Synthesis and Photoconductivity of Polystyrene Containing *N*-Substituted 5-(*p*-Diethylaminobenzylidene)rhodanine Group in Side Chains

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ABSTRACT: Polystyrene containing *N*-substituted 5-(*p*-diethylaminobenzylidene)rhodanine in the side chains (PSt-Rhod) was synthesized by esterification of chloromethylated polystyrene with 3-carboxymethyl-5-(*p*-diethylaminobenzylidene)rhodanine. The content of *N*-Substituted 5-(*p*-diethylaminobenzylidene)rhodanine in polystyrene was 20 mol%. Since PSt-Rhod was soluble in tetrahydrofuran (THF) and chloroform, a homogeneous film was prepared from its solution. The wavelength of the peak absorbance of the polymer solution in THF was 473 nm. The photo-carrier generation of this polymer was investigated by measuring current-voltage characteristics. A solid solution of the PSt-Rhod and a carrier transport material such as 4-diethylaminobenzaldehyde-1,2-diphenylhydrazone exhibited very large photoconductivity. It could be seen from a photocurrent action spectrum that the *N*-substituted 5-(*p*-diethylaminobenzylidene) rhodanine group existing in side chains of polystyrene generates free carriers by visible light. The photoconductivity was greatly influenced by the atmosphere and an electrode. From these results, it is concluded that exciton dissociation is caused (1) by an electric field due to the Schottky-barrier, and (2) by a local electric field formed by ionically-absorbed oxygen molecules.

KEY WORDS Chloromethylated Polystyrene / Rhodanine Dye /
Hydrazone Derivative / Solid Solution / Current-Voltage Characteristic /
Photocurrent / Dark Current /

Photoconductive polymers such as poly-*N*-vinylcarbazole (PVCz) have been extensively investigated.¹⁻¹⁰ These polymers have no photoconductivity in the visible light region. Other photoconductive polymers reported by Hirohashi *et al.*¹¹ and Schopov¹² have photoconductivity in the visible light region, but are insoluble in all solvents except concentrated sulfuric acid or *N,N*-dimethylformamide (DMF). So far, there is no report on soluble polymers which have simple structures and show photoconductivity in the visible light region.

In many cases where organic photoconductive materials are used in the electrophot-

ographic photoreceptor, the carrier generation materials and carrier transport materials are dispersed in the binder matrix polymer. But, it is difficult to prepare a homogeneous film by this method. Accordingly, we tried to synthesize a soluble photoconductive polymer which is sensitized in the visible light region. We successfully synthesized the above polymer by reacting a polystyrene derivative with a photoconductive, low molecular weight compound.

Substitution reactions of chloromethylated polystyrene with a number of nucleophilic reagents have been widely carried out to obtain polymeric reagents and ion exchange resins. Applying this method, we synthesized a

Figure 1. Schematic diagram of a sample structure and circuit used in measuring current-voltage characteristics.

source, and monochromatic light was obtained using an interference filter. A schematic diagram of a sample structure and the circuit used in the measurement of current-voltage characteristics are shown in Figure 1.

RESULTS AND DISCUSSION

Photoconductive Properties of PSt-Rhod

Rhodanine dyes crystallize at the concentration of more than 8 wt% in PSt-CH₂Cl film. The photoconductivity of a PSt-CH₂Cl film doped with 3-carboxymethyl-5-(*p*-diethylaminobenzylidene)rhodanine was examined by measuring current-voltage characteristics using a raster-type cell. In Figure 2, the photoconductivity of Rhodanine dye in PSt-CH₂Cl film is plotted as the ratio of photocurrent to dark current against applied voltage. The ratio of photocurrent to dark current is large for the crystalline state (15 wt%), but small for the molecular dispersion state (6 wt%).

Using the same measuring system, the photoconductivity of a PSt-Rhod was examined, but no photoconductivity was observed. Although the PSt-Rhod contained 38 wt% of

Figure 2. Voltage dependence of the ratio of photocurrent to dark current of a PSt-CH₂Cl film doped Rhodanine dye and PSt-Rhod under vacuum at room temperature. (1) crystalline state (15 wt%); (2) molecular dispersion state (6 wt%); (3) PSt-Rhod.

Figure 3. Structure of 4-diethylaminobenzaldehyde-1,2-diphenylhydrazone.

Table I. Absorption maximum and molecular extinction coefficient

Structural formula		Substituent		$\lambda_{\max}$ (nm)	$\epsilon (\times 10^4)$
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_1-\text{N}-\text{C}-\text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{R}_2 \\ \parallel \\ \text{S} \end{array}$		R ₁	R ₂		
		H	N(C ₂ H ₅) ₂	467	1.25
		CH ₃	N(C ₂ H ₅) ₂	473	5.25
		CH ₂ COOH	N(C ₂ H ₅) ₂	469	5.18
		NH ₂	N(C ₂ H ₅) ₂	481	4.10
		C ₆ H ₅ SO ₃ Na	N(C ₂ H ₅) ₂	400	3.68
		CH ₂ COOH	H	376	3.05
		CH ₂ COOH	OH	397	3.65
		CH ₂ COOH	N(C ₂ H ₅) ₂	469	5.18

Figure 4. Spectral dependence of photocurrent and absorbance of a solid solution of PSt-Rhod and 4-diethylaminobenzaldehyde-1,2-diphenylhydrazine (40 wt%) under vacuum at room temperature. (1) absorbance; (2) photocurrent.

a Rhodanine dye, the ratio of photocurrent to dark current was about one. It is reasonable to consider that free carriers were generated at the chromophore side chains but they could not migrate in the film.

Next, the photoconductivity of a solid solution of PSt-Rhod and a carrier transport material (Figure 3) was investigated.

The photocurrent observed in a solid solution with PSt-Rhod was almost coincident with the absorption of PSt-Rhod, as shown in Figure 4. Even though the amount of hydrazone in the solid solution changed, the shape of the photocurrent action spectrum was not changed. From these findings, the photoconductivity of the solid solution may be described as follows. The excitons are generated by absorption of light by PSt-Rhod and dissociated into free carriers (holes and electrons) by an internal electric field. The holes migrate through hydrazone molecules in compliance with an external electric field.

Influence of Atmosphere (Oxygen) on Photoconductivity

For a solid solution of PSt-Rhod and hy-

Figure 5. Influence of the atmosphere on the ratio of photocurrent to dark current of a solid solution of PSt-Rhod and 4-diethylaminobenzaldehyde-1,2-diphenylhydrazine (40 wt%). (1) atmosphere; (2) vacuum.

Figure 6. Voltage dependence of the ratio of atmospheric current and vacuum current of a solid solution of PSt-Rhod and 4-diethylaminobenzaldehyde-1,2-diphenylhydrazine (40 wt%). (1) photocurrent; (2) dark current.

drazone, the influence of the atmosphere on photoconductivity was investigated. The ratio of photocurrent to dark current in the atmosphere was approximately four times that under vacuum as shown in Figure 5.

In addition, the ratio of atmospheric dark current to vacuum dark current was approximately one, but the ratio of atmospheric photocurrent and photocurrent under vacuum was approximately five (Figure 6). The influence of the atmosphere on photoconductivity became more remarkable when the V/I measurement was carried out under a higher vacuum.

It was also revealed that the influence of the atmosphere is greater on photocurrent than on dark current. This effect of the atmosphere on the photocurrent may be caused by adsorption of oxygen toward the solid solution. Because the local electric field formed by oxygen anions induces the dissociation of excitons,¹⁴ a large photoconductivity was observed in the atmosphere. The dissociation of excitons due to the local electric field caused by ionically-absorbed oxygen molecules has already been reported in the other organic systems such as phthalocyanine.¹⁵

Potential Interface between a Metal and a Solid Solution of PSt-Rhod and Hydrazone

The interface between a metal and a solid solution of PS-Rhod and hydrazone was investigated. Figure 7 shows the absorption spectrum of the PSt-Rhod, the photocurrent action spectrum of ITO/PSt-Rhod hydrazone/AI, and ITO/PSt-Rhod hydrazone/Au cells. The action spectrum was measured by passing the light through the ITO electrode. As can be seen from the photocurrent action spectrum shown in Figure 7, the masking effect due to the absorption of PSt-Rhod was clearly observed and the Schottky-barrier seemed to be formed at the interface between the metal and solid solution of PSt-Rhod and hydrazone. A similar relation between absorption spectrum and photocurrent action spectrum was observed in other organic systems.^{16,17}

The interface between the solid solution of PSt-Rhod and hydrazone, and the metal was examined by measuring current-voltage char-

Figure 7. Spectral dependence of photocurrent in a sandwich-type cell of a solid solution of PSt-Rhod and 4-diethylaminobenzaldehyde-1,2-diphenylhydrazone (40 wt%) under vacuum at room temperature. (1) ITO/PSt-Rhod hydrazone/AI; (2) ITO/PSt-Rhod hydrazone/Au.

Figure 8. J-V characteristics of an Al/PSt-Rhod hydrazone/Au cell. (1) Al/PSt-Rhod hydrazone/Au; (2) Al/PSt-CH₂Cl hydrazone/Au; (3) Al/PSt-Rhod/Au.

acteristics. The typical J-V curves for Al/Pst-Rhod/Au, Al/PSt-CH₂Cl hydrazone/Au and Al/PSt-Rhod hydrazone/Au cells, all measured in the dark, are shown in Figure 8. In the Al/RSt-Rhod/Au cell, the relation between current and voltage was ohmic. But in the Al/PSt-CH₂Cl hydrazone/Au and the Al/PSt-Rhod hydrazone/Au cells, the relation was not

Figure 9. Cycle photoresponse characteristic of a solid solution of PSt-Rhod and 4-diethylaminobenzaldehyde-1,2-diphenylhydrazone (20 wt%) under vacuum at room temperature.

ohmic and exhibited rectification as was also observed in other organic systems.^{18,19} The excitons were assumed to be dissociated by an internal electric field possibly due to the Schottky-barrier formed at the interface between the metal and hydrazone molecules in PSt-Rhod. Free carriers were thereby generated and caused a photocurrent. A representative photoresponse characteristic of the solid solution of PSt-Rhod and hydrazone is shown in Figure 9. The photoresponse characteristics of the solid solution of PSt-Rhod and hydrazone were stable during many repeated exposures in the case of the sandwich and raster-type cells. For example, differences between the photocurrent and dark current were unchanged for a hundred times of repeated exposure in case of the raster-type cell as shown in Figure 9.

CONCLUSION

PSt-Rhod is soluble in organic solvents and forms a homogeneous film. A solid solution with a carrier transport material such as 4-diethylamino-benzaldehyde-1,2-diphenylhydrazone has large photoconductivity in the

visible region. The photoconductivity of the solid solution seems to be based on the following process. In the first step, excitons are generated by absorption of light by PSt-Rhod and are dissociated into free carriers (holes and electrons) by internal electric field. Secondly, the holes migrate through the hydrazone molecules in compliance with the external electric field. It seems that two kinds of internal electric fields act on the dissociation processes of excitons. One is a local electric field formed by ionically-absorbed oxygen molecules as was seen in other organic systems such as phthalocyanine, and the another is an electric field due to Schottky-barrier formed at the interface between the metal and hydrazone molecules in PSt-Rhod.

REFERENCES

1. P. J. Reucroft, S. K. Ghosh, and D. Keever, *J. Polym. Sci., A-2*, **10**, 2305 (1972); *Phys. Rev.*, **138**, 803 (1973).
2. K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 1953 (1973).
3. J. E. Carnes, and P. J. Warter, Jr., *Phys. Rev.*, **B5**, 1557 (1972).
4. R. C. Hughes, *J. Chem. Phys.*, **58**, 2212 (1973).
5. C. F. Hackett, *J. Chem. Phys.*, **55**, 3178 (1971).
6. G. Pfister, M. Abkowitz, and D. J. Williams, *J. Chem. Phys.*, **57**, 2979 (1972).
7. P. J. Meltz, *J. Chem. Phys.*, **57**, 1694 (1972).
8. W. D. Gill, *J. Appl. Phys.*, **43**, 5033 (1972).
9. J. Mort, *Phys. Rev.*, **B5**, 3329 (1972).
10. K. Okamoto, S. Kusabayashi, and H. Mikawa, *Bull. Chem. Soc. Jpn.*, **46**, 1948, 2324, 2613, 2883 (1973).
11. R. Hirohashi, Y. Hishiki, and M. Dohi, *Kogyokagaku*, **73**, 1450 (1970).
12. I. Schopov, *Polym. Lett.*, **4**, 1023 (1966).
13. K. W. Pepper, H. M. Paiseley, and M. A. Yung, *J. Chem. Soc.*, **1953**, 4097 (1953).
14. F. Gutmann and L. E. Lyons, "Organic Semiconductors," John Wiley & Sons, New York, 1967.
15. J. Mizuguchi, *Denshishyasin*, **26**, 216 (1987).
16. A. K. Ghosh and T. Feng, *J. Appl. Phys.*, **49**, 5982 (1978); *ibid.*, **44**, 2781 (1973).
17. A. K. Ghosh, D. L. Morel, T. Feng, R. F. Shaw, and C. A. Rowe, Jr., *J. Appl. Phys.*, **45**, 230 (1974).
18. R. O. Loutfy and J. H. Sharp, *J. Chem. Phys.*, **71**, 1211 (1979).
19. R. O. Loutfy, J. H. Sharp, C. K. Hsiao, and R. Ho, *J. Appl. Phys.*, **52**, 5218 (1981).