TWO-PHOTON IONIZATION OF AROMATIC MOLECULES IN POLYMER MATRICES

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1. Introduction

Many photochromic systems have been studied for the application of optical recording usage [1]. Recently, we reported a new type of photochromic system [2-4]. By intense laser excitation of an aromatic chromophore doped in a polymer bulk, an electron is ejected from a higher excited state of the chromophore by the two-photon absorption and the electron is trapped in the polymer matrix. As a result, the colorless polymer gives a clear color of the formed radical cation of the chromophore. Various colors can be given by the selection of appropriate chromophores. When the *N,N,N',N'*-tetramethyl-*p*-phenylenediamine chromophore is photoexcited in the poly(methyl methacrylate) (PMMA) matrix, this color lasts so long that it is recognized even after one year's storage at room temperature [2]. So far, we have prepared the samples of poly(methacrylate)s and polystyrene by bulk polymerization of the corresponding monomers. In this investigation polymer cast films which have a perylene (Pe) dopant were prepared and photochromism induced by the two-photon ionization was studied for practical usage.

2. Method

Figure 1 shows the chromophores and polymers used in this work. Chromophore Pe (1, Aldrich) and dimethylterephthalate (2, DMTP, Wako) were purified by chromatography and recrystallization. Polymer films of purified poly(vinyl chloride) (3, PVCl, Nakarai), U-polymer (4, UP, Unitika), Vylon (5, VL, Toyobo), PMMA (6, Nakarai), poly(vinyl acetate) (7, PVAc, Nakarai), and

cellulose triacetate (8, CTA, Fuji Film) were prepared by the solution-casting method from spectrograde dichloromethane, 1,2-dichloroethane, and tetrahydrofuran solvents. The films were cast in a dry box. Then they were evacuated to remove the remaining solvent for 2 days at room temperature and for the following 2 days at 80 °C. The thickness of the film was 0.2 mm. The Pe chromophore is durable enough to heat and light and its absorption and emission spectra were unchanged by these treatments.

Photoexcitation of the films was made selectively on the Pe chromophore by a 351-nm pulse (ca. 17 ns fwhm) from a XeF excimer laser (Lambda Physik, EMG101MSC). About 50-mJ energy was fed into a 1 x 10 mm slit to excite the samples. The absorption spectrum of the Pe radical cation ($\text{Pe}^{\cdot+}$) formed was obtained at 77 K, and the decay of $\text{Pe}^{\cdot+}$ absorbance at 550 nm was measured in a temperature-controlled sample box immediately after the laser excitation.

3. Results and Discussion

Prepared cast films were initially yellow colored due to the Pe dopant. By a laser excitation the films changed in color to purple instantaneously, and then gradually the color faded within a few hours in an aerated condition at room temperature. This color fading did not occur at 77 K, whereas it was accelerated by raising the temperature, and finally the initial yellow color of the Pe was recovered. As already reported [2-4], this purple coloration is due to Pe radical cation formation by the two-photon excitation and the successive fading is caused by the recombination of an ejected electron with the parent $\text{Pe}^{\cdot+}$. In a degassed condition, the Pe chromophore whose ionization potential is low formed stable $\text{Pe}^{\cdot+}$ and the color could be seen even after one year at room temperature [3], whereas in an aerated condition the decay was fast. The

Fig. 1 Molecular Structures of Dopants and Polymers

trapped electron in the polymer matrix seems to be carried by O_2 to recombine with Pe^+ . The amount of Pe^+ initially formed by a laser pulse was almost the same for all polymers used, even in the presence of O_2 . The photoejection of an electron from Pe is too fast to be affected by O_2 in the polymer.

The recombination rate of an ejected electron with the parent cation radical is determined by the electron affinity of polymers, the T_g of the polymers, ionization potential of chromophores, and ambient temperature [2]. Fig. 2(a) shows the temperature effects on the color fading of Pe^+ in the UP matrix; fast decay could be observed at higher temperatures. The recombination rate of an electron with Pe^+ is accelerated by the thermal motion of polymer chain. It is noticeable that a considerable amount of Pe^+ still remains at 110 °C in the time range of the figure. This is because UP has a rather high T_g (195 °C) which slows down the charge recombination at 110 °C; in other polymers with lower T_g , Pe^+ decayed at considerably faster rates at this temperature. In this work, polymers which have rather strong electron affinity were selected and the effect of acceptor groups of polymers was compared as seen in Fig. 2(b). The aromatic polyester UP showed better electron acceptability than the aliphatic PMMA and PVCl. The high acceptor character of the aliphatic ester of PMMA has previously been reported [3], and electron capture detachment of HCl from PVCl is well known. Fig. 2(b) shows stronger stabilization of photoejected electrons by the aromatic polyester.

Fig. 2 Temperature Effects on Pe^+ Survival Ratio

a) UP at various temperatures, b) (1) PMMA, 20 °C, (2) PMMA, 60 °C, (3) PVCl, 20 °C, (4) PVCl, 60 °C, (5) UP, 20 °C, and (6) UP, 60 °C.

Fig. 3 Absorption Spectra of Pe^+ Formed in Polymer Films
(1) UP film, (2) PVCl film, and (3) difference

Figure 3 shows the absorption spectra of Pe^+ formed in polymer films by the two-photon ionization at 77 K. When the spectrum in UP (spectrum No. 1) is compared with that in PVCl (No. 2), the overlap of another absorption band can be recognized at 500–600 nm region. Therefore, both spectra were normalized at the 735-nm peak and the spectrum No. 2 was subtracted from No. 1, then the curve No. 3 was obtained. The position and shape of this absorption band quite resembles that of DMTP^- , and hence in UP film the ejected electron is considered to be trapped as a radical anion of the aromatic ester. The strong electron affinity of the aromatic ester stabilizes ejected electrons and suppresses the fast recombination. Similar results were obtained for aromatic VL and aliphatic PVAc and CTA films. We conclude that aliphatic and aromatic ester groups are crucial in the suppression of the recombination of an electron with the parent radical cation.

This work was supported by the Asahi Glass Foundation for Industrial Technology.

References

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