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Ionization Potential Dependence of Photoconductive Properties of Polysiloxanes Bearing Hole-Conductors Sensitized with C_{60}

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Photo-charge generation efficiencies and photoconductivities were measured at 632.8 nm in a series of polysiloxanes bearing hole-conductors doped with C_{60} as sensitizer. Generation and transport of mobile carriers were strongly dependant on the charge-transfer (CT) complex formed between the hole conducting polymer and the sensitizer. We investigated the dependence of the ionization potential of hole conducting polymer on the photoconductive properties of the CT complex. The composite containing polymer with lower ionization potential had the highest photo-charge generation efficiency and photoconductivity.

Keywords Hole conducting polymer; ionization potential; photo-charge generation efficiency; photoconductivity

1. Introduction

Since doped polymers were used as xerographic photoreceptors [1], and the potential use of molecular glasses in electroluminescence [2] and photovoltaic devices [3], there has been considerable interest in generation and transport of mobile photo-carrier in disordered composite system during the past two decades [4]. The photoconductive properties are strongly dependant on the charge transfer (*CT*) interaction between a electron donor (hole conducting polymer) and a electron acceptor (photosensitizer). The hole conducting polymers having lower ionization potential (*IP*) are stronger electron donor and can bind more strongly to identical photosensitizer [5].

In this work, we investigated the dependence of the ionization potential of hole conducting polymer on the photo-charge generation efficiency (ϕ) and photoconductivity (σ_{ph}). We measured on the photo-charge generation efficiencies and photoconductivities of a series of composites based polysiloxanes bearing hole-conductors sensitized with C_{60}. The photoconductive properties were closely related to the ionization potential of the hole conducting polymers.

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2. Experimental

2.1. *Materials and Sample Fabrications*

Several composites were prepared by blending hole conducting polymer matrix and photosensitizer, C_{60}, in the ratio of 99: 1 by wt%, respectively. Figure 1 shows the chemical structure of the hole conducting polymers used in this work. Their synthesis will be reported elsewhere [6]. The ionization potentials of all polymers are shown in Table 1. The *IP* of polysiloxane based polymers was adjusted by electron-donating group. To obtain homogeneous samples all components were dissolved in toluene followed by evaporation of solvent. For photo-charge generation efficiency measurement, the films were fabricated by doctor-blade technique on a $2.5 \times 2.5\,\mathrm{cm}^2$ ITO glass substrate. For photoconductivity measurement, the devices were prepared by sandwiching of the heat-softened composite between two ITO coated glass plates [7]. The thickness of active layer was 100 μm.

2.2. *Measurements*

The ionization potential of the hole conducting polymers and sensitizer was calculated by geometry optimization of materials using the semi-empirical method, VAMP-AM1 in the Material Studio 4.1 program (Accelrys co.). The photo-charge generation efficiency of samples was calculated from the amplitude of the photovoltage measured by electrometer (TREK model 344) under the He-Ne laser ($I = 3.6$ mW/cm^2) which is 1 cm in diameter [8]. The photoconductivity of samples was measured by simple *dc* method using He-Ne laser with intensity of 20 mW/cm^2 while applying bias field of 30 and 60 V/μm [9].

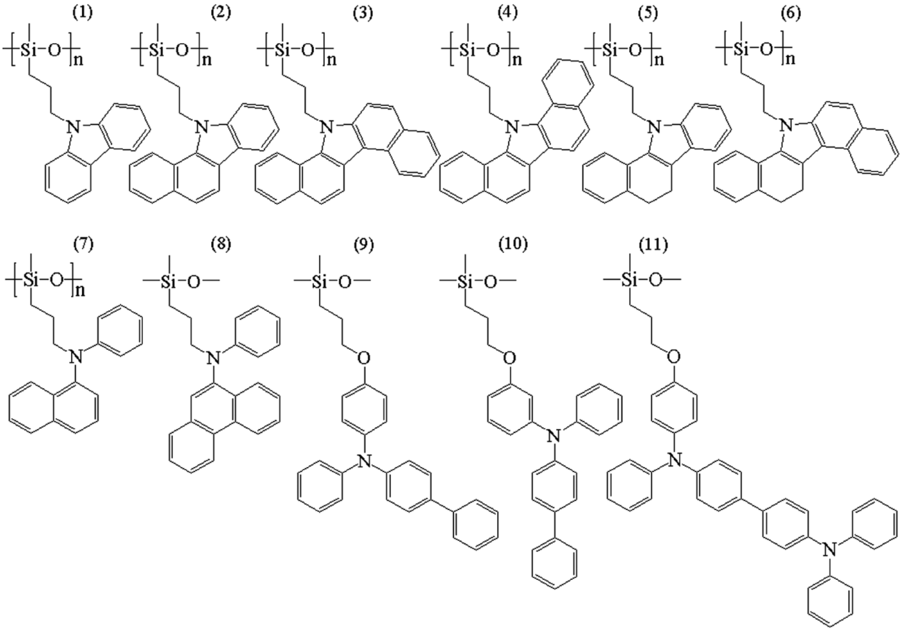

Figure 1. Chemical structure of the hole conducting polymers used in this work.

Table 1. Sample identification scheme, composition and ionization potential of the hole conducting polymers, respectively. For the numbering of polymers **1**–**11** see Figure 1

Sample	Composition (wt%)	Polymer *IP* (eV)	Sample	Composition (wt%)	Polymer *IP* (eV)
A	1:C_{60} (99:1)	8.28	G	7:C_{60} (99:1)	8.22
B	2:C_{60} (99:1)	8.01	H	8:C_{60} (99:1)	8.33
C	3:C_{60} (99:1)	7.80	I	9:C_{60} (99:1)	7.72
D	4:C_{60} (99:1)	8.08	J	10:C_{60} (99:1)	7.88
E	5:C_{60} (99:1)	7.99	K	11:C_{60} (99:1)	7.71
F	6:C_{60} (99:1)	7.76			

3. Results and Discussion

As can be seen from the data in Table 1, the triphenylamine (TPD) derivatives have a lower ionization potential than carbazole derivatives. The ionization potential of hole conducting polymers **1**–**11** could be varied by 0.57 eV by substitution with the electron donating groups [5].

The photo-charge generation efficiency, that is, the number of free carriers produced divided by the number of absorbed photons, is a basic parameter in the evaluation of photoconductor performance [5]. Figure 2 shows ionization potential dependences of photo-charge generation efficiency of samples **A**-**K**. As shown Figure 2, samples containing hole conducting polymers with lower ionization potential have the higher photo-charge generation efficiency. Sample **K** containing polymer **11** with lowest *IP* (7.71 eV) has highest photo-charge generation efficiency (0.0304). The *IP* dependence of photo-charge generation efficiency can also be explained by following equation [10]:

$$\phi = \left[1 + \theta \exp\left(\frac{\Delta(U=0) - U_{ph} - \beta E^{1/2}}{2kT}\right)\right]^{-1} \quad (1)$$

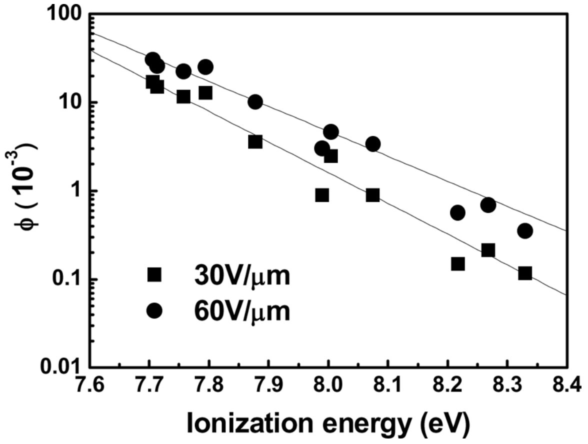

Figure 2. Ionization potential dependence of photo-charge generation efficiency for samples **A**-**K**. The line is calculated by Eq. (1).

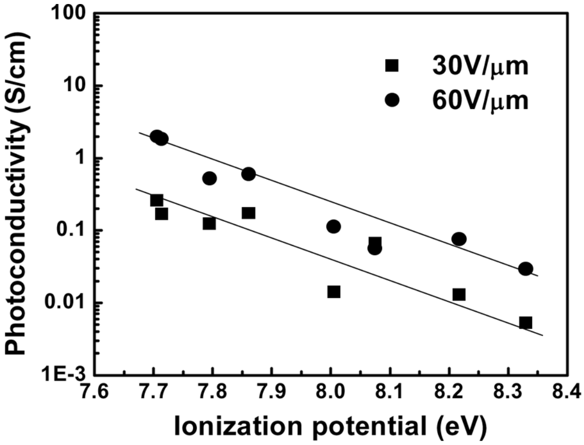

Figure 3. Ionization potential dependence of photoconductivity for samples **A**-**K**. The line is a guide to the eye.

where $\Delta U = \Delta(U = 0) - \beta E^{1/2}$, $\beta = (e^3/\pi\epsilon\epsilon_0)^{1/2}$, ΔU is ionization potential energy in the presence of a field, $\Delta(U = 0)$ is the zero-field energy, U_{ph} is photon energy, E is electric field, ε is dielectric constant, ε_0 is vacuum permittivity, k is Boltzmann constant. As shown in Figure 2, the experimental data for the *IP* dependence of the photo-charge generation efficiency are in excellent agreement with the simulation results of the above equation over the whole *IP* range. From these results, we can confirm that the correlation between ionization potential of the hole conducting polymer and photo-charge generation efficiency of the CT complex is clear.

The photoconductivity is closely related to the charge generation and the transport of photo carriers by [11,12]:

$$\sigma ph = ne\mu = \left(\frac{\varphi\alpha I\tau}{h\nu}\right)e\mu \tag{2}$$

where n is the density of carriers, e the elementary charge, μ the mobility, α the absorption coefficient, I the optical intensity, τ the life time of carrier, and $h\nu$ is the photon energy. Figure 3 shows photoconductivities of samples **A**-**K** as a function of the ionization potential of hole conducting polymers. The photoconductivity was calculated as the difference between the total conductivity in the presence of light and the dark conductivity in the absence of light. We can see that the photoconductivity exhibited a strong *IP* dependence; as the ionization potential was decreased, the photoconductivity increased. This tendency was similar to the *IP* dependence of photo-charge generation efficiency. For sample **K**, decreasing ionization potential leads to a larger photoconductivity through a higher photo-charge generation and a faster electron-transfer.

4. Conclusion

In this work, we have measured the photo-charge generation efficiencies and photoconductivities of series of polysiloxanes bearing hole-conductors with different electron donating groups, sensitized with C_{60}. The photoconductive properties was found to correlate with the ionization potential of hole conducting polymer. The sample containing polymer with lowest ionization potential has highest photo-charge generation efficiency and photoconductivity. All experimental results were in excellent agreement with theoretical simulation data.

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