High Photosensitivity in *cis*-Polyphenylacetylene Films Irradiated with ^{60}Co γ-Ray

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Synopsis

This paper reports that ^{60}Co γ-ray irradiation can convert *cis*-polyphenylacetylene (*cis*-PPA) films prepared with rare-earth coordination catalysts to highly photosensitive materials. The dependence of the photosensitivity on irradiation dose, preparation methods, and microstructure of the PPA films has been investigated by means of a potential discharge technique. The photosensitivity was enhanced with increasing irradiation dose. The critical dose to produce a light response was 5×10^3 Gy. The maximum surface potential discharge rate was 618 V/s, and the dark decay was approximately 2 V/s for *cis*-PPA films irradiated with ^{60}Co γ-ray (dose: 2×10^5 Gy). The *cis*-transoidal-PPA and an electrophotographic photoreceptor device incorporating *cis*-PPA showed a higher irradiation effect. The structure and properties of ^{60}Co γ-ray irradiated rare-earth PPA films are similar to the unirradiated films.

INTRODUCTION

Polyphenylacetylene (PPA) is a conjugated polymer. Theoretically, it has four geometric isomers, i.e., *cis*-cisoidal, *cis*-transoidal, *trans*-cisoidal, and *trans*-transoidal. Kang et al. reported that *trans*-PPA was a semiconducting photoconductor and showed higher photosensitivity in the red and near-infrared regions when doped with electron acceptors and sensitized with dyes.[1,2] This paper presents a novel method using ^{60}Co γ-rays to induce high photosensitivity in *cis*-PPA films. This method is completely different from the chemical methods reported in the literature. Some studies on the photosensitivity in ^{60}Co γ-ray irradiated *cis*-PPA films, and results of characterization of the ^{60}Co γ-ray irradiated *cis*-PPA films are reported.

EXPERIMENTAL

Preparation of PPA Films

The *cis*-PPA films were prepared by a direct method of simultaneously polymerizing and forming PPA films with rare-earth coordination catalysts in a hexane/toluene mixed solvent at 30°C.[3] The cis-content of the PPA films is more than 90%. The number-average molecular weight is about 10^5, as measured by GPC.

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The *trans*-PPA film was obtained by thermal isomerization of the *cis*-PPA film in a nitrogen atmosphere at 190°C for 30 min. The trans-content is approximately 100%.

An Electrophotographic Photoreceptor (P/R) Device

A photoreceptor (P/R) device incorporating *cis*-PPA consisted of three layers: aluminum substrate, a PMMA barrier layer, and a *cis*-PPA charge

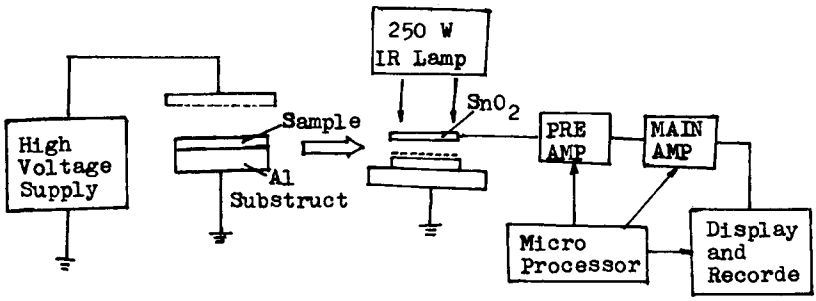

Fig. 1. Experimental arrangement for photosensitivity studies.

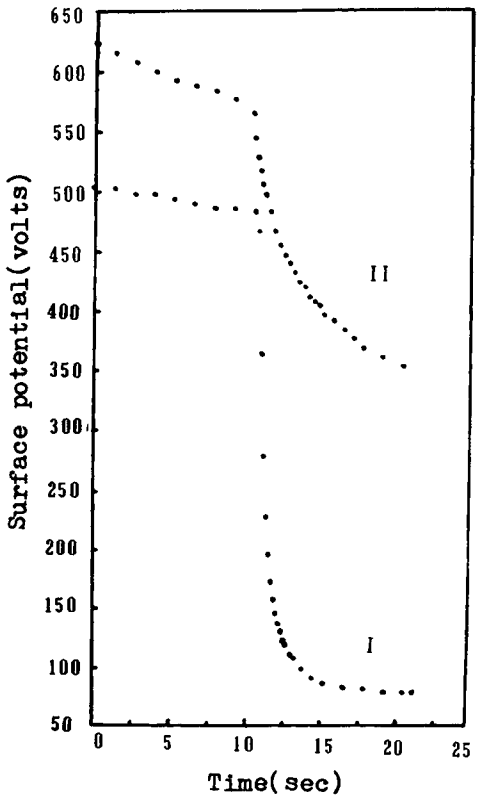

Fig. 2. Typical photoinduced discharge curves (PIDC) for negatively charged samples: (I) ^{60}Co γ-ray irradiated *cis*-PPA film (dose: 2×10^5 Gy), (II) unirradiated *cis*-PPA film.

generator layer. Each of the layers was solution coated and dried before adding successive layers.

Preparation of Highly Photosensitive Samples

The *cis*-PPA films pressed at 600 kg/cm^2 (thickness: 70–100 μm) and the photoreceptor (P/R) device incorporating the *cis*-PPA were exposed to ^{60}Co γ-ray irradiation in air atmosphere at room temperature.

Measurements

The infrared (IR) spectra were recorded on a Nicolet 5-DX FTIR spectrophotometer. Electron spin resonance (ESR) measurements were carried out using a JES-FEIXG ESR spectrometer. Gel permeation chromatography (GPC) measurements were performed at 30°C on a Waters GPC Model 208. The reference was polystyrene. DTA was carried out by a CDR-1 calorimeter.

The technique used in photosensitivity studies employs the photoinduced discharge of a corona-charged sample. A schematic diagram of the experimental arrangement is shown in Figure 1. The sample was charged to a negative potential by the corona discharge, then exposed under a 250 W IR-lamp. The distance between the lamp and the sample was just 10 cm. The surface potential discharge curves were recorded by a Z-80 microprocessor.

RESULTS AND DISCUSSION

The photosensitivity in ^{60}Co γ-ray irradiated samples has been investigated by means of the potential discharge technique. The greater the photosensitivity of a sample, the smaller its dark decay, the higher its surface potential discharge rate, and the lower its residual surface potential. Figure 2 shows typical photoinduced discharge curves (PIDC) of negatively charged samples under a 250 W IR lamp exposure. The ^{60}CO γ-ray (dose: 2×10^5 Gy) irradiated *cis*-PPA film (sample I) and unirradiated one (sample II) were charged to the initial potential of 502 and 623 V, respectively. During the dark period ($t < 10$ s), the dark decay for sample I is about 2 V/s; i.e., slower than that of sample II. During the light period ($t > 10$ s), the maximum surface potential discharge rate of sample I is 618 V/s; i.e., much faster than that of

TABLE I
The Dependence of Potential Discharge on the Irradiation Dose of ^{60}Co γ-Ray

Irradiation dose (Gy)	Dark: Maximum rate of Discharge (V/s)	Light: Maximum rate of discharge (V/s)	Discharge (%)
2×10^5	1.86	617.6	84.8
1×10^5	2.63	451.5	58.6
5×10^4	1.85	354.5	56.3
2×10^4	2.83	237.6	54.6
1×10^4	3.65	166.7	50.4
5×10^3	4.07	190.3	47.2
0	5.29	118.8	43.4

sample II. The residual voltage for sample I was 78 V; i.e., much lower than that for sample II. This indicated that the photosensitivity in the ^{60}Co γ-ray irradiated *cis*-PPA film is much higher than that in the unirradiated film.

The dependence of surface potential discharge rates on the dose of ^{60}Co γ-ray is shown in Table I. For ^{60}Co γ-ray irradiated *cis*-PPA films, the discharge rate increased and the dark decay rate decreased with increasing irradiation dose. The critical dose required to produce a light response was 5×10^3 Gy.

It is worth noting that ^{60}Co γ-ray irradiated an electrophotographic photoreceptor (P/R) device incorporating the *cis*-PPA showed a higher photosensitivity than ^{60}Co γ-ray irradiated *cis*-PPA films under the same experimental conditions, as shown in Figure 3. It can be seen that there is a certain influence of preparation methods on the photosensitivity of the material.

It has been found that the irradiation effect for ^{60}Co γ-ray is strongly dependent on the microstructure of the polymer. The rare-earth *cis*-PPA film has two different isomers: *cis*-transoidal and *cis-cis*oidal. The former is soluble in toluene and of low crystallinity, and the latter is insoluble in toluene and of high crystallinity.[4,5] Different irradiation effects for ^{60}Co γ-ray were observed for above two isomers, as shown in Figure 4. It is apparent that the photosensitivity in the *cis*-transoidal-PPA is higher than that in the *cis-cis*oidal-PPA, when irradiated with ^{60}Co γ-ray for the same dose. Therefore the irradiation effect of *cis*-transoidal PPA is much higher than *cis*-cisoidal PPA (as seen in Figure 4, Curves I and II). In fact, no irradiation effect for

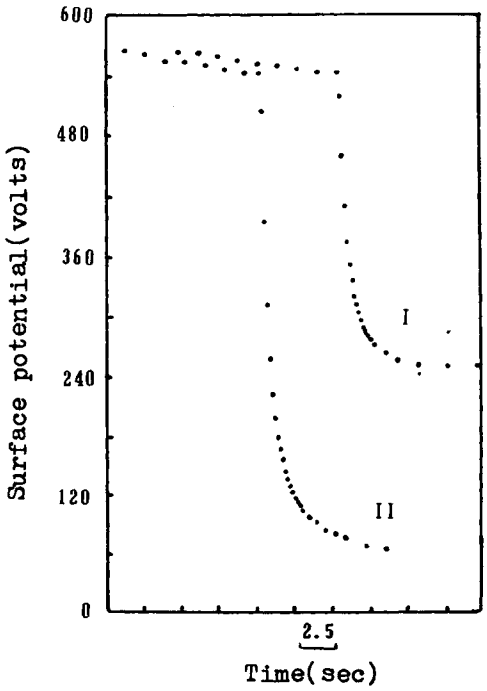

Fig. 3. The comparison of potential discharge for samples prepared with different methods: (I) ^{60}Co γ-ray irradiated *cis*-PPA film; (II) ^{60}Co γ-ray irradiated P/R device. Irradiation dose: 5×10^4 Gy.

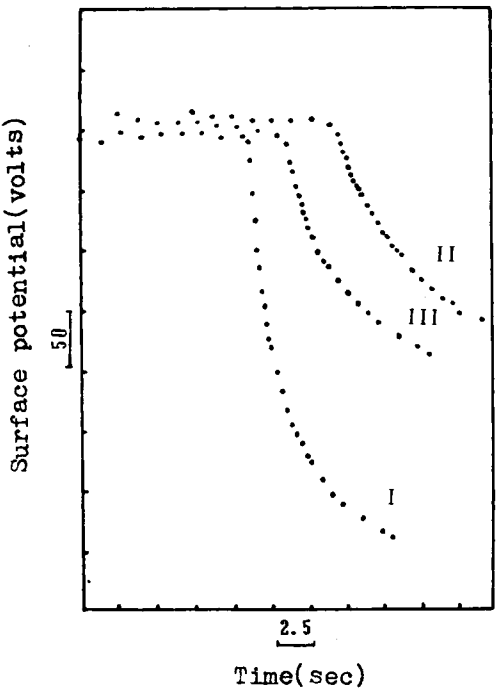

Fig. 4. Potential discharge of samples with different configuration: (I) *cis*-transoidal-PPA, (II) *cis*-cisoidal-PPA; (I, II) for irradiation with ^{60}Co γ-ray (5×10^4 Gy); (III) unirradiated *cis*-PPA film.

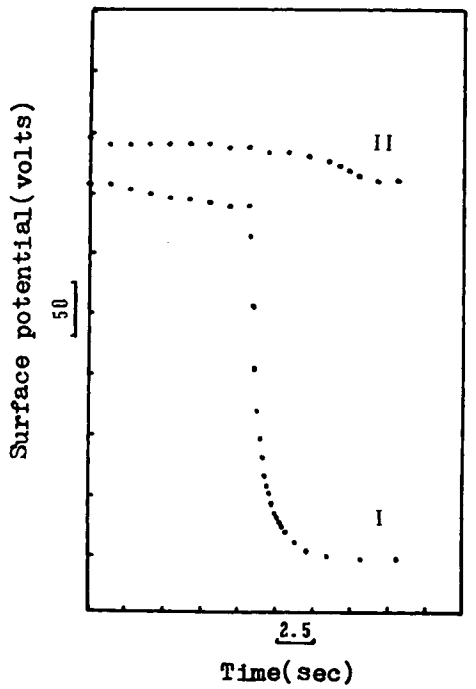

Fig. 5. Potential discharge of *cis*- (I) and *trans*- (II) PPA films for irradiation with ^{60}Co γ-ray. Irradiation dose: 5×10^4 Gy.

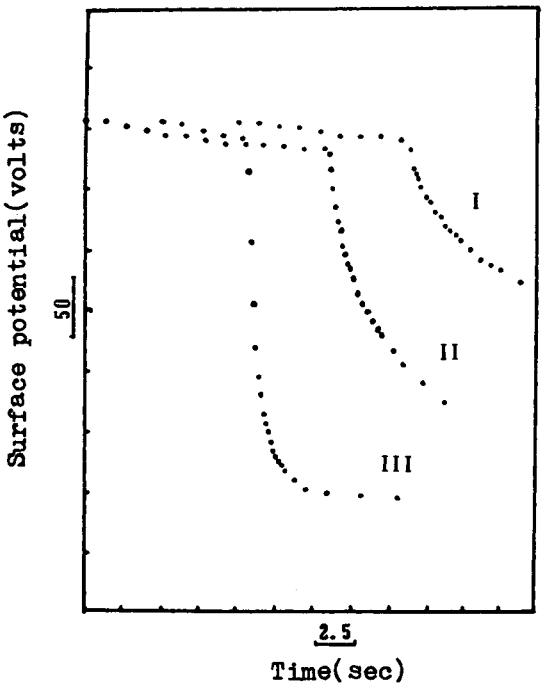

Fig. 6. Effect of heat treatment on potential discharge for samples: (I) ^{60}Co γ-ray (5×10^4 Gy) irradiated *cis*-PPA film after heat treatment in N_2 at 50°C for 30 min, (II) unirradiated *cis*-PPA film, (III) ^{60}Co γ-ray (5×10^4 Gy) irradiated *cis*-PPA film.

PPA with the *cis*-cisoidal configuration was observed, as its potential discharge as a function of time is nearly the same as that for the unirradiated film (as seen in Figure 4, Curves II and III).

Figure 5 shows that the *trans*-PPA films irradiated with ^{60}Co γ-ray had no noticeable light response. This illustrates that the *trans*-PPA has no irradiation effect for ^{60}Co γ-ray. It should be pointed out that the photosensitivity in ^{60}Co γ-ray irradiated *cis*-PPA films disappeared after being heated in a nitrogen atmosphere at 50°C for 30 min (Fig. 6).

The structure and the properties of ^{60}Co γ-ray irradiated *cis*-PPA films have been characterized by using the techniques of IR, ESR, GPC, and DTA. The ^{60}Co γ-ray irradiated *cis*-PPA films showed paramagnetics, a high *cis*-content (90%), good thermal stability, and high molecular weights ($\bar{M}_n$: $\sim 10^5$; $\bar{M}_w$: $\sim 2 \times 10^5$), that were similar to the unirradiated films. These results revealed that no noticeable *cis–trans* isomerization, oxidation, and chain degradation occurred in PPA while irradiated with ^{60}Co γ-ray in air atmosphere at room temperature.

This research shows that ^{60}Co γ-ray irradiation can convert *cis*-PPA films prepared with rare-earth coordination catalysts to highly photosensitive materials. This novel method is completely different from the chemical methods reported in the literature. Further investigation on a mechanism for the photosensitivity in the ^{60}Co γ-ray irradiated *cis*-PPA films is in progress and will be published later.

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