CHEMISTRY LETTERS, pp. 1575-1578, 1989.

Photo-induced Stable Radicals in Organic Photoconductors

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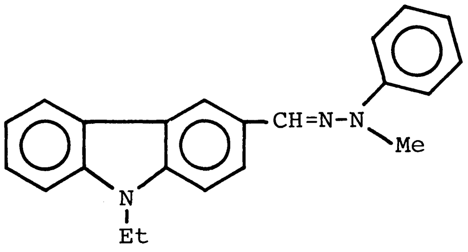
Irradiation of fluorescent light onto a solid solution containing a hydrazone compound and a polymer generated stable polymer radicals at room temperature. Spin concentration was 10^{13} spins/g and saturated within 6 h under 10 Klx fluorescent light. The factors affecting the stable radical formation are discussed.

Observation of stable free radicals has been reported for many polymer matrices. Oxidation, pyrolysis, mechanical degradation, and irradiation of high energy rays, such as γ-rays, cause polymer free radicals, and some of them are very stable.1) In the field of photochemistry, UV rays have been used for the generation of free radicals, but its ESR signals have been generally observed only at low temperatures.2,3)

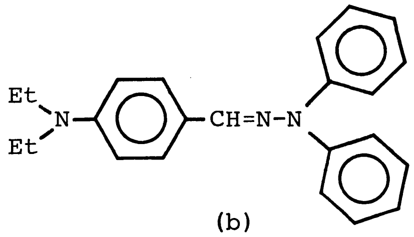
Recently, solid solutions containing a hydrazone compound and a polymer have been used as the charge transportation layer of organic photoconductors for electrophotography.4,5) In this system, the cation radicals seem to carry holes at the moment of photo irradiation onto the organic photoconductors,6) but the existence of the cation radicals and details of the mechanism of radical formation have not been confirmed.

Stolle, et al. reported stable radicals induced by photo-irradiation of photoconductive polyvinylcarbazole.7) They suggested that cation radicals were photo-induced, which caused alkyl-abstraction leading to degradation of the organic photoconductor.

The authors report here the formation of stable radicals in polymer solid solutions containing a hydrazone compound, which do not actually show photoconductivity under irradiation of fluorescent light.



(a)



(b)

A given amount of hydrazone (a)[8] was dissolved in a 10 wt% polyarylate (polyester from 4,4'-isopropylidendiphenol and terephthalic acid and isophthalic acid) solution of 1,1,2-trichloroethane. This solution[10] was dropped on a silicon rubber sheet and dried at 80 °C. More than one hundred solid samples (ca. 200 mg, 3 mm ⌀, and 0.2 mm thickness) were placed in a dry N_2 purged ESR tube. The states of samples were almost the same as in a practical charge transportation layer of an organic photoconductor. When the drying time was longer than 10 h, the samples became opaque due to deposit of the hydrazone compound. Thus opaque samples were prepared. Samples with different concentrations of hydrazones (a) and (b)[11] were prepared similarly. During a 10 Klx fluorescent light[12] was irradiated to the samples in ESR tube, ESR spectra were recorded at room temperature.[13]

Figure 1 shows the behaviors of the ESR signal in a polyarylate solid solution of hydrazone (a) under fluorescent light irradiation. When the ratio of (a) to polymer was 0.5 wt/wt., the spin concentration almost saturated after 2 h. Longer times were needed for saturation when this ratio was larger than 1.0. This trend was almost the same in all cases.

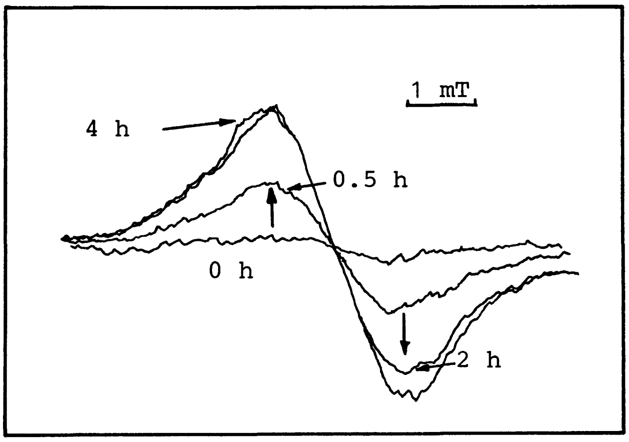


Fig. 1. ESR spectra of photo-irradiated sample.
(a)/polyarylate = 0.5

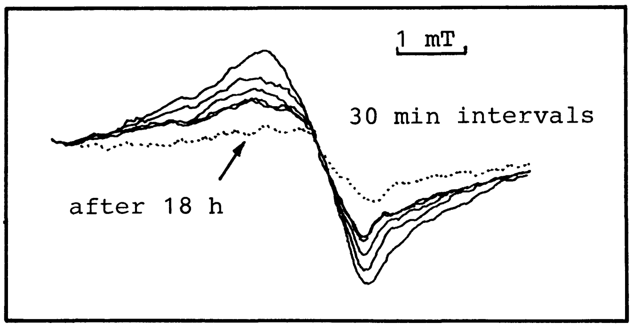


Fig. 2. The dark decay of ESR signal.
(a)/polyarylate = 1.0

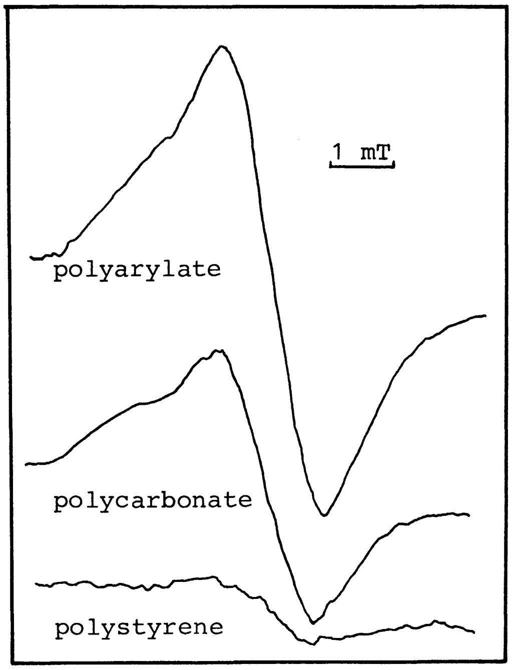


Fig. 3. ESR spectra of photo-irradiated samples for three kinds of polymer.
(a)/polymer = 1.0

Table 1. ESR Parameters for Photo-irradiated Samples

Run	Sample (wt ratio)		g-values[a]	spins/g (x 10^{-13})[b]
1	(a)/polystyrene	(= 0.5)	2.0048	<0.1
2	"	(= 1.0)	2.0087	<0.1
3	(a)/polycarbonate	(= 0.5)	2.0037	1.3
4	"	(= 1.0)	2.0046	1.3
5	"	(= 1.0)[c]	2.0042	1.7
6	"	(= 1.5)[c]	2.0039	1.8
7	(a)/polyarylate	(= 0.5)	2.0047	0.9
8	"	(= 1.0)	2.0051	1.3
9	"	(= 1.0)[c]	2.0038	4.5
10	"	(= 1.5)[c]	2.0039	3.8
11	(b)/polycarbonate	(= 1.0)[c]	2.0057	1.1
12	"	(= 1.5)[c]	2.0057	0.8

a) ± 0.0003

b) Values after irradiation of fluorescent light 4 h.

c) Opaque sample due to hydrazone deposit.

After stopping irradiation the ESR signal gradually reduced in dark at room temperature as shown in Fig. 2. The sample containing a large amount of hydrazone (a) showed a radical life time longer than a week. The sample prepared in dark did not show any ESR signal.

The data for the photo-irradiated samples are summarized in Table 1. The g-values were calculated by using a Mn^{2+} marker as a standard. The values of spin concentration were estimated comparing with the signal intensity of DPPH for a sample of known concentration.

The hydrazone molecules appear to disperse homogeneously in the transparent samples. The opaque samples contained heterogeneously deposited hydrazone.[14] Comparing the transparent with opaque samples of hydrazone and polymer 1 : 1 wt/wt, the spin concentrations of opaque samples were higher than those of the transparent samples (run 4 to 5, and 8 to 9). Small differences in the spin concentrations for opaque samples were observed for different hydrazone concentrations (run 5 to 6, 9 to 10, and 11 to 12). A shoulder and an asymmetrical line broadening were observed in the ESR spectra in all cases with a high hydrazone concentrations. This is probably due to that the motions of hydrazone molecules are depressed by deposit.[15]

The effect of the nature of polymer on ESR signals is shown in Fig. 3. The ESR signal intensity decreased in the following order: polyarylate > polycarbonate > polystyrene. The relative amount of the carbonyl group to the polymer unit were 0.15 for polyarylate, 0.11 for polycarbonate, and 0.0 for polystyrene, respectively. Hence, it seems reasonable that the amount of the carbonyl groups in the polymer chain influences generation of photo-induced radicals and their stability. Electron transfer from the hydrazone to the carbonyl groups in the polymer chain under photo-irradiation will produce a radical ion pair.[16]

This seems to be a main feature of the radical forming mechanism. But this is clearly not the case of polystyrene which has no carbonyl group. Irradiation of fluorescent light to hydrazone crystals also generated a small amount of radicals as in polystyrene samples. Further study is needed for the mechanism of generation of these photo-induced stable radicals.

References

1) B. Ranby and J. F. Rabeck, "ESR Spectroscopy in Polymer Research," Springer Verlag, New York (1977).
2) L. H. Piette, "Photo Chemical Studies with ESR," in "NMR and ESR Spectroscopy," Pergamon Press, London (1960), Chap. 20, pp. 241-251.
3) S. Ya. Psheztskii, A. G. Kotov, V. K. Milinchuk, V. A. Roginskii, and V. I. Tupikov, "EPR of Free Radicals in Radiation Chemistry," John Wiley & Sons, New York (1974).
4) Y. Shirota, "Dodensei-kobunshi-zairyo," ed by H. Sasabe, CMC, Tokyo (1983).
5) T. Murayama, Nippon Shashin Gakkai Shi, 50, 3 (1987).
6) J. Stevens and K. A. Zaklika, Photogr. Sci., 26, 2, 75 (1982).
7) T. H. Stolle, H. Pietsch, and I. Evert, Acta Polym., 38, 340 (1987).
8) K. Sakai, U. S. Patent 4454212 (1986). Commercially available.
9) All polymers were commercially available, and were purified by reprecipitation.
10) When a solution of DPPH was added to this solution, the color of DPPH disappeared rapidly, much faster than the air oxidation speed of color disappearance of an individual DPPH solution.
11) H. Y. Anderson, U. S. Patent 264737 (1981). Commercially available.
12) Irradiation was carried out by a FL10 (TOSHIBA) fluorescent light.
13) The ESR spectra were recorded by a JES FE2XG (JEOL) spectrometer.
14) Deposit of hydrazone crystals was confirmed by a polarizing microscope.
15) M. C. R. Symons, "The Identification of Organic Free Radicals by Electron Spin Resonance," Academic Press Inc, London (1963).
16) The ionization potentials were estimated as 5.1 eV for (a) and 5.2 eV for (b) by a AC-1 (RIKENKEIKI) low energy electron spectrometer.

(Received June 15, 1989)