lead to significantly greater bond weakening than is seen in the excited B' state.

The B' state cannot be ruled out as the precursor to photochemistry from our observations of a risetime shorter than the normal luminescence decay time, since the excited-state population may decay more rapidly in a nonlinear fashion at high excitation density. Luminescence lifetimes have not as yet been measured for the polysilanes with high-energy, short-pulsed laser systems. Singlet exciton-exciton annihilation has been deduced³¹ to be occurring in a poly(*n*-propylmethylsilane) film, by the reduction in fluorescence quantum yield with increase in excitation energy density. The very fast rise of the transient could be evidence for the mobility of excitations in this system and for the involvement of a nonlinear process in the fluorescence decay of the excited state. Annihilation would require a nonlinear dependence on the pump strength of fluorescence intensity. This is indeed observed as shown in Figure 3, although saturation of the transition (ground-state depletion) at the high excitation density used might also contribute to this effect. We emphasize that this figure also shows that the transient itself is not the direct result of a nonlinear interaction, for even at the high excitation density generated, the transient signal shows the same dependence on the pump strength as the fluorescence. The possibility that a biexciton state or photoionized state created by excitation migration is largely responsible for photodecay is thus ruled out. We note that the absorption rise is in any case slower than would be predicted if the transient were the immediate product of two-photon or excited-state absorption by the polysilane. The calculated curve for such a case would rise faster than the 16-ps curve of Figure 2.

In summary, we are unable to distinguish, on the basis of our experiment, between the possible short-lived precursor states for the photochemistry we observe at room temperature for the reason that all such states are extremely short-lived. Low-temperature studies might permit a distinction to be made, but these are made difficult by the extreme photosensitivity of the materials. The likelihood that the rate of transient formation is not a singleexponential process requires investigation with higher temporal resolution than was available here (30 ps). Such studies are currently in progress in our laboratory; these might also prove more fruitful in locating short-lived excited-state absorptions.

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The position and width of the photobleaching signal deserve further comment. It has been noted that the polysilane absorption spectrum reflects an inhomogeneous distribution of chain segment

lengths.^{11a-c} The width of the bleaching spectrum shown in Figure 5 is significantly narrower than that of the absorption. Furthermore, the bleaching peak was not found at the laser pump wavelength (355 nm) but shifted to shorter wavelength. The bleaching spectrum was more similar in position and width (348 and 8 nm) to the fluorescence (353 and 15 nm) than to the absorption (340 and 30 nm). These results suggest that the long-chain portion of the segment distribution, normally considered responsible for the fluorescence, is in fact being directly excited by the 355-nm pulse and that bleaching is occurring without significant energy transfer being required. Thus the 8-nm width of the bleaching spectrum places an upper limit on the dephasing rate of these excitations in solution. The blue shift of the burnt hole is probably partially the result of excitation at the red edge of a line having an appreciable homogeneous width, but may also reflect a greater susceptibility to photochemistry of the higher energy excitations in the system. Photochemical hole burning has been observed in polysilanes at 77 K in glasses³² and in solid films:³³ we have now shown that some site selection is achievable in solution at room temperature.

Summary

We have observed transient absorptions at 450 and 370 nm in room temperature solutions of poly(phenylmethylsilane). We attribute the long-lived transient absorption at 450 nm to photogenerated phenylmethylsilylene. The precursor state is likely to be the relaxed state which emits at 430 nm. Photochemical selection from the length distribution occurs for the solution-phase polymer at ambient temperature.

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A Time-Resolved EPR Study of One- and Two-Photon Processes in the Photochemical Reactions of Benzil

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A time-resolved EPR study of the photochemical reactions of benzil in isopropyl alcohol and a benzene-triethylamine (TEA) mixed solvent is reported. Emissive and absorptive chemically induced dynamic electron polarization signals of the intermediate radicals were observed in these two systems. The observed radicals are assigned as the benzoyl and benzil ketyl radicals in the former case and the benzil anion radical in the latter case. It is found that these photochemical reactions occur from the higher excited triplet state through a two-photon process in isopropyl alcohol and from the lowest excited triplet state through a one-photon process in the benzene-TEA mixed solvent, respectively.

Introduction

Benzil is one of the most typical α -dicarbonyls. Many studies have been reported on the excited-state structures and photochemical reactions. The structure of benzil is considered to be flexible with respect to the dihedral angle (θ) between the planes of two carbonyl groups.¹⁻³ A skewed ($\theta \sim 111^{\circ}$)⁴ and a near-trans $(\theta \sim 157^{\circ})^{5}$ form were found to be stable in the ground (S₀) state

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Figure 1. Time-resolved EPR spectra of intermediate radicals observed at 0.8 μ s after the laser pulse for benzil (10⁻² M) (a) in isopropyl alcohol at -10 °C and (b) in a benzene-triethylamine (1 M) mixed solvent at room temperature. (c) and (d) are simulated spectra for (a) and (b), respectively. See the text for assignments of the radicals.

and the lowest excited triplet (T_1) state in solids, respectively. In solution, a dipole moment of T_1 benzil has been reported as ~ 0 D,⁶ suggesting a stable trans planar form.

The photochemical reactions of benzil have been studied by means of product analysis,^{7,8} flash photolysis,^{9,10} and time-resolved EPR (TREPR).^{11,12} In the transient absorption experiments Scaiano measured rise and decay rates of an intermediate radical and found that the reaction rate increases with an addition of amines.9 Recently, McGimpsey and Scaiano have proposed that a cleavage reaction occurs from a higher excited triplet state by observing quenching of T_1 benzil with the second laser excitation.¹⁰ However, the detailed reaction mechanisms including definitive assignments of the intermediate radicals have not been determined yet. In the TREPR experiments quite different results have been reported by Grant and McLauchlan (GM)¹¹ and by us.¹² GM observed a net absorptive CIDEP (chemically induced dynamic electron polarization) signal in isopropyl alcohol containing a triplet-state quencher such as triethylamine or di-tert-butylphenol. In contrast, we observed two kinds of net emissive CIDEP signals in a pure isopropyl alcohol solution.¹² As the polarization of a CIDEP signal should reflect the nature of the precursory excited state of the reaction, the opposite polarizations observed in these two systems are very interesting in relation to a state selective reaction and/or a flexible geometry in the excited state of benzil.

In this Letter we report preliminary results of the TREPR experiment on this phenomenon of polarization inversion. We first discuss assignments of the intermediate radicals observed in GM's and our systems on the basis of the obtained EPR parameters. We next show that different types of reactions (electron transfer, hydrogen abstraction, and cleavage) occur from the different electronic states of benzil by investigating the dependences of the TREPR signals on laser power and concentration of amine.

Experimental Section

Benzil (Nacalai Tesque) was recrystallized from ethanol several times and was zone-refined through 200 band-passes. Benzene and isopropyl alcohol (Wako Pure Chemicals Ltd., spectrograde) were used without further purification. Triethylamine (Nacalai Tesque) was purified by repeated distillation. Concentrations of benzil in solutions were 10^{-2} – 10^{-3} M. The solutions were deaerated

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TABLE I: Hyperfine Coupling Constants (in G) Used To Simulate the TREPR Spectrum of the Benzil Ketyl Radical $(C_6H_5)\dot{C}(OH)CO(C_6H_5)$

$a_{\rm c} = a_{\rm p}$	2.50	$a_{\mathrm{m}'}$	0.20
a _m .	1.05	$a_{OH} (a_{OD})$	1.40 (0.20)
$a_{o'} = a_{p'}$	0.30		

by blowing helium gas and flowed in a quartz tube of 2.5-mm i.d. at a rate of $\sim 0.3 \text{ mL/min}$. The TREPR signals were detected without field modulation with a JEOL-FE3X EPR spectrometer at 0.4–1.0 μ s after a laser excitation (a Lumonics TE861M excimer laser with a XeCl fill, $\lambda = 308$ nm, and a power of ~ 60 mJ/pulse or a Lumonics HE440UBB excimer laser with ~ 300 mJ/pulse).¹² The spectra were taken by feeding an output of a modified preamplifier of a microwave unit to a PAR 160 boxcar integrator. The relative laser power was measured by using a 10% beam splitter and a power meter (Scientech 380105).

Results and Discussion

Figure 1a,b shows time-resolved EPR (TREPR) spectra of intermediate radicals produced by photochemical reactions of benzil in two different kinds of solvent systems at 0.8 μ s after the laser excitation. The spectrum in Figure 1a was taken in isopropyl alcohol at -10 °C and is analyzed by a superposition of spectra of two radicals. From the reported g value and hyperfine coupling constants (hfcc, a)¹³ the radical with g = 2.0009, $a^{m}_{H} = 1.18$ G, and a^{p}_{H} , $a^{o}_{H} < 0.3$ G is assigned as the benzoyl radical. The other radical with g = 2.0046 and a rather complicated hyperfine structure is assigned as the benzil ketyl radical from the computer simulation of the spectrum (Figure 1c). The hyperfine coupling constants of the benzil ketyl radical are determined as summarized in Table I. The spectrum of the corresponding radical obtained in isopropyl- d_8 alcohol can be simulated with $a_{OD} = 0.2$ G and other hfcc being kept the same, which supports the validity of the assignment. These results clearly indicate that the photochemical reactions of benzil occurring in isopropyl alcohol are the Norrish type I cleavage reaction and a hydrogen abstraction reaction from the solvent alcohol as described by the following scheme:

$$Ph-CO-CO-Ph \xrightarrow{n\nu} (Ph-CO-CO-Ph)^*$$
(1a)

$$(Ph-CO-CO-Ph)^* \rightarrow 2Ph-\dot{C}O$$
 (1b)

From Figure 1a we find that the TREPR signals of both radicals show net emissions (E pattern).

On the other hand, an absorptive TREPR spectrum (Figure 1b) of an intermediate radical was observed in a benzene-triethylamine (TEA, 1 M) mixed solvent at room temperature. This radical having g = 2.0042 and a line width ($\Delta H_{1/2}$) of 3.7 G is not the ketyl radical but is assigned as the benzil anion radical on the basis of the reported g value (g = 2.0038) and hyperfine coupling constants.¹⁴ The simulation of the spectrum is shown in Figure 1d. This assignment does not agree with the result by Scaiano⁹ that the ketyl radical is generally produced in a TEAnonpolar mixed solvent system. However, as the absorptive CI-DEP signals having the same EPR parameters were observed in TEA-isopropyl alcohol and in KOH-isopropyl alcohol, our interpretation that not the benzil ketyl but benzil anion radical is observed even in TEA-benzene is reasonable. In this case an electron-transfer reaction occurs as the following:

Ph-CO-CO-Ph
$$\xrightarrow{h\nu}$$
 (Ph-CO-CO-Ph)* (2a)

$$(Ph-CO-CO-Ph)^* \xrightarrow{TEA} (Ph-CO-CO-Ph)^{\bullet-} (2b)$$

Here the TREPR spectrum also showed a net polarization pattern, but the polarity is reversed to an absorption.

There are two possibilities for the net polarization pattern. One is a radical pair mechanism (RPM) involving a $S-T_0$ mixing with

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Figure 2. Dependence of the intensities (Is) of the time-resolved EPR signals on the laser power (P) for the benzil ketyl and benzoyl radicals in isopropyl alcohol (\bullet) and the benzil anion radical in benzene-triethylamine (O). Straight lines A and B indicate that Is $\propto P^1$ and Is $\propto P^2$ relationships, respectively.

different g values of pair radicals. The other is a triplet mechanism (TM).^{15,16} In the former case polarizations of pair radicals are opposite, but these are the same in the latter case. In the present case, there is no $\Delta g (=g_1 - g_2)$ mechanism for the formation of the benzoyl radical because of $\Delta g = 0$. Δg is considered to be too small to produce such a large polarization for the benzil ketyl radical ($\Delta g = 0.0014$; $g((CH_3)_2COH) = 2.0032$) and the benzil anion radical ($\Delta g \sim 0.0011$; $g((C_2H_5)_2NCHCH_3) = 2.0031$). Therefore, TM is dominant and the observed intermediate radicals are produced from the reactions in the excited triplet states of benzil. In TM a difference in the polarization is due to a difference in populations of triplet sublevels of precursory excited states of reactions. Then in isopropyl alcohol, the upper sublevels of the reactive benzil triplet are more populated than the lower sublevel, but in the benzene-TEA mixed solvent the upper sublevels are populated less than the lower sublevel. These results suggest that the photochemical reactions of benzil may occur from the different excited triplet states or different structures of the same triplet state.

In order to ensure this difference, we examined the dependence of the intensities of TREPR signals (Is) on the laser power (P) in the two systems. The plots of log Is vs log P are shown in Figure 2, where P was changed by a factor of 3. From the figure we find a nice correlation between Is and P, a linear (n = 1) and square (n = 2) dependence of Is on Pⁿ for the benzil anion radical, and the benzoyl and ketyl radicals, respectively. It is apparent that the anion radical is produced through a one-photon process and the other two radicals are produced through two-photon processes.¹⁷ The benzil anion radical, and the benzil ketyl and benzoyl radicals, therefore, come from the different excited electronic states of benzil.

From these obtained results, the electron transfer in benzil is found to occur through the one-photon process from the lower excited triplet states, giving rise to the net absorptive CIDEP signal of the benzil anion radical. It is noted that the TREPR spectra of T_1 benzil in various kinds of glassy solutions show the same absorptive patterns indicating that the lower triplet sublevel is more



Figure 3. Dependences of the time-resolved EPR spectra (a) on the relative laser power and (b) on the concentration of triethylamine (TEA) in benzene. The concentrations of benzil used are 5×10^{-3} M (TEA, 7×10^{-3} M) and 10^{-2} M in the cases of (a) and (b), respectively. The observed radicals are assigned as the benzil ketyl (O), benzil anion (Δ), and benzoyl (\Box) radicals.

populated than the upper sublevels,¹⁸ though the structures of T_1 benzil are considered to vary remarkably in these solvents.^{3,19} These results strongly indicate that the electron transfer occurs from the T_1 state of benzil in the benzene-TEA system. The result of the transient absorption experiment for the intermediate radical9 is consistent with this conclusion, though the assignment of the radical was different. As for the formation of the benzil ketvl and benzoyl radicals, they were produced from the triplet state through the two-photon processes, indicating that the reactions occur from the higher excited triplet state (T_n) of benzil. This result is also consistent with the suggestion from the transient absorption experiment for T₁ benzil using two-color lasers.¹⁰ The observed emissive polarization indicated that T_n is populated more in the upper sublevels. Although the exact reason why the population scheme is opposite between the T_1 and T_n states is not clear at present, the skewed structure ($\theta \sim 90^{\circ}$) may be involved in the reactions from the T_n state in contrast to the nearly planar T_1 structure ($\theta = 150-180^\circ$). In the former structure more population in the upper sublevels and emissive CIDEP signals are expected just as in T₁ benzaldehydes.²⁰

If one- and two-photon processes really occur, the second photon absorption and the reaction with TEA are expected to be competing with each other in the T_1 state of benzil in benzene-TEA. To make certain of this point, we examined the dependences of the TREPR signals on the laser power and the concentration of TEA under the condition that three radicals are coexisting. The results are shown in Figure 3a,b, which shows that the ketyl and benzoyl radicals increase their intensities with increasing the laser intensity more than the anion radical. In contrast, the anion radical increases and the other two radicals decrease with the concentration of TEA. The results are qualitatively consistent with the above conclusion.

We summarize the photochemical reaction mechanisms of benzil as follows: the benzil ketyl and benzoyl radicals are produced from the higher excited triplet state of benzil involving the two-photon processes, and the benzil anion radical is produced from the lowest excited triplet state in the benzene-TEA mixed solvent. It is interesting to note that the bond cleavage reaction and the hydrogen abstraction do not occur efficiently in the T_1 -($n\pi^*$) state of benzil. Further investigation on the cause of the polarization inversion is in progress.

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