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Absorption Spectra and Dynamics of the Triplet State in *p*-Terphenyl Powder Systems: A Diffuse Reflectance Laser Photolysis Study

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A microcomputer-controlled nanosecond diffuse reflectance laser photolysis system was developed and applied to *p*-terphenyl powder systems. The triplet absorption spectrum of microcrystalline powders is broader and red-shifted compared to the molecular triplet state in solution. Possible contributions of an optical artifact and an impurity were rejected by examining powder systems doped with naphthacene and diluted with NaCl as well as poly(methyl methacrylate). *p*-Terphenyl adsorbed on silica gel and included in β-cyclodextrin gave different triplet spectra, which are interpreted in terms of conformational structure of *p*-terphenyl. Decay processes and an oxygen effect are also discussed.

Laser photolysis method is now recognized as an indispensable technique to study photophysical as well as photochemical primary processes. A variety of systems from gas, solution, solid to biology have been investigated, however, all of them should be optically transparent, since the laser photolysis is usually performed under a transmittance optical alignment. In 1981, a nanosecond diffuse reflectance laser photolysis method was proposed by Kessler and Wilkinson.1) This is very powerful because it gives absorption spectra of transient species in opaque and scattering materials. Several laboratories are elucidating primary processes of microcrystals, semiconductor as well as insoluble polymer powders, dyed fabrics, molecules adsorbed on silica gels, etc., using this technique.2—5) The present authors have improved its time-resolution from the nanosecond to picosecond domains and studied the excited singlet state absorption spectra and fast intersystem crossing process of organic microcrystals.6)

Now the similar analysis on relaxation and reaction mechanisms as that for gas and solution systems can be given for optically scattering materials. It is possible to examine and compare photochemical processes of the same molecule with each other under different conditions such as in dilute solution, in microcrystalline powders, and in adsorption. This type of study is quite scarce as far as we know. We measured transient absorption spectra of various organic microcrystals and found that most of them are similar to the absorption of the corresponding molecular triplet state.7) An exceptional case was observed for *p*-terphenyl whose absorption band in the nanosecond time domains is different from that of the solution system. Therefore, we considered that the dynamics of the present microcrystal is an interesting topic in the diffuse reflectance photolysis studies. The absorption spectrum of the excited singlet state of this microcrystalline *p*-terphenyl was already measured by the picosecond diffuse reflectance spectroscopy and its decay time was obtained to be very short (ca. 2.4 ns).8) In the present work we have applied the nanosecond diffuse reflectance laser photolysis method to various *p*-terphenyl systems and found that the triplet absorption spectral shape of this molecule is very sensitive to the sample condition and changes from system to system. Their phosphorescence spectra are not generally observed at room temperature, so that the laser photolysis study is indispensable.

Experimental

A nanosecond microcomputer-controlled diffuse reflectance laser photolysis system with an excimer laser has been used. Figure 1 shows a schematic diagram of the system set in this laboratory. Excimer lasers (Lumonics TE 430-T2; 308 nm, 6 ns, Lumonics EX 400; 351 nm, 20 ns (or 337 nm, 2 ns) and Lambda Physik EMG101 MSG; 248 nm, 18 ns) were used as an excitation light source. The analyzing lamp was a 150 W DC Xenon lamp (Wacom KXL 150) which is additionally pulsed for ca. 200 μs in fwhm, synchronized with laser oscillation. A hot filter and some UV cut filters were used to avoid a sample heating and photochemical reactions by the analyzing light. The sample was contained in a suprasil cell with 2 mm or 1 cm thickness. The diffuse reflected light of the analyzing lamp was detected by a photomultiplier (Hamamatsu 1P28 or R928) through a monochromator. The signal was digitized by a transient memory (Kawasaki Electronica M-50E, 50 ns/ch) and transferred to a microcomputer (NEC PC9801F2). The spectral data were averaged over multiple measurements (20—100 times). The present system is completely automated, namely, triggering of laser oscillation, operation of shutters for blocking excitation as well as analyzing lights, slit adjustment, wavelength driving of monochromator, and voltage adjustment of photomultiplier are controlled by the microcomputer.

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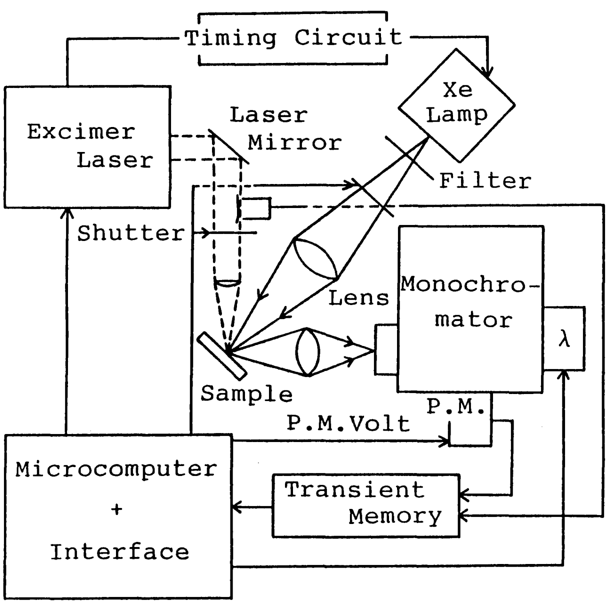

Fig. 1. Schematic diagram of a nanosecond diffuse reflectance laser photolysis system. P.M.; photomultiplier.

For some measurements a Nd^{3+}: YAG laser (Lumonics HY750; 355nm, ca. 5ns) and multichannel photodiode array were used as an excitation light source and detector, respectively. In this case a monitoring lamp is a Xe flash lamp (Hamamatsu L2188; fwhm 1.6 μs) which determines the time resolution.

The transient absorption intensity in diffuse reflectance laser photolysis was displayed as % absorption,[9] defined as

$$\%\mathrm{Abs}(\lambda)=(R_0(\lambda)-R(\lambda)+E(\lambda))/R_0(\lambda)$$

where $R(\lambda)$ and $R_0(\lambda)$ represent the intensity of the diffuse reflected analyzing light at wavelength λ with and without excitation, respectively. $E(\lambda)$ is emission intensity induced by laser excitation. Actually, it is important to correct the contribution of sample fluorescence or phosphorescence.

Transient absorption spectrum in solution was measured by a conventional laser photolysis system where the same excimer laser is used and the optical alignment was changed to a transmittance one. Emission spectra were measured by a laboratory-made or Nippon Bunko (FP-770) spectrophotometer.

Microcrystalline *p*-terphenyl (Dotite scintillation grade) was zone refined (100 passes). After purification, samples were ground on a mortar. Particle sizes ranged from several to hundred micrometers. Silica gels (Toso TSK Silica 60: average diameter 5 μm, surface area ca. 500 $m^2 g^{-1}$ and Nippon Aerosil OX-380; 7 nm, 380 $m^2 g^{-1}$) were heated at 400 °C for 5 h and used as an adsorbent. For adsorption procedure, 2 g of silica gel was stirred for 24 h in 10^{-3} M *p*-terphenyl cyclohexane solution ($M=mol\,dm^{-3}$), taken out from the latter, washed several times with cyclohexane, and was evaporated. β-Cyclodextrin (Wako-GR) was recrystallized two times from aqueous solution. For inclusion procedure, 0.02 M β-cyclodextrin aqueous solution with a few mg of *p*-terphenyl was stirred for 3 h, and water was slowly evaporated on a hot plate.

Powder samples of *p*-terphenyl diluted with inactive poly(methyl methacrylate) (PMMA) were prepared by the following way. Benzene solution of *p*-terphenyl and PMMA (Kuraray) was solidified on the flask wall by cooling down to −10 °C and degassed, which results in an evaporation of benzene. The content of *p*-terphenyl in amorphous PMMA powders was 0.08—83.4 wt%. The precipitated microcrystals of *p*-terphenyl were identified even by naked eye for polymer powders containing *p*-terphenyl more than 51.2 wt%.

All the powder samples were deaerated at least for 10 h, while the solution samples were bubbled with N_2 gas. All the measurements were performed at room temperature.

Results and Discussion

Triplet Absorption Spectra of *p*-Terphenyl Microcrystalline Powders. Transient absorption spectra of microcrystalline powders and its hexane solution are shown in Fig. 2. The absorption band of *p*-terphenyl in hexane at 450 nm can be ascribed to the triplet state according to the literature.[10] We consider the spectrum of the powders is also due to the triplet state, however, we have to examine at first whether the present spectral shift is intrinsic or due to some artifacts. Since optical conditions of diffuse reflectance laser photolysis have not been established completely, scattering condition of powders have been examined as a factor of the artifact.

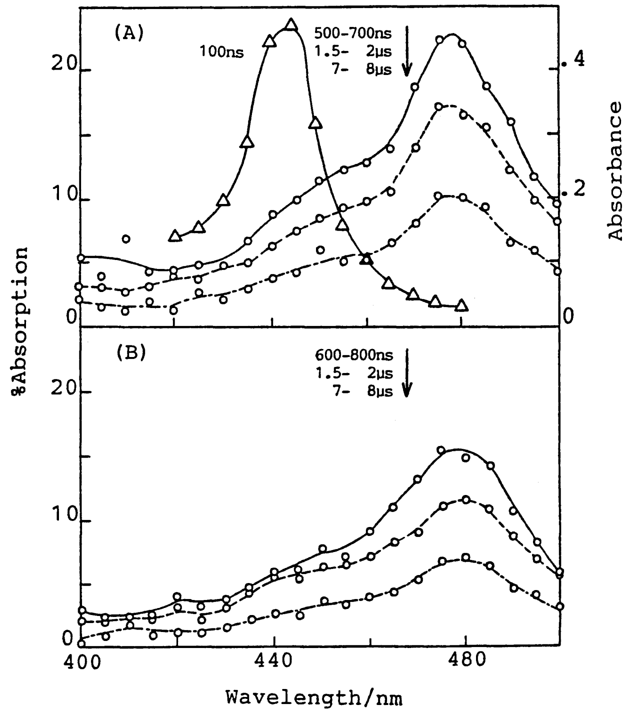

Fig. 2. Transient absorption spectra of *p*-terphenyl systems. (A) Pure microcrystalline powders, and (B) mixed powders of 5% *p*-terphenyl and 95% NaCl. The triplet absorption spectrum in hexane (—△—), measured by transmittance laser photolysis, is also shown in (A).

The first is to measure transient absorption spectrum of mixed powders of *p*-terphenyl and NaCl crystals. NaCl powders are transparent at excitation and observation wavelength, and may have a different distribution of particle size and scattering coefficient from that of *p*-terphenyl crystals. As shown in Fig. 2, however, absorption spectral shape and decay behavior were not affected so much by the change of diffuse reflectance condition.

As the second, mixed powder systems of *p*-terphenyl and PMMA were investigated in detail. As phosphorescence spectra were very weak at room temperature, fluorescence spectra were examined to obtain an information on the dispersed state of *p*-terphenyl. A series of spectra are given in Fig. 3. The spectra of the 0.08 and 0.2 wt% *p*-terphenyl samples are close to that in solution. This indicates that *p*-terphenyl in these samples is molecularly dispersed in polymer powders and the fluorescent state takes the same geometrical structure as that of solution. Increasing the wt%, fluorescence spectra changed. All the observed spectra can be reproduced by a superposition of the bands of the hexane and microcrystalline samples, except that the latter vibrational structure is not intrinsic but modified by re-absorption effect.

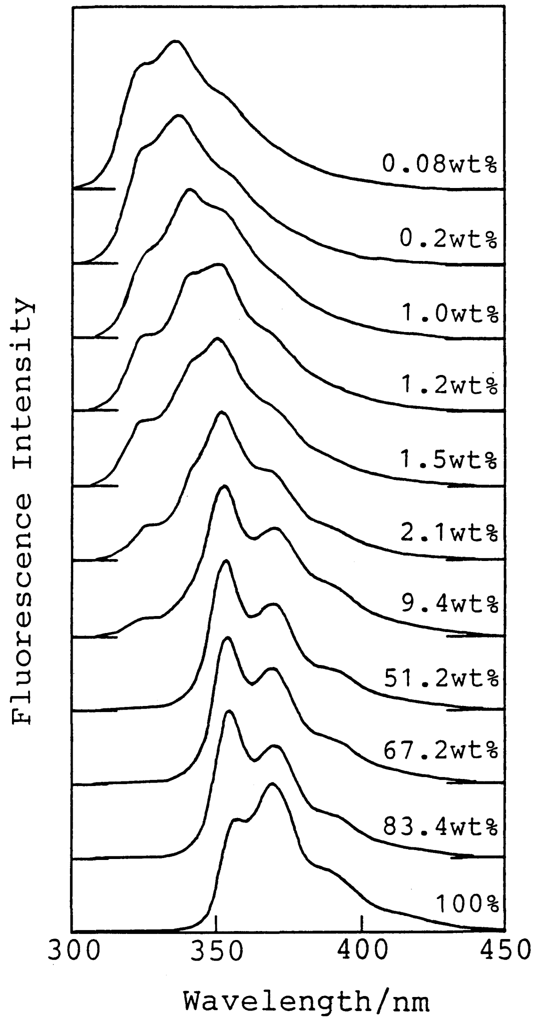

Fig. 3. Fluorescence spectra of mixed powders of *p*-terphenyl and poly(methyl methacrylate). The weight % of *p*-terphenyl is given in the Figure.

In accord with this fluorescence spectral change, the transient absorption spectra were also changed from low to high wt% of *p*-terphenyl. As shown in Fig. 4, the absorption maxima of the 0.08—1.2 wt% samples are similar to that of the molecular triplet state in hexane, while another band was overlapped around 480 nm for the samples with high wt% of *p*-terphenyl. These spectra were also interpreted by a superposition of the spectra of the most dilute sample and pure microcrystals. On the basis of these results, it is

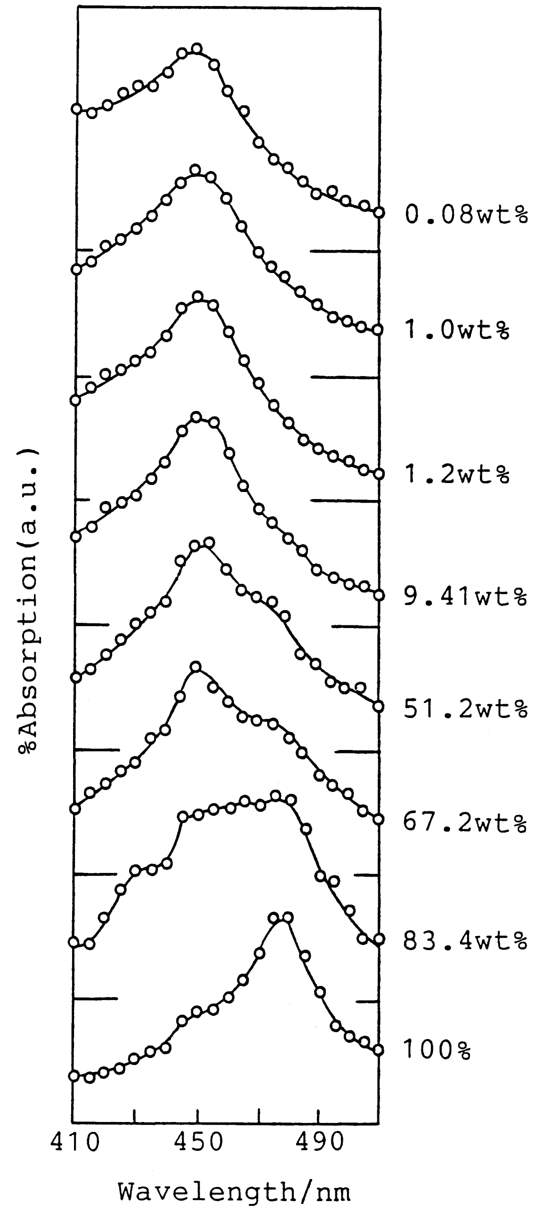

Fig. 4. Transient absorption spectra of mixed powders of *p*-terphenyl and poly(methyl methacrylate). The weight % of *p*-terphenyl is given in the Figure. The gated time is 1.5—2.5 μs.

concluded that *p*-terphenyl is molecularly dispersed and partly forms microcrystal in polymer powders, their ratio depending upon its wt%. The fact that the 450 nm band of the *p*-terphenyl molecular triplet state is observed in PMMA powders is a critical experimental foundation that the present spectral data are intrinsic.

Another artifact is due to an interpretation that an impurity contained in the crystal is responsible to the 480 nm absorption band in microcrystalline powders. Excitation energy migrates over *p*-terphenyl molecules and is trapped by an impurity, namely, the excited state of the latter should have an electronic energy level lower than that of the former. It is well known that the most representative impurity in *p*-terphenyl crystal is naphthacene and its photophysical properties have been studied in detail.[11] It is crucial to measure photophysical processes of *p*-terphenyl doped with known amounts of naphthacene by the diffuse reflectance laser photolysis.

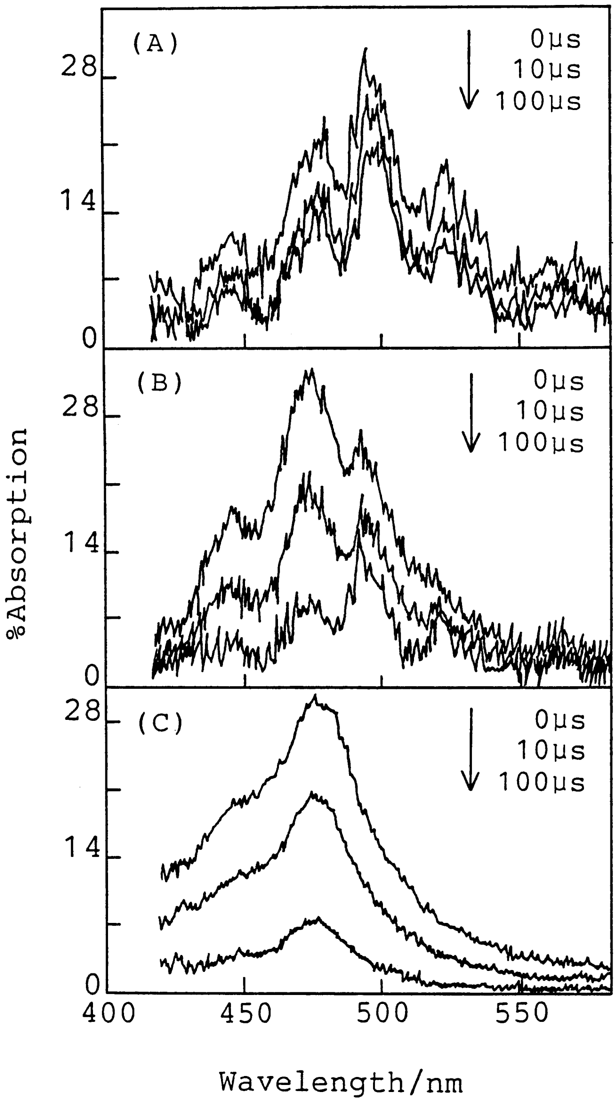

Fig. 5. Transient absorption spectra of *p*-terphenyl powders, (A) doped with 1×10^{-5} mole naphthacene per mol *p*-terphenyl, (B) doped with 3×10^{-6} mole naphthacene per mol *p*-terphenyl, and (C) without dopants. The gated time is given in the Figure.

In Fig. 5 are shown transient absorption spectra of *p*-terphenyl microcrystals containing 1×10^{-5} and $3\text{x}10^{-6}$ mol naphthacene per mol *p*-terphenyl which were measured with a Nd^{3+} : YAG laser-multichannel photodiode array combination. The vibrational structures were observed in 430—550 nm region and their spectral shape was almost independent upon the delay time for the 1×10^{-5} mol/mol sample. On the other hand, the sample doped with 3×10^{-6} mol naphthacene per mol *p*-terphenyl showed that the peak was at 480 nm immediately after excitation and approached to the spectral shape of the 1×10^{-5} mol/mol sample. The peak position at the early stage is identical to that of pure crystals, as shown in Fig. 5. The spectral shape at the late stages is similar to the vibrational structure of the triplet absorption spectrum of naphthacene in rigid solvent,[12] although the former is shifted to the red by about 25 nm. Therefore, this behavior can be explained by assuming singlet or triplet energy transfer from *p*-terphenyl to the doped naphthacene. In the latter case the triplet states of *p*-terphenyl and naphthacene may decay independently in the present time scale. Now it is concluded that the 480 nm band of the microcrystalline sample is not ascribed to the impurity but due to *p*-terphenyl itself.

The transient spectrum of microcrystals decayed monotonously, its time range is a few tens of μs, and no appreciable chemical reaction was induced, so that the spectrum is assigned to the triplet state. This is consistent with the behavior observed for the crystals doped with naphthacene.

Electronic Nature of the Triplet State in *p*-Terphenyl Microcrystals. As electronic and geometrical structure of *p*-terphenyl is sensitive to the surrounding condition, we summarize here the relevant reports. An angle between the edge and central benzene rings in solution is about 10° and upon excitation the relaxation from the excited Franck-Condon to the excited equilibrium states results in a planar structure.[13] The large Stokes shift of fluorescence can be explained by this structural change. In the case of crystal, the geometry at room temperature and below 190 K is planar and skewed, respectively, and phase transition occurs between these temperatures.[14]

Concerning a relation between absorption spectral shift and conformation in the molecular triplet state, Menzel et al. presented a series of data of the triplet-triplet absorption spectrum of *p*-terphenyl derivatives in solution.[15] At room temperature the band position was 455 nm, while its spectral shift and another peak at 480 nm was observed by lowering the temperature. The latter corresponds to the unrelaxed, not completely rotated conformer. Namely, the triplet state of *p*-terphenyl molecule is very sensitive to the geometrical structure, and the planar and skewed triplet states give the 455 nm and the 480 nm bands, respectively.

Combining these considerations with our experimental results, it is concluded that the planar triplet state in microcrystal gives the absorption band at 480 nm. Why the different absorption spectrum is observed in crystal and solution inspite of the common planar geometry should be ascribed to their electronic nature. Namely, the triplet exciton in microcrystalline powders has a different electronic structure from that of the molecular triplet state.

Dynamics of the Triplet Exciton of *p*-Terphenyl Microcrystals. The decay in the present microcrystals is in the order of tens microseconds and showed an excitation wavelength dependence (Fig. 6), although the triplet absorption spectral shape is common to all excitation conditions. This result can be explained in terms of triplet-triplet annihilation which is sometimes the rate-determining process in laser photolysis of solution and crystal systems. As the molar extinction coefficient at the laser wavelength is larger, the triplet concentration is higher, leading to an efficient contribution of the triplet-triplet annihilation, namely, the decay became faster in the order of the excitation wavelength; 308 nm>337 nm>351 nm.

An oxygen effect upon the triplet decay curve, one of the triplet characteristics, is different between exciton and molecular triplet states. In Fig. 7, decay curves of the 51.2 wt% *p*-terphenyl in PMMA sample where both triplet states are involved are given. The initial spike was brought about by a scattering of the intense fluorescence. Both decay curves observed at 450 and 480 nm are complicated and not analyzed by a simple kinectis. The fast decay component is larger

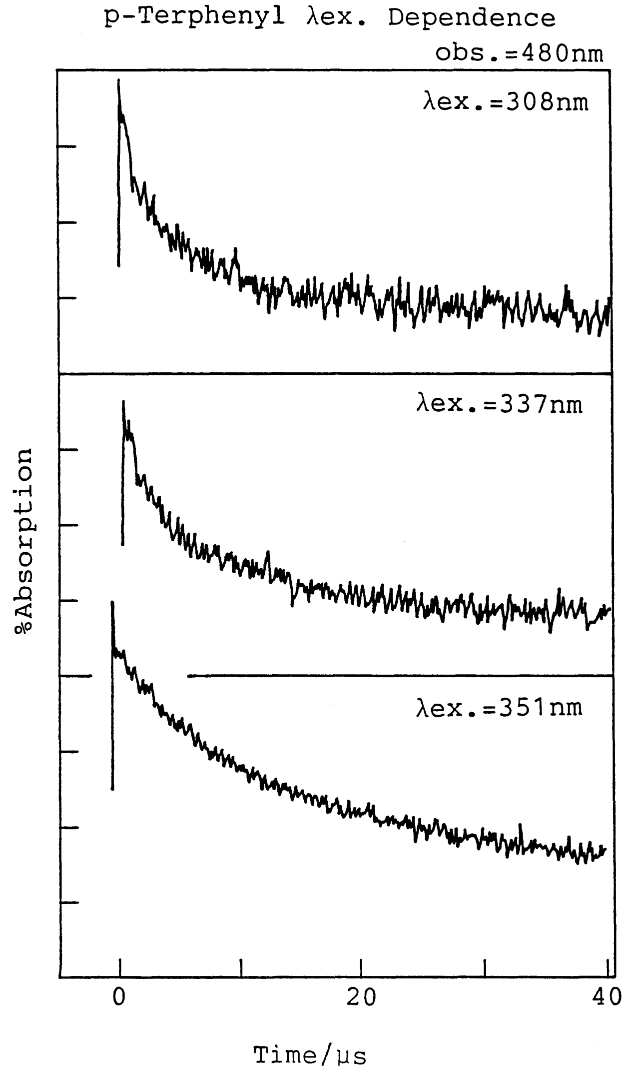

Fig. 6. Absorption decay curves of *p*-terphenyl microcrystals. The excitation and observation wavelength is shown in the Figure. Vertical scale is 6%/div.

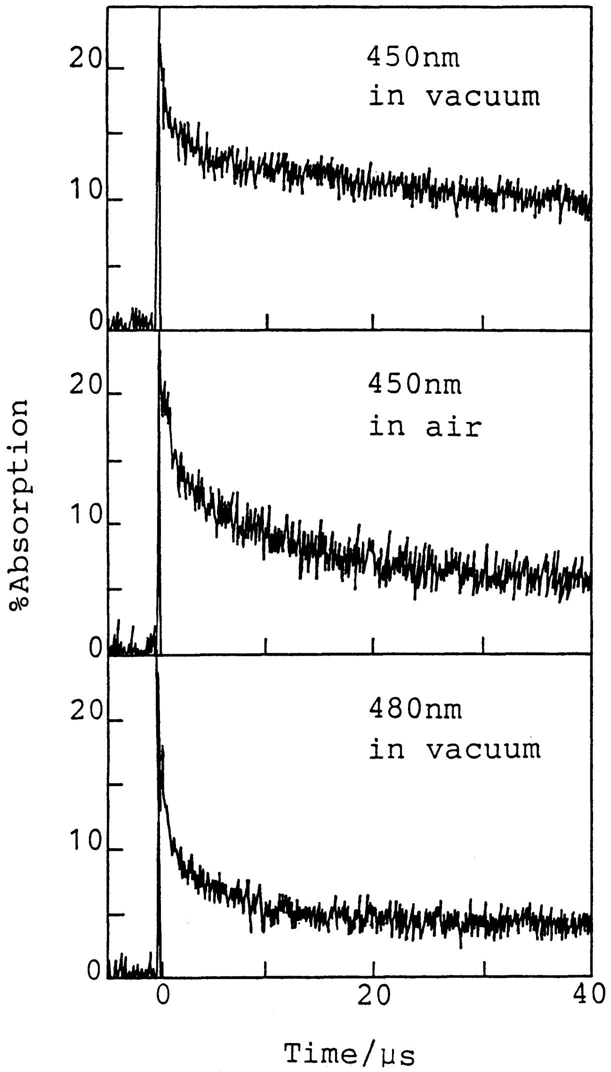

Fig. 7. Absorption decay curves of mixed powders of 51.2 wt% *p*-terphenyl and 48.8 wt% poly(methyl methacrylate). The observation wavelength and conditions are given in the Figure.

at 480 nm than at 450 nm in vacuum, so that the exciton band of the crystal (peak at 480 nm) decayed faster than that of the molecular triplet state (peak at 450 nm). In the case that the samples are aerated, the decay of the 450 nm band is accelerated while no appreciable effect was observed for the 480 nm band. Namely, the triplet state of the molecularly dispersed *p*-terphenyl in PMMA is sensitive to oxygen, while not in crystals. This means that molecular oxygen can diffuse in PMMA powders but not penetrate into each *p*-terphenyl microcrystals. We consider that the triplet exciton is not trapped on the surface which can interact with oxygen. The present result is worth noting from photochemical viewpoint, since oxygen effect is one of the standards for identifying the triplet state.

Triplet Absorption Spectra and Dynamics of Some *p*-Terphenyl Powder Systems. Nanosecond absorption spectra of *p*-terphenyl in microcrystals, adsorbed on silica gel, and included in β-cyclodextrin are summarized and compared with each other in Fig. 8. The absorption bands of powder systems are broader than in solution. The spectrum of powders of inclusion complexes is just between the spectra of micro-

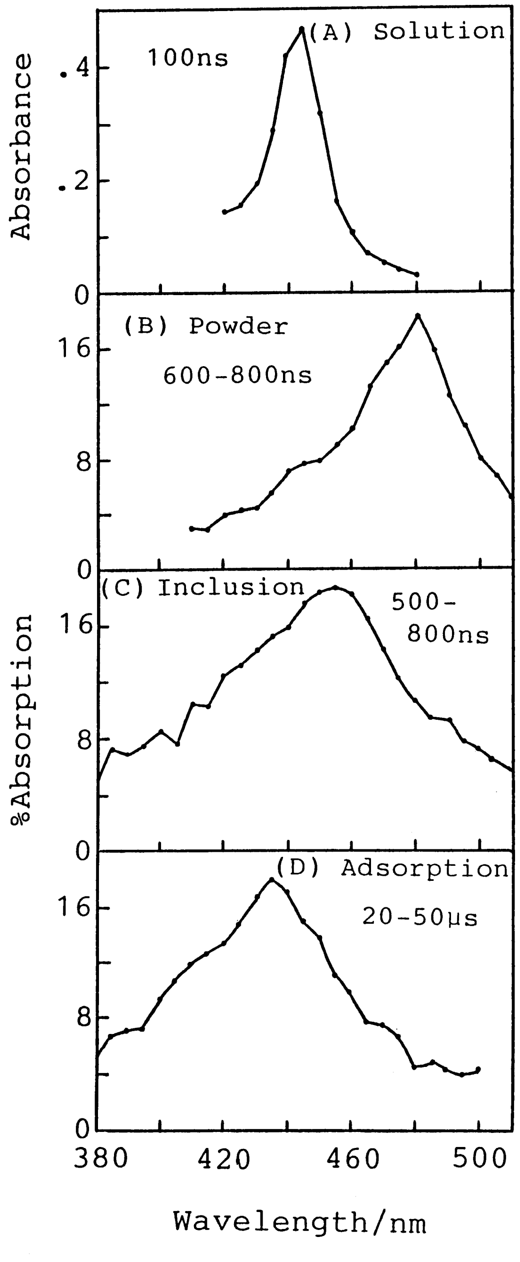

Fig. 8. Transient absorption spectra of some *p*-terphenyl systems. (A) 3×10^{-5} M hexane solution, (B) microcrystalline powders, (C) β-cyclodextrin powders including *p*-terphenyl, and (D) adsorbed on silica gel.

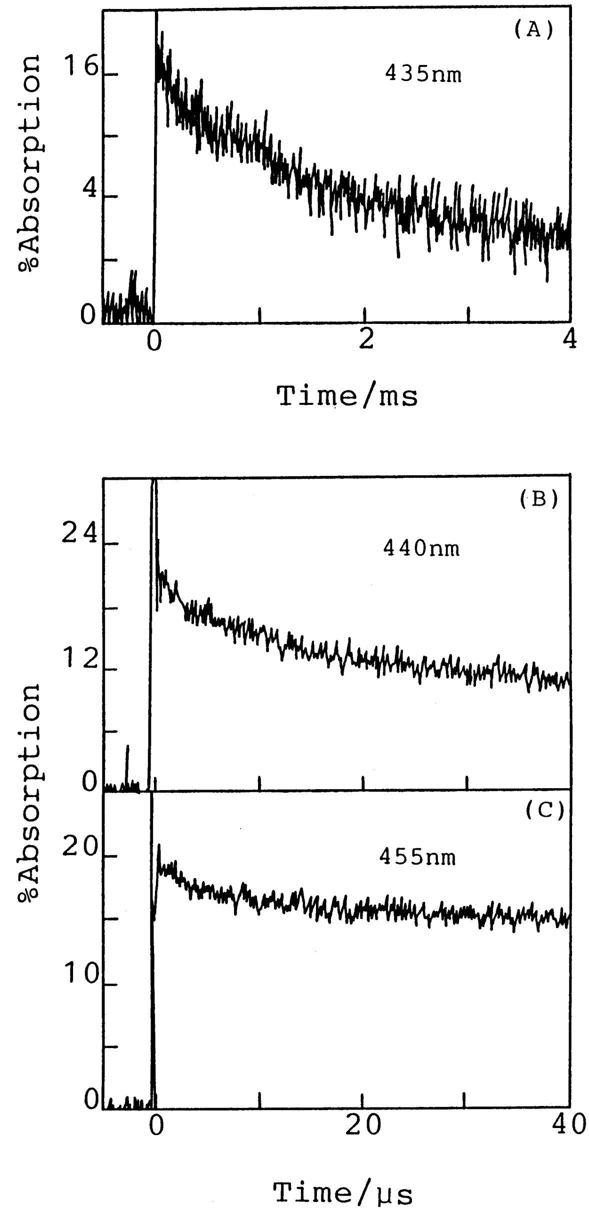

Fig. 9. Absorption decay curves of some *p*-terphenyl systems. (A) Silica gel (average diameter 5 μm) adsorbing *p*-terphenyl, (B) silica gel (average diameter 7 nm) adsorbing *p*-terphenyl, and (C) β-cyclodextrin powders including *p*-terphenyl. The observation wavelength is given in the Figure.

crystals and solution, while the adsorbed *p*-terphenyl on silica gel, gave an absorption peak below 450 nm. As the absorption spectral shape of *p*-terphenyl is sensitive to the rotational angle between benzene rings, we consider that absorption spectra of silica gel and *β*-cyclodextrin systems are also ascribed to the respective triplet states and the spectral shift is due to the differences of electronic and geometrical structures. These spectra decayed monotonously and no appreciable chemical reaction was induced, although their decay processes are complex and characteristic of the powder condition.

In Fig. 9, the triplet decay curves at the peak position are summarized. Compared to the microcrystals, a rather slow decay was observed for *p*-terphenyl adsorbed on the silica gel with 7 nm diameter and a very slow process for that with 5 μm diameter. In the case of inclusion complexes, the triplet decay consists of fast and slow components. Although the present result is qualitative, it is suggested that kinetic analysis of the excited states in powder systems provide a promising subject.

Closing Remarks. We have succeeded to measure absorption spectra and dynamics of the triplet exciton in *p*-terphenyl microcrystals. The relevant triplet state in silica gel and *β*-cyclodextrin systems has also been elucidated. In crystal a high density excitation usually brings about efficient interactions between excited states which lead to no transient absorption. Our success in measuring the absorption spectra of the excited states is due to rather small molar extinction coefficient of *p*-terphenyl at the laser wavelength. Furthermore, the absorption spectra of its excited singlet and triplet states have a high molar extinction coefficient, so that *p*-terphenyl powders are one of the best target systems for diffuse reflectance laser photolysis study.

Finally we comment a difficulty for analyzing photochemical processes by diffuse reflectance laser photolysis. In transmittance spectroscopy of solution, examinations of additives such as electron, energy, and proton acceptors are very effective for assigning transient species and the analysis method is almost established. On the other hand, a history of diffuse reflectance laser photolysis is quite short, the target powders are inhomogeneous, diffusion process is slow or almost impossible, and a contribution of surface photoprocess is sometimes appreciable. Therefore, we have to develop how to assign transient species and examine their dynamics. The present work is one of answers for such problems.

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