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Long-lived cation radical formation of aromatic amines in poly(methyl methacrylate) matrix at room temperature by two-photon excitation

Akira Tsuchida[1], Mitsuru Nakano[1], Masaaki Yoshida[1], Masahide Yamamoto[1*], and Yoshio Wada[2]

[1] Department of Polymer Chemistry, Faculty of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto, 606 Japan

[2] Department of Photographic Engineering, Kyoto Institute of Technology,
Matsugasaki, Sakyo-ku, Kyoto, 606 Japan

SUMMARY

Very stable cation radicals of N,N,N',N'-tetramethyl-p-phenylenediamine and N,N,N',N'-tetramethylbenzidine were produced in poly(methyl methacrylate) matrix by the intense photoexcitation of pulsed UV lasers or by a focused Xenon lamp. The color of the ion radicals could be recognized even a year after the photoexcitation at room temperature, although the rate of fading was accelerated by raising the temperature to the glass-transition temperature of the polymer (ca. 120 ^{o}C). The light intensity dependence of the produced cation radicals proved the two-photonic nature of this photoionization.

INTRODUCTION

Extensive studies have been made on the radiolysis (1) and photolysis (2) of aromatic molecules in low temperature organic matrices such as sec-butyl chloride and 2-methyltetrahydrofuran, but few have been made on the aromatic solutes in polymer matrices. The cation and/or anion radical formation in polyethylene, polystyrene (PSt), poly(methyl methacrylate) (PMMA) and a few other polymers have been studied by pulse radiolysis (3-5) and gamma-radiolysis measurements (6-9). Among the polymers, the PMMA matrix shows very efficient formation of solute ion radicals (5).

In this study, we found that the two-photon excitation of the aromatic solute N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) or N,N,N',N'-tetramethylbenzidine in PMMA produces very stable cation radicals. For example, the colorless sample block of TMPD doped PMMA gives the Würster's blue color of $TMPD^{\dot{+}}$ by high density photoexcitation at 308 nm. This $TMPD^{\dot{+}}$ formed in PMMA is so stable that the color can be recognized even after a year's storage at room temperature after the photoexcitation. Some other pairs of chromophores (e.g., N-ethylcarbazole, perylene) and polymers (e.g., polyacrylate derivatives, PSt) were examined to elucidate the effects of the kind of chromophore, polymer matrix, and the ambient temperature on the lifetime of the cation radicals formed in polymer matrices.

EXPERIMENTAL

N,N,N',N'-Tetramethyl-p-phenylenediamine (TMPD, Aldrich), N,N,N',N'-tetramethylbenzidine (TMB, Wako), N-ethylcarbazole

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* To whom offprint requests should be sent

(ECZ, Aldrich), and perylene (Pe, Nakarai) were purified by recrystallization. Polymer samples were prepared by the bulk polymerization of the corresponding monomers (3). Methyl methacrylate monomer (Wako) was washed with aqueous 5% NaOH solution and dried by Na_2SO_4, and then distilled under reduced pressure. Appropriate amounts of dopant and 5 x 10^{-4} mol l^{-1} of 2,2'-azobisisobutyronitrile (Nakarai) as an initiator were added to the monomer. The polymerization was made in a degassed Pyrex cell (3 x 1 x 1 cm): the polymerization conditions were 10 h at 60 °C, then 10 h at 70 °C, and 10 h at 120 °C. The residual monomer was confirmed by GPC to be less than 0.1%. The absorption and emission spectra and the excited lifetimes of the doped chromophores were the same as those of the reference samples obtained by the solution casting method. Therefore, thermal degradation of the chromophores seems to be negligible. Samples of other polymer matrices were prepared in a similar manner.

Photoexcitation of the polymer samples was done by a focused laser pulse or Xe arc light. The light pulse (308 nm, 17 ns) from a XeCl excimer laser (Lambda Physik, EMG101E) was 4 x 10^{-6} E cm^{-2}. The laser photolysis apparatus was the same as that described elsewhere (10) except that an excimer laser was used as the light source. The focused Xe arc light was obtained from a 500-W Xe lamp (Ushio) through a Pyrex filter. Absorption and emission spectra were measured by a spectrophotometer (Shimadzu, UV200S) and a spectrofluorophotometer (Hitachi, 850), respectively. Fluorescence lifetime was measured by the single-photon counting technique (PRA Inc., model 510B). The thermal bleaching of colored samples was measured in a Dewar cell fitted in a spectrophotometer. Photobleaching by the analyzing light of the spectrophotometer was negligible. All the spectroscopic and decay measurements were carried out on the freshly prepared polymer samples under a degassed condition. The effect of oxygen on the formation of ion radicals and their decay rates was checked by exposing the sample block (3 x 1 x 1 cm) in air: the color fading of $TMPD^{\cdot+}$ in PMMA, whose color withstands for a year in the degassed condition, was accelerated to a few months, but neither noticeable spectral change nor the decrease of ion radical formation was found.

RESULTS AND DISCUSSION

Photoexcitation of the TMPD doped PMMA block by the excimer laser made the sample deep blue instantaneously. This blue color is produced by the formation of $TMPD^{\cdot+}$ and is known as Würster's blue (11). The colored region of the sample was about 3 mm in thickness of the 1-cm cell. This inhomogeneous coloration is probably because of the inner-filter effect of the produced $TMPD^{\cdot+}$ and $^3TMPD^*$, as the molar extinction coefficients of these species at 308 nm are much larger than that of the ground state TMPD. The coloration also occurred by the focused Xe lamp excitation. TMB doped PMMA gave a yellow color by the laser excitation. Figure 1 (a) shows the absorption spectra of the TMPD and TMB doped PMMA samples after excimer laser excitation. These spectra were obtained

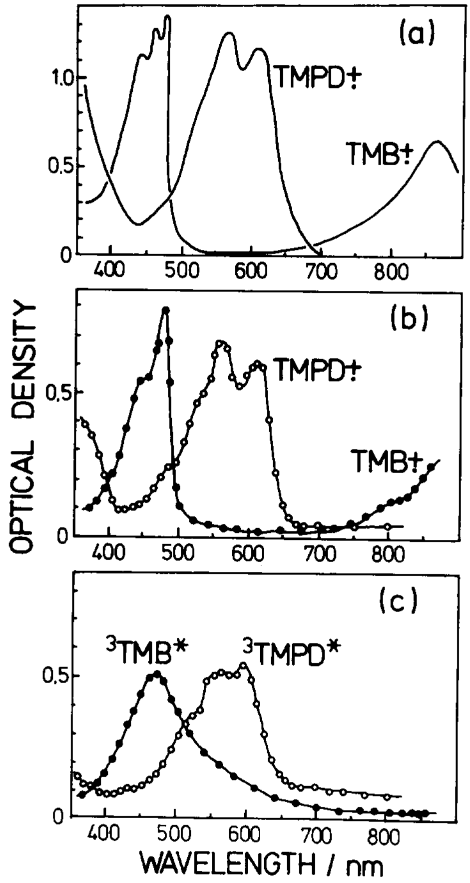

Figure 1 Absorption spectra of cation radicals and triplet states. (a): cation radicals formed in PMMA matrix by high-photon density excitation, (b): cation radicals in acetonitrile at 2 μs after excitation by laser photolysis, (c): triplet states in benzene at 2 μs after excitation by laser photolysis. [TMPD] = 5.8 x 10^{-4} mol l^{-1}, [TMB] = 4.0 x 10^{-5} mol l^{-1}.

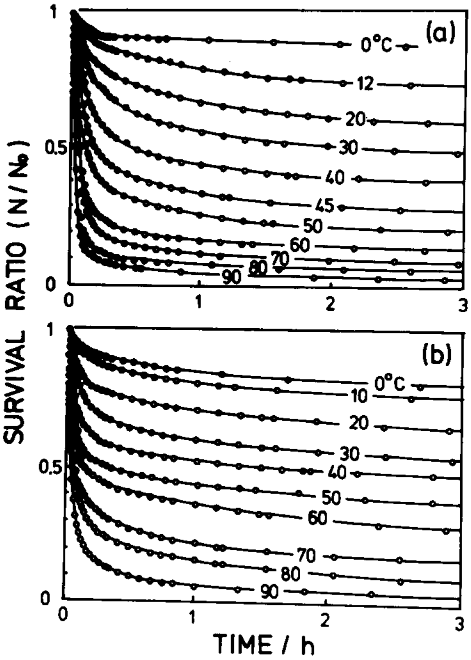

Figure 2 Thermal bleaching of cation radicals formed in PMMA. (a): TMPD$^{\cdot+}$ monitored at 619 nm, (b): TMB$^{\cdot+}$ monitored at 471 nm.

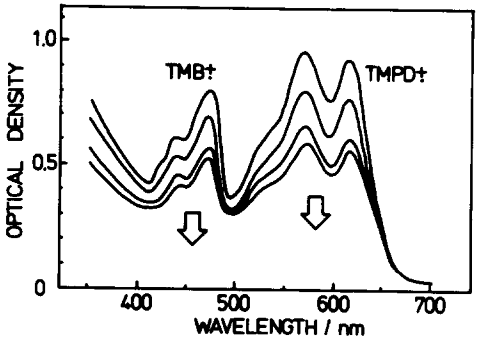

Figure 3 Thermal breaching of cation radicals of the two-chromophore system in PMMA. [TMPD] = 1.9 x 10^{-4} mol l^{-1}, [TMB] = 2.6 x 10^{-5} mol l^{-1}.

by a conventional spectrophotometer since they decayed extremely slowly as described below. Figures 1 (b) and (c) show the transient absorption spectra measured by laser photolysis in the solutions for reference. It is well established that these solutes in a polar acetonitrile solvent and in a non-polar benzene solvent produce the cation radicals (b) and the triplet states (c), respectively (12). In comparison with the transient absorption spectra of (b) and (c), the absorption spectra of (a) are ascribed to those of the cation radicals of TMPD and TMB. The absorption spectra of the cation radicals (b) and the triplet states (c) are well distinguishable though they look similar (13).

As for the photoionization of TMPD in the PMMA matrix, low photon-density laser photolysis of the sample gave only a ^{3}TMPD* absorption spectrum, whereas high photon-density excitation showed the spectrum of TMPD$^{+\cdot}$. The rise rate of TMPD$^{+\cdot}$ absorption was within the exciting light pulse. In the steady state excitation by Xe lamp, the concentration of TMB$^{+\cdot}$ increased with irradiation time but the formation of TMB$^{+\cdot}$ reached a plateau after a short irradiation time and the optical density at 471 nm (TMB$^{+\cdot}$) did not exceed 0.25. The initial rate of TMB$^{+\cdot}$ formation was proportional to the second-power of the exciting light intensity. The energy of near-UV light is only 3-4 eV and the low dielectric constant of polymers is not enough to produce ion radicals by one-photon excitation (2), hence at least a two-photon energy seems to be required for the photoionization. The lifetime of ^{3}TMB* in PMMA was 1.0 s, determined by the phosphorimetry at room temperature. This lifetime is long enough to absorb the second photon from the Xe lamp the light of which is less intense than that of the laser. To confirm the two-photonic nature of the photoionization, double-beam experiments (11) is desirable and is in planning. In the case of pulsed laser excitation (17 ns FWHM), some part of TMB$^{+\cdot}$ may be formed via the S_1-S_n absorption of ^{1}TMB* as the lifetime of ^{1}TMB* is 10.3 ns which is comparable to the exciting laser pulse width (14). As for the excitation photon density, the TMPD in PMMA is irradiated by ca. 30 incident photons per TMPD molecule. Of course such a large number of photons cannot be absorbed by the chromophore, and most of the photons are considered to pass through by the ground-state depression of a TMPD molecule or to be absorbed by the products such as TMPD$^{+\cdot}$ and ^{3}TMPD* with the inner-filter effect. When 6×10^{-4} mol l^{-1} of TMPD in PMMA is excited by a 150-mJ laser pulse at 308 nm, about half of the TMPD is estimated to be ionized according to the absorption spectra. In this concentration of [TMPD$^{+\cdot}$] = 3×10^{-4} mol l^{-1}, the average distance between TMPD$^{+\cdot}$ molecules is calculated to be ca. 150 Å.

The TMPD$^{+\cdot}$ and TMB$^{+\cdot}$ formed in PMMA are as stable at room temperature as those produced in an organic glass at 77 K. When they were stored at 240 K, the color was scarcely bleached, but the color disappeared instantaneously when the sample was immersed in an oil bath at 140 °C, which is higher than the glass-transition temperature (Tg) of PMMA (120 °C). Figures 2 (a) and (b) show the thermal effects on the photobleaching for TMPD$^{+\cdot}$ and TMB$^{+\cdot}$, respectively. The decay has almost the same shape, although TMPD$^{+\cdot}$ decreases slightly faster. This bleaching of ion radicals is caused by the recombination of the cation radical with a photo-ejected electron. However, the decay shown in Figure 2 cannot be explained by the conventional first- or second-order kinetics. As shown in Figure 2, the recombination in the initial 30 min is fast, and the tail of the decay lasts afterward: the color of TMPD$^{+\cdot}$, although it became very pale, could be observed even after a year's storage at room temperature after the photoexcitation. The decay within a few minutes is limited by thermal diffusion in the samples.

In this experimental condition, the concentration of cation radicals produced is low (ca. 10^{-4} mol l^{-1}) and the average distance between them is large (ca. 100 Å). Judging from the very low mobility of the trapped electron in the polymer, the electron is expected to return to the molecule where it was generated. The following experiment was done to elucidate the recombination mechanism (15) of the cation radical with a photo-ejected electron in PMMA. The PMMA sample which contains two chromophores of TMPD and TMB were photoexcited, and the cation radicals of both solutes, TMPD$^{+\cdot}$ and TMB$^{+\cdot}$ were produced in the sample. Figure 3 shows the thermal bleaching of TMPD$^{+\cdot}$ and TMB$^{+\cdot}$ in the PMMA sample. The decay rates of TMPD$^{+\cdot}$ and TMB$^{+\cdot}$ are independent of each other and were the same as those shown in Figure 2. This suggests the independent geminate-ion recombination mechanism of ion radicals: the electron ejected from a TMPD returns to the same TMPD and the one from a TMB returns to the same TMB.

The kinetics of recombination of the cation radical with a photo-ejected electron is necessary to analyze the color fading quantitatively. In this system, the decays of ion-radicals can be well simulated by using a distance-dependent rate constant (15) and the result will be given elsewhere. This model is based on the geminate-ion recombination mechanism as mentioned above: very low concentration of cation radical and low mobility of photo-ejected electron for this system will satisfy the condition. However, at high concentration of cation radicals, bimolecular mechanism (16) may become predominant. This bulk-recombination condition is attained by the high concentration of chromophore and by high density photon excitation. As for decay kinetics, it is interesting to compare the recombination kinetics of this system with those of the color centers of inorganic systems. In ionic crystals, however, the existence of many types of color centers, e.g., F, H, Vk centers, makes the situation complicated and the unique solution have not been established (17,18). For photochromic glasses containing silver halides, some kinetic treatments for color fading have been made (19) on the basis of the geminate-recombination mechanism.

As for the location of ejected electrons, no spectroscopic information has been obtained so far. Solvent-trapped electrons in methylpentane at 77 K give the absorption in a near-IR region (20). The absorption spectrum in this region was scrutinized in detail, but no noticeable absorption band was observed. An absorption band at ca. 725 nm or 440 nm for the PMMA anion radical has been proposed (21,22). Precise examination of the absorption spectra, however, gave no noticeable band in this range. The colored PMMA sample became transparent again by heating it above the Tg of PMMA and almost the same absorption spectra were reproduced by photoirradiation: the samples could withstand a few tenth of repeated cycles.

As an example of other pairs of chromophore-polymer systems, Figure 4 shows the transient absorption spectrum of ECZ in PMMA and the decays (insert) in PMMA and PSt matrices measured by laser photolysis. ECZ has a higher ionization potential than TMB. In the PMMA matrix, a strong absorption band of $^3ECZ^*$ with small bands of $ECZ^{\dot{+}}$ was recognized. This is not the case for TMPD or TMB doped PMMA: almost no absorption bands for triplet state were found for these systems at the same excitation intensity or time after excitation. This shows that the cation radical formation of TMPD and TMB from their triplet states is efficient. The lifetime of $ECZ^{\dot{+}}$ in PMMA is ca. 1 h, which is very short compared with those of $TMPD^{\dot{+}}$ and $TMB^{\dot{+}}$. In general, the chromophores which have a low ionization potential, such as aromatic amines or Pe, give efficient cation radical formation with a long lifetime. In the PSt matrix, the lifetime of $ECZ^{\dot{+}}$ is a few tens of nanosecond. The electron-accepting ability of PSt does not seem so large as that of PMMA.

The two-photon ionization behavior of aromatic molecules in polymer matrices is described as follows. The yield and

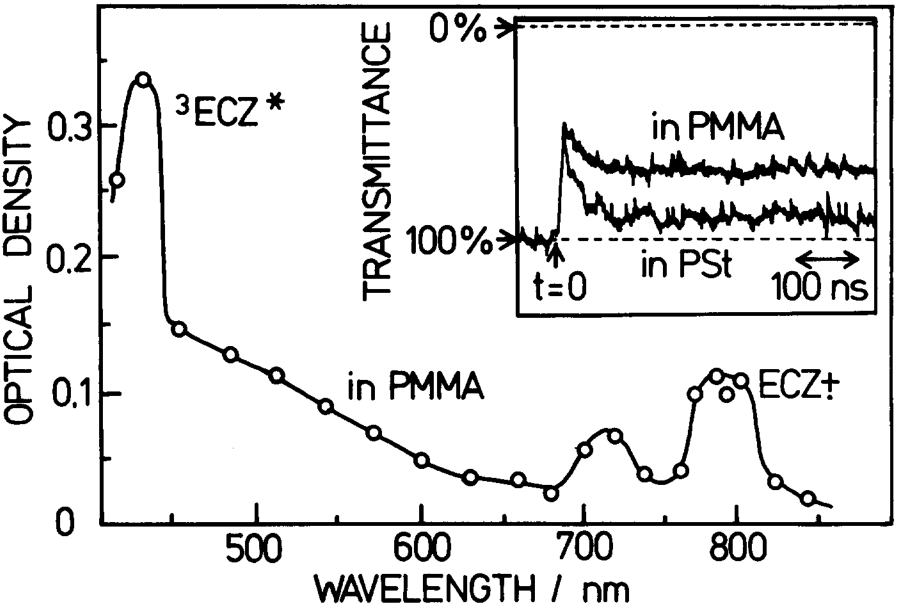

Figure 4 Transient absorption spectra of ECZ in PMMA at 300 ns after excitation. Insert: oscillograms of transient absorption of $ECZ^{\dot{+}}$ at 780 nm in PMMA and in PSt matrices.

lifetime of the cation radicals produced are greatly affected by the ionization potential of chromophores, kind of polymer matrices, and ambient temperature. First, the chromophores of low ionization potential such as aromatic amines and perylene have high yields of cation radical formation and a long cation radical lifetime. Secondly, acrylate polymers have a good electron-accepting ability probably due to carbonyl group (23) and stabilize the cation radicals. Thirdly, suppression of molecular motion in polymer matrices prolongs the lifetimes of cation radicals. The lifetimes of cation radicals are shortened rapidly as the ambient temperature is raised to the Tg of polymers. PMMA was the best among the polymers we have examined so far, poly(alkyl methacrylate)s, poly(acrylate)s and PSt, i.e., PMMA has high electron-accepting ability and high Tg. The phenomenon is important to elucidate ion radical structures, electron transfer kinetics, and photochromic devices. This phenomenon can be used as a photochromic material of image recording systems. Though practical examination of samples as a recording material has not been made yet, the resolution of this system is expected to be in a molecular order similarly to those of other organic photochromic compounds. A more detailed study on the phenomenon is now in progress.

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