidate for photoreceptor materials to be used in the digital optical imaging systems.

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