

PHOTOCHROMISM AND LUMINESCENCE OF DOPANT CHROMOPHORES THROUGH TWO-PHOTON IONIZATION IN POLYMER FILMS

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Abstract Two-photon ionization and recombination processes of an aromatic chromophore doped in polymer films were studied and the features of these processes were discussed in relation to photofunctional polymers. An aromatic molecule having low ionization potential, e.g., *N,N,N',N'*-tetramethyl-*p*-phenylene diamine doped in poly(methyl methacrylate) (PMMA) film was easily photoionized by intense laser light excitation, giving a colored radical cation (photochromism) and a trapped electron in PMMA matrix. As a reversed process, the radical cation recombined with the trapped electron, showing discoloration and emitting luminescence, either isothermal luminescence (ITL), or thermoluminescence (TL). In this report, ITL and TL through the charge recombination process were studied and the luminescence was suggested as a mean of the read-out of photorecording.

Keywords Two-photon ionization, Photochromism, Charge recombination, Trapped electron, Isothermal luminescence, Thermoluminescence, Aromatic amines, Poly(methyl methacrylate)

INTRODUCTION

Photofunctional polymers such as photochromic, electroluminescent materials have been investigated extensively. Recently we found that aromatic molecules molecularly doped in polymer films are easily photoionized by intense laser light excitation, giving colored radical cations, which subsequently recombine with the ejected electrons, emitting luminescence. The former process shows photochromism and the latter process emits fluorescence and/or phosphorescence. Herein, we review our findings on multiphotonic ionization and recombination processes of a dopant chromophore in polymer films, and discuss the features of the present system and its applications

PHOTOCHROMISM THROUGH TWO-PHOTON IONIZATION

Two-photon excitation of an aromatic dopant in a polymer solid ejects an electron from the dopant molecule, producing a radical cation of the dopant and a trapped electron^[1-4] (Fig. 1). For example, intense laser pulse excitation of *N,N,N',N'*-tetramethyl-*p*-phenylene diamine (TMPD) doped in poly(methyl methacrylate) (PMMA) solid produces a TMPD radical cation (TMPD^{•+}) with Wurster's Blue color. The photoionization can be accomplished through both singlet and triplet processes. The laser used in this study is an XeF excimer laser (Lambda Physik EMG101 MSC, 351 nm, ca. 30 mJ cm⁻², ca. 20 ns fwhm). The ionization potential of TMPD in the gas phase is 6.2 eV and the polarization energy is ca. 1.5 eV; the ionization potential in the solid state is ca. 4.7 eV^[5].

The radical cation formed is so stable that the color of the radical cation can be recognized even after one-

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year storage at room temperature (Fig. 2). The color fades away on raising the temperature near the glass transition temperature of the PMMA matrix ($T_g = \text{ca. } 105^\circ\text{C}$). This reversible phenomenon is a new kind of photochromism. The stability of color depends on the kind of chromophore and polymer: in polystyrene (PSt) matrix the color decayed rather fast, in a few minutes. This is because the ester group of PMMA becomes an electron trap, and the photoejected electron is trapped by the ester group. While the electron affinity of phenyl group of PSt is not large enough for phenyl group to become an electron trap, *i.e.*, in PSt matrix an ejected electron recombines with the parent radical cation immediately after photoionization.

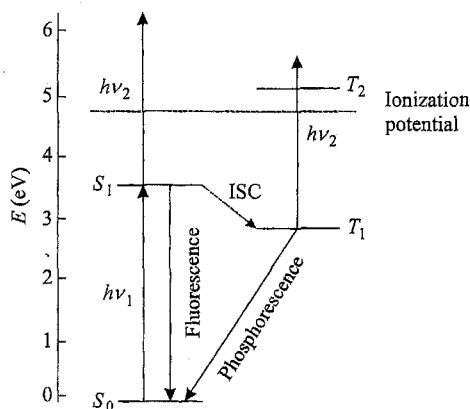


Fig. 1 Two-photon ionization mechanism of TMPD in the solids

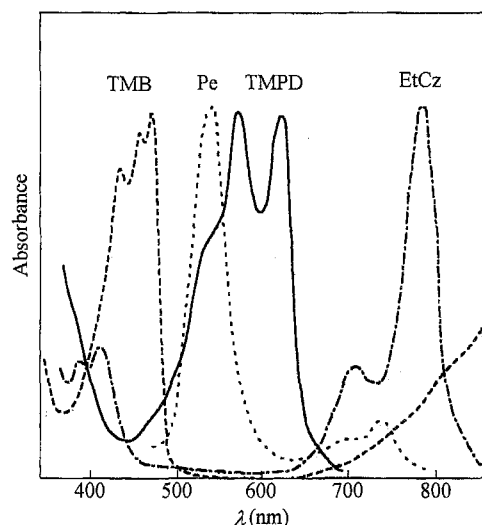


Fig. 2 Absorption spectra of the radical cations of various aromatic molecules in PMMA matrix at room temperature
TMB: *N,N,N',N'*-tetramethylbenzidine, Pe: perylene,
EtCz: *N*-ethylcarbazole

As for the absorption spectra of produced anion species, the electrons captured in PMMA matrix were not observed in the visible and infra-red region, probably because the absorption coefficient of aliphatic ester radical anion is too small to be observed. However, the addition of a weak electron acceptor, *p*-dicyanobenzene, to the TMPD/PMMA system clearly showed the absorption band of the anion radical (430 nm)^[2].

Further evidence of the formation of aliphatic ester radical anion in the TMPD/PMMA system was given by ESR spectroscopy. The ESR signal after photoionization at 77 K gave a strong peak accompanying a quartet of $\cdot\text{CH}_3$. The saturation effect of the central singlet on changing the microwave power revealed a strong singlet peak of $g = 2.0037$, $H_{pp} = 6.3$ gauss: this singlet peak was assigned to the radical anion of the aliphatic ester group^[6]. Furthermore, in the chromophore doped film of an aromatic polyester having a weak electron accepting group in the main chain, the absorption bands of both the radical cation and the radical anion could be observed after two-photon ionization^[7].

LUMINESCENCE THROUGH CHARGE RECOMBINATION

The charge recombination process was also observed through isothermal luminescence (ITL, preglow) and thermoluminescence (TL, glow).

Experimentally the preglow decay curve $I(t)$ followed an empirical equation:

$$I(t) = I_0 / (1 + \alpha t)^m \quad m \approx 1 \quad (1)$$

Figure 3 shows the ITL decay curves of *N,N,N',N'*-tetramethylbenzidine (TMB) doped in several polymer matrices at 20 K. The result shows that Eq. (1) holds well with $m \approx 1$ and the decay is extremely slow.

Theoretically the preglow decay curve $I(t)$ was analyzed in terms of long-range electron transfer by electron

tunneling. Then, the decay curve $I(t)$ is expressed by Eq. (2).

$$I(t) = \lambda \int_0^{\infty} n(r, 0) k(r) \exp(-k(r)t) dr \quad (2)$$

where $k(r)$ is the recombination rate constant dependent on the distance r of an electron from the parent cation, $n(r, 0)$ is the distribution function of electrons from a parent radical cation at time $t = 0$, and λ is a proportional constant.

Here, the empirical decay curve $I(t)$ in Eq. (1) is equal to the theoretical one in Eq. (2). Then, the Laplace inverse transformation of this relation gives explicitly the distribution function $n(r, 0)$ of electrons when we assume $k(r) = \nu \exp(-\beta r)$ ^[8, 9], where $\nu/\alpha = 10^{13}$ and $\beta = 10 \text{ nm}^{-1}$. Figure 4 shows the result obtained on the basis of this analysis: the initial distribution function $n(r, 0)$ with the maximum of $2\sim 3 \text{ nm}$ ^[10-12]. The ejected electrons are located rather remotely from the parent radical cation and broad. This is the reason why the charge recombination process is so slow with a long tail.

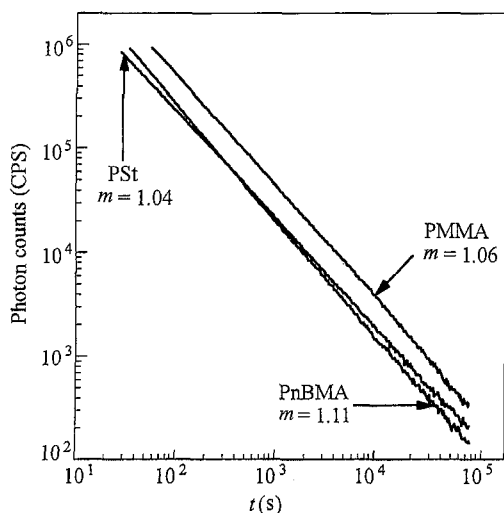


Fig. 3 ITL decay of TMB doped in polymer solids at 20 K
PnBMA: poly(*n*-butyl methacrylate)

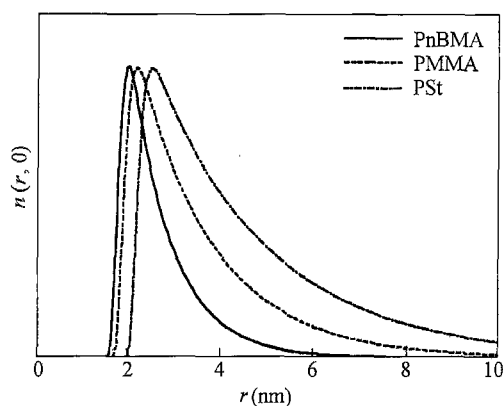


Fig. 4 Initial distribution function $n(r, 0)$ of an ejected electron from the parent radical cation

The thermoluminescence is caused by thermally stimulated recombination of a parent radical cation with the trapped electron, that is, by thermally stimulated recombination of trapped electrons the doped chromophore is electronically excited to S_1 and/or T_1 states, emitting fluorescence and/or phosphorescence. Then, the thermal stimulation depends on the local motion of the polymer chain in the solid, and the glow curve depends on the glass transition and sub-transition of polymer solids^[13]. For example, in the case of perylene/PnBMA (poly(*n*-butyl methacrylate)) film, the fluorescence intensity showed a peak at ca. 100 K and then rose to the highest peak at ca. 250 K (Fig. 5). The former peak is ascribable to the rotation of ester alkyl group and the latter to the local mode relaxation of the polymer main chain^[14]. The highest temperature peak appeared at a few tens of Kelvin lower than the T_g of the matrix polymer, because the molecular motion of the polymer matrix accelerates the recombination and the trapped electrons are exhausted before the T_g . In Fig. 5, the main peak was not observed for glow curves of PMMA and PSt films, because the T_g 's of these polymers are at ca. 380 K. To obtain direct evidence that the glow is caused by the charge recombination of a photo-ejected electron with the parent radical cation the decrease of absorbance of the radical cation was measured with the glow intensity. The result shows that the decrease of the radical cation absorbance is roughly proportional to the integration of the glow curve^[13]. This means that the charge recombination of the produced radical cation of dopant with the ejected electron is the cause of the thermoluminescence of dopant chromophore.

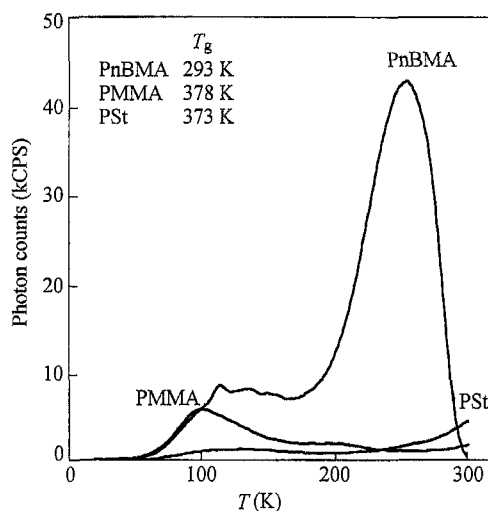


Fig. 5 TL curves of several polymer films doped with perylene
Excitation: 351 nm at 20 K
Heating rate: 5 K/min

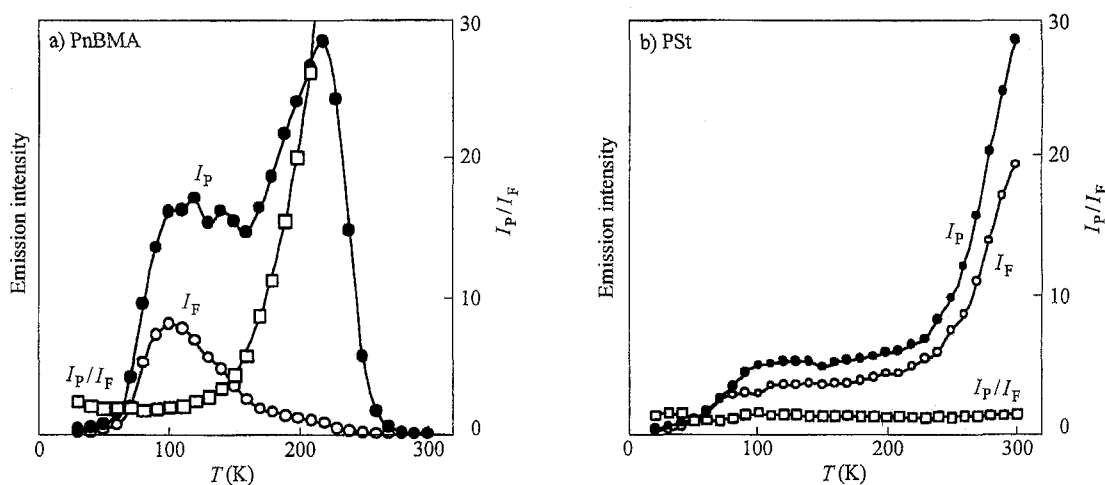


Fig. 6 Temperature dependence of TL emission spectra in polymer solids
a) TMB/PnBMA; b) TMB/PSt

The thermoluminescence of TMB doped in PnBMA (Fig. 6a) and in PSt (Fig. 6b) films was spectroscopically analyzed^[10]. The fluorescence intensity I_F , phosphorescence intensity I_P , and the ratio I_P/I_F are plotted against temperature. The ratio I_P/I_F for PSt film is almost constant from 20–300 K, while the ratio I_P/I_F for PnBMA film increases with the increase of temperature. In other words, the ratio of the concentration of T_1 state to that of S_1 state is constant for the PSt film, while for the PnBMA film the concentration of S_1 state decreases and the concentration of T_1 state increases with increasing temperature above ca. 100 K. These results can be explained by the scheme (Fig. 7) that the energy level of trapped electrons for the PSt matrix is shallow and the charge recombination forms both S_1 and T_1 states of TMB in a constant fraction, whereas for the PnBMA matrix the energy level of trapped electrons becomes deeper with the increase of temperature, and at higher temperature the charge recombination cannot form the S_1 state of TMB, but the T_1 state. Interestingly this fact means that the population of the spin states of excited chromophore is determined by the energy level of trapped electrons.

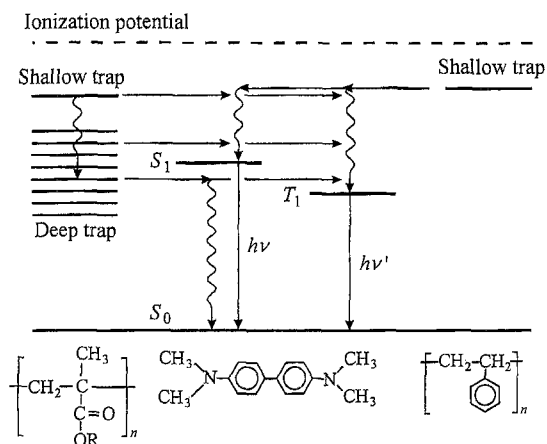


Fig. 7 Scheme for the charge recombination of electron-cation pairs in polymer solids

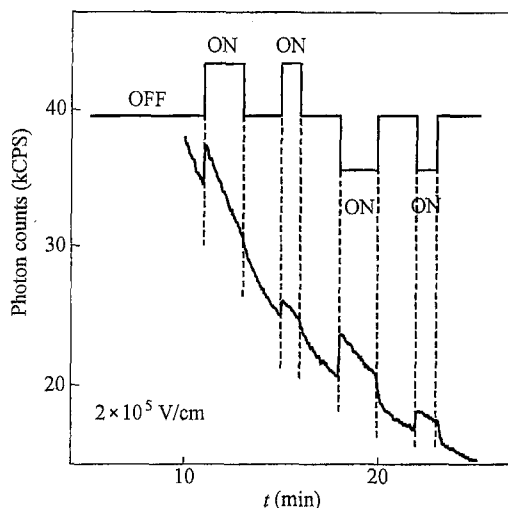


Fig. 8 Electric field effect on ITL for the TMB/PMMA system at 77 K

The upper signal is applied electric field, and the lower signal is enhanced ITL intensity.

The electric field effect on ITL clearly demonstrates the charge recombination of a trapped electron with the parent radical cation. Figure 8 shows the electric field effect on ITL: ITL was enhanced by applying an electric field. Both plus and minus polarities are effective to enhance the ITL intensity. The enhancement is caused by release of trapped electrons under application of an electric field.

SUMMARY

Recently the high power laser has become popular as a light source enabling multiphotonic excitation of chromophores, in other words, for single photonic excitation, care must be taken to eliminate the multiphotonic process. However, this process can be used effectively, *e.g.*, photoionization of aromatic molecules, laser ablation of polymers, and in this study photochromism, charge recombination luminescence. The present photochromism has two features: one is a threshold intensity of light due to two-photon ionization and the other is a very fast response because the mechanism is the electron transfer process. The charge recombination luminescence is analogous to electroluminescence where a hole recombines with an electron, producing the excited state of a chromophore. It can be used for information storage where the read-out process of photo-recording is accomplished in an emissive way. The electric field effect may be used for the intensification of ITL and TL signals.

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