Macromolecules **1987**, *20*, 54–58

Photochemistry in Polymer Solids. 8. Mechanism of Photoreaction of Benzophenone in Poly(vinyl alcohol)

Kazuyuki Horie,* Harumi Ando, and Itaru Mita

Institute of Interdisciplinary Research, Faculty of Engineering, University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153, Japan. *Received May 28, 1986*

ABSTRACT: The decay of benzophenone phosphorescence in poly(vinyl alcohol) film and the quantum yields for benzophenone disappearance were measured over a wide temperature range. The decay curves deviate markedly from single-exponential type in the temperature range between T_γ (−100 °C) and T_g (85 °C), but the phosphorescence decays single-exponentially for temperatures below T_γ and above T_g. The origin of non-single-exponential decay was attributed to the diffusion-controlled hydrogen abstraction by benzophenone triplet from the matrix polymer with a time-dependent rate coefficient. Comparison of the quantum yields for benzophenone disappearance with the results of transient decay measurements suggests the existence of a cage backward reaction, and the proposed mechanism is supported by transient absorption measurements of benzophenone ketyl radical.

Introduction

Organic photosensitive polymers are widely used as key materials for photoimaging systems, photoresists, printing, and painting, and they have potential applicability to erasable photomemory systems. As most photosensitive materials are used in the form of polymer films, the elucidation of the rates and mechanism of photoreactions in polymer solids as a function of not only the molecular structure of the chromophores but also the molecular structure and motion of the matrix polymers has a special importance in developing more efficient organic photosensitive polymers with higher sensitivity, resolution, and selectivity.

In our previous papers, the decay of benzophenone phosphorescence in poly(methyl methacrylate) (PMMA) and other acrylic polymers[1-3] and in polystyrene and polycarbonate[4] and the rates of photochromic reactions[5] as well as fluorescence decay[6] of spirobenzopyran in polycarbonate were measured over a very wide temperature range (80–453 K) by using nitrogen laser pulses. In the case of benzophenone phosphorescence, the decay curves in the polymer matrices were observed to deviate markedly from the single-exponential type in the temperature range between T_β (onset of ester group rotation in acrylic polymers) or T_γ (onset of phenyl or phenylene group rotation in polystyrene or polycarbonate) and T_g (glass transition temperature), while the phosphorescence decays exponentially for temperatures below T_β or T_γ and above T_g of the matrix polymers. The deviation was attributed to the diffusion-controlled dynamic quenching (endothermic energy transfer) of benzophenone triplet by the side-chain ester group or by the phenyl or phenylene group in these polymers.[2-4]

The nonexponential decay of benzophenone phosphorescence in PMMA was also observed at room temperature by Salmassi et al.[7] and Fraser et al.[8] under the condition of very high intensity and/or repeated laser pulse irradiation, and the possibility of triplet–triplet (T–T) annihilation was suggested as a cause for the nonexponential decay, based on a mechanism[8] that consists of energy transfer from benzophenone triplet to polymer, triplet energy migration in the polymer matrix, and T–T annihilation between polymer triplet and benzophenone triplet. The irradiation intensity independence, however, of the non-single-exponential decay profile of benzophenone phosphorescence in PMMA was ascertained by the present authors,[3] indicating the absence of biphotonic T–T annihilation under the present experimental conditions.

Moreover, our preliminary results[9] on the phosphorescence decay of benzophenone on poly(vinyl alcohol) where there is no possibility of triplet energy migration have shown the presence of nonexponential decay of benzophenone phosphorescence in the polymer matrix where T–T annihilation does not occur. Thus, we expanded the decay study of benzophenone phosphorescence to the case of poly(vinyl alcohol).

Poly(vinyl alcohol) is sometimes used as a matrix for dispersing various chromophores by making use of its hydrogen-bonding ability and/or its solubility in water. For example, photochemical hole burning of 1,4-dihydroxyanthraquinone was realized in poly(vinyl alcohol) film.[10] However, poly(vinyl alcohol) is usually regarded as an inert rigid matrix for photophysical processes of excited chromophores dispersed in it. In the present paper, nonexponential decay of benzophenone phosphorescence in poly(vinyl alcohol) is analyzed based on the diffusion-controlled hydrogen abstraction with a time-dependent rate coefficient, and then the quantum yield for benzophenone disappearance under steady-state irradiation is compared with the results of transient decay measurements. The proposed mechanism of the photoreaction including cage backward reaction is supported by the transient absorption measurements of benzophenone ketyl radical.

Experimental Section

Materials. Benzophenone was purified by recrystallization from ethanol solution. Reagent grade poly(vinyl alcohol) (M_n = 7.7 × 10^4) and extrapure grade formic acid were obtained from Tokyo-Kasei Chemicals.

Sample Preparation. A poly(vinyl alcohol) film containing 0.15–2.0% benzophenone (250–400 μm) was prepared by solvent casting on a quartz plate from poly(vinyl alcohol) and benzophenone solution in formic acid. Evacuation was carried out at room temperature for 24 h and at 100 °C for 24 h. The purge of oxygen is important in the study of triplet reactions. In the case of phosphorescence decay measurements, the evacuated sample was set in a cryostat and was evacuated again under high vacuum. For quantum yield measurements, the evacuated sample was covered by another quartz plate quickly and then was evacuated again at 100 °C for 1 h.

Measurements of Phosphorescence Decay and Transient Absorption. A schematic diagram of the laser flash photolysis apparatus used for the measurements of phosphorescence decay and transient absorption during the photoreaction of benzophenone in poly(vinyl alcohol) is shown in Figure 1. A pulse nitrogen laser (Avco C950B) with a pulse width of 10 ns as an exciting light at 337 nm, cryostat (Oxford DN704), monochromator (Jasco CT10), photomultiplier (HTV R1464), transient time

0024-9297/87/2220-0054$01.50/0

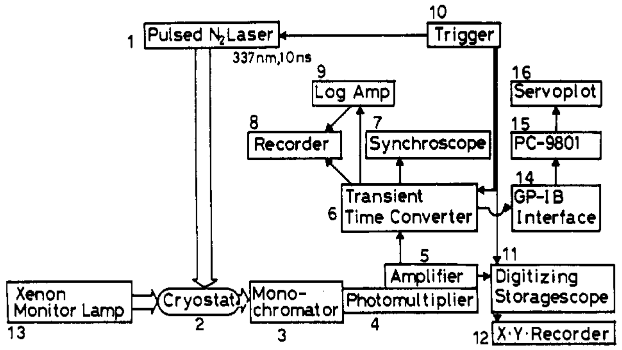

Figure 1. Laser flash photolysis apparatus.

converter (Riken Denshi TCG 8000) or digitizing storage scope (Iwatsu Denshi TS8123), and a personal computer (PC-9801) were used for measuring the phosphorescence decay of benzophenone. The continuous light from a 500-W xenon lamp (Ushio UXL-500D) was used as a monitoring light for measuring the transient absorption spectra of intermediate ketyl radical from benzophenone in poly(vinyl alcohol).

Measurements of Change in Benzophenone Concentration during Continuous Irradiation. Steady-state photoirradiation of a sample film placed between quartz plates by 365-nm light from a 450-W high-pressure mercury lamp (Ushio UM-452) with a UV-D36A glass filter and a Pyrex glass plate was carried out in a merry-go-round type photoreaction apparatus or in a high-temperature type photoreaction apparatus, both prepared in the workshop of the Institute. Actinometry for the irradiation light was carried out with an International IL-411T type photoresist photometer calibrated by the potassium ferrioxalate/*o*-phenanthroline system.[11] The decrease in benzophenone concentration of the sample during continuous irradiation was measured by the change in optical density of the $\pi\pi^*$ absorption of benzophenone at 256 nm by using a Shimadzu MPS-5000 type spectrophotometer.

Kinetics for Nonexponential Decay of Benzophenone Phosphorescence in Poly(vinyl alcohol)

Typical decay curves at various temperatures of benzophenone phosphorescence at 450 nm in poly(vinyl alcohol) films excited by a 10-ns nitrogen laser puse at 337 nm are shown in Figure 2. The phosphorescence intensity, $I_p(t)$, decreases single-exponentially at temperatures below −100 °C. When the temperature rises above −100 °C, deviation from the straight line in the semilogarithmic decay of $I_p(t)$ is observed, and the deviation becomes more marked with increasing temperature until the temperature reaches the T_g of poly(vinyl alcohol) (85 °C); then the deviation becomes less marked. These temperature dependences of the decay profiles of benzophenone triplet in poly(vinyl alcohol) are similar to those previously observed in poly(methyl methacrylate) and other acrylic polymers[2] and in polystyrene and polycarbonate.[4] Though there seem to be no physically quenching groups in poly(vinyl alcohol), in contrast to the case of previously measured polymers, the tertiary hydrogen atom in the main chain of poly(vinyl alcohol) (PVA) is supposed to be easily abstracted by benzophenone triplet (^{3}BP*), forming benzophenone ketyl radical (BPH$^\bullet$) and poly(vinyl alcohol) on-chain radical (PVA$^\bullet$), based on the model hydrogen abstraction reaction[12] of benzophenone triplet from 2-propanol.

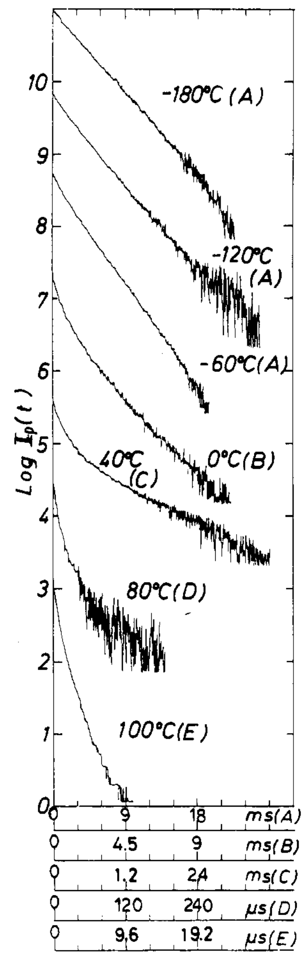

Figure 2. Semilogarithmic decay curves of benzophenone phosphorescence in poly(vinyl alcohol) at various temperatures.

The kinetic scheme for the decay process of benzophenone triplet can be given by eq 1 and 2, where $k_0 = k_{PT}$

$$^3\mathrm{BP}^* \xrightarrow{k_0} \mathrm{BP} \qquad (1)$$

$$^3\mathrm{BP}^* + \mathrm{PVA} \xrightarrow{k_a} \mathrm{BPH}^\bullet + \mathrm{PVA}^\bullet \qquad (2)$$

$+ k_{IT}$ is the rate constant for spontaneous deactivation consisting of phosphorescence (k_{PT}) and nonradiative deactivation (k_{IT}) processes and k_a is the rate coefficient of hydrogen abstraction by benzophenone triplet from poly(vinyl alcohol). The bimolecular rate coefficient k_a in the solid state is given by eq 3, as were the previous cases

$$k_a = \frac{4\pi RDN}{1 + 4\pi RDN/k}\left(1 + \frac{R}{(1 + 4\pi RDN/k)(\pi Dt)^{1/2}}\right) \qquad (3)$$

of dynamic quenching of benzophenone triplet by polymeric chains. In eq 3 D is the sum of the diffusion coefficient for the carbonyl group in benzophenone and that for hydrogen in poly(vinyl alcohol), R is the reaction radius between the two reacting groups, k is the intrinsic (chemical) rate constant for hydrogen abstraction, and N is the Avogadro number divided by 10^3. When k_a is controlled by the diffusion process of the two groups ($k \gg 4\pi RDN$), eq 3 is reduced to

$$k_a = 4\pi RDN(1 + R/(\pi Dt)^{1/2}) = A + B/t^{1/2} \qquad (4)$$

with $A = 4\pi RDN$ and $B = 4R^2(\pi D)^{1/2}N$. The rate coefficient k_a includes a time-dependent term that is important at the very early stage of reaction where the steady-state diffusion flux of the reacting group is not yet attained.

As the decay rate of benzophenone triplet and its concentration, [^{3}BP*], at time t are given by eq 5 and 6, respectively, the decay curve of the phosphorescence inten-

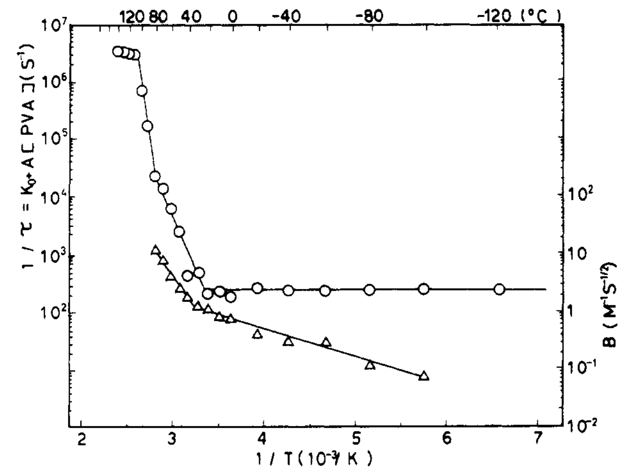

Figure 3. Arrhenius plots of the parameters $1/\tau$ (○) and B (△) for phosphoresecence decay of benzophenone in poly(vinyl alcohol).

sity, $I_p(t)$, which is proportional to $k_{PT}[^3BP^*]$, is finally expressed by eq 7

$$-d[^3BP^*]/dt = (k_0 + k_a[PVA])[^3BP^*] = (k_0 + A[PVA] + B[PVA]t^{-1/2})[^3BP^*] \quad (5)$$

$$[^3BP^*] = [^3BP^*]_0 \exp\{-(k_0 + A[PVA])t - 2B[PVA]t^{1/2}\} \quad (6)$$

$$\ln I_p(t) = -(k_0 + A[PVA])t - 2B[PVA]t^{1/2} = -(t/\tau) - C(t/\tau)^{1/2} \quad (7)$$

where

$$1/\tau = k_0 + A[PVA] = k_0 + 4\pi RDN[PVA] \quad (8)$$

$$B = C\tau^{-1/2}/(2[PVA]) = 4R^2(\pi D)^{1/2}N \quad (9)$$

The curve fitting for the non-single-exponential phosphorescence decay with eq 7 by the nonlinear least-squares method calculated with an NEC PC-9801 type personal computer gives the values of τ and C, and hence B from eq 9, for each decay curve. The standard deviation was 2–3% in normal cases, but sometimes several percent at temperatures near T_g of the matrix polymer. The temperature dependence of the parameters $1/\tau$ and B calculated by using the tertiary hydrogen concentration in poly(vinyl alcohol), [PVA] = 28.9 mol/L, is given in Figure 3.

The onset of deviation from single-exponential decay is observed in Figure 3 as the appearance of parameter B at −100 °C. This temperature is equal to the temperature corresponding to the onset of phenyl or phenylene group rotation in polystyrene and polycarbonate (T_γ = −100 °C)[4] and is supposedly due to the onset of benzophenone rotation in the poly(vinyl alcohol) matrix, which makes possible the hydrogen abstraction reaction. The parameter $1/\tau$ is almost constant over a wide range of the low-temperature region by as much as −30 °C and has almost the same value as k_0 in other polymer matrices (k_0 = 200–220 s^{-1}).[2] This suggests that $4\pi RDN[PVA] \ll k_0$ in eq 8, so that $1/\tau \cong k_0$ in this temperature range. The lifetime, $\tau_0 = 1/k_0$, was 5.0 ms at 80 K. The break for $1/\tau$ at 30 °C suggests that $4\pi RDN$[PVA] becomes larger than k_0 in the higher temperature range. The approximation

$$1/\tau \simeq 4\pi RDN[PVA] \qquad \text{for } 30\ ^\circ C < T < T_g \quad (10)$$

is supported by the fact that the activation energy, E, for

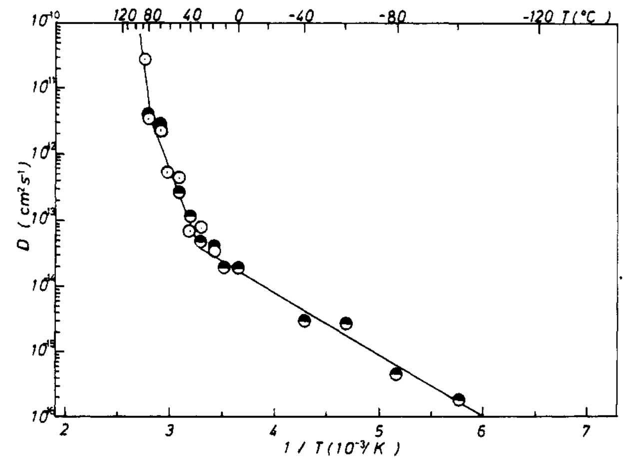

Figure 4. Arrhenius plots of diffusion coefficients, D, of reacting groups for hydrogen abstraction by benzophenone triplet in poly(vinyl alcohol) calculated from $1/\tau$ (○) or B (◓).

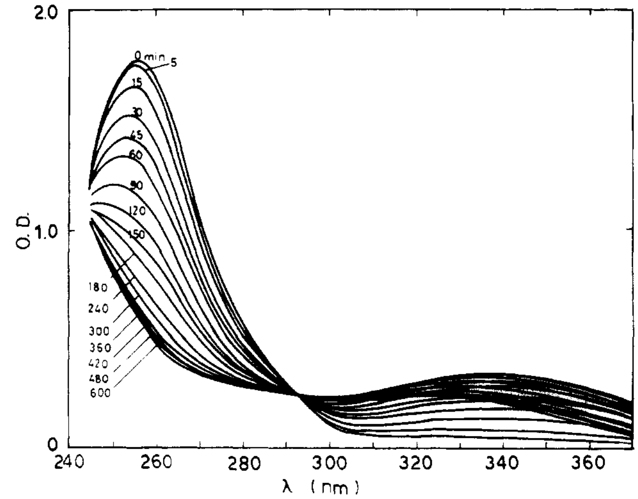

Figure 5. Change in UV spectra of benzophenone in poly(vinyl alcohol) film during 365-nm high-pressure mercury lamp irradiation at 30 °C.

$1/\tau$ (68 kJ/mol) is almost twice as large as E for B in the same temperature range. The break at 85 °C for the Arrhenius plot of $1/\tau$ corresponds to glass transition temperature, T_g, of poly(vinyl alcohol), due to the change in the temperature dependence of D from below to above T_g.

A break observed at 110 °C for $1/\tau$ in Figure 3 is supposed to correspond to the crossover of k_a from a diffusion-controlled to an activation-controlled reaction. Thus, at $T >$ 110 °C, $1/\tau = k$[PVA] holds. The value of k at 110 °C and its activation energy E were obtained as 1×10^5 M^{-1} s^{-1} and 8.2 kJ/mol, respectively, which are comparable to the literature values for hydrogen abstraction of benzophenone triplet in solution ($k = 10^5$–10^6 M^{-1} s^{-1}, E = 9–11 kJ/mol).[12]

The parameter B appears at T_γ = −100 °C and shows a break at 30 °C. This temperature corresponds to the β transition, reflecting the local mode relaxation of several monomer units in the main chain of poly(vinyl alcohol) ($T_\beta \simeq$ 30 °C at 10^5 Hz).[13] The combination of eq 9 and 10 with two unknowns, R and D, at each temperature for $T_\beta < T < T_g$ gave the value of the reaction radius, R, independent of temperature and $R \simeq$ 3.5 Å on the average.

The diffusion coefficient, D, for reacting carbonyl groups was calculated from eq 9 and 10 by using this average value of R and is shown against $1/T$ in Figure 4. Breaks in the slope of D are observed at T_g and T_β, and activation energies for D are 220 kJ/mol for $T > T_g$, 68 kJ/mol for T_g

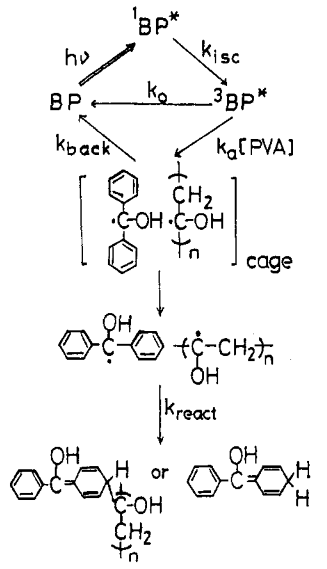

Figure 6. Reaction scheme of photoexcited benzophenone in poly(vinyl alcohol).

$> T > T_\beta$, and 19 kJ/mol for $T < T_\beta$. The absolute value of D at 20 °C amounts to 3×10^{-14} cm^2/s which is comparable with the value in PMMA (4×10^{-14} cm^2/s at 20 °C).[2]

Quantum Yields for Benzophenone Disappearance in Poly(vinyl alcohol) under Continuous Irradiation. In order to ascertain that the deviation of the decay curve from single-exponential is due to the hydrogen abstraction reaction, benzophenone disappearance during the photoirradiation of benzophenone in poly(vinyl alcohol) was followed by spectrophotometry. Typical changes in absorption spectra of poly(vinyl alcohol) film containing 0.15% benzophenone under 365-nm light irradiation is illustrated in Figure 5. The $\pi\pi^*$ absorption of benzophenone at 256 nm decreases with increasing irradiation time, but the $n\pi^*$ absorption at 340 nm first increases with irradiation and then decreases. This increase in $n\pi^*$ absorption of benzophenone during photoirradiation was also observed in benzene solution[14-15] and in PMMA matrix[13] and is attributed to some reaction product having absorption at 340 nm (Figure 6).

The change in benzophenone concentration, [BP], during stationary-state photoirradiation can be related to the quantum yield for benzophenone disappearance, $\Phi_{(-\mathrm{BP})}$, by eq 11, which is reduced to eq 12 and 13 for $\epsilon[\mathrm{BP}]l < 0.1$. I_0 (einstein cm^{-2} s^{-1}) is the intensity of incident light,

$$-\mathrm{d}[\mathrm{BP}]/\mathrm{d}t = \Phi_{(-\mathrm{BP})} \times 10^3 I_0(1 - 10^{-\epsilon[\mathrm{BP}]l})/l \quad (11)$$

$$\simeq \Phi_{(-\mathrm{BP})} \times 10^3 I_0 \times 2.3\epsilon[\mathrm{BP}] \quad (12)$$

$$\ln ([\mathrm{BP}]/[\mathrm{BP}]_0) = -2.3 \times 10^3 I_0 \epsilon \Phi_{(-\mathrm{BP})} t \quad (13)$$

ϵ (l mol^{-1} cm^{-1}) is the molar extinction coefficient, l (cm) is the film thickness, and the product $I_0\epsilon$ was summed over the wavelengths of incident light. As semilogarithmic plots of benzophenone concentration, [BP], evaluated from the absorbance at 256 nm in Figure 5 against time gave a straight line, the quantum yield, $\Phi_{(-\mathrm{BP})}$, was calcuated from its slope by using eq 13.

The results are summarized in Table I. The independence of $\Phi_{(-\mathrm{BP})}$ against I_0 at 30 °C ascertains that the hydrogen abstraction by benzophenone triplet in poly(vinyl alcohol) proceeds as a one-photon process, different from the case in PMMA.[2,13] The values of $\Phi_{(-\mathrm{BP})}$ for $T < T_g$ are very small in contrast to the fraction of ketyl radical formation, f_a

Table I
Quantum Yield, $\Phi_{(-\mathrm{BP})}$, for Benzophenone Disappearance during 365-nm Irradiation with Incident Intensity, I_0, and the Fraction of Ketyl Radical Formation, f_a, from Transient Measurements

temp, °C	I_0, einstein cm^{-2} s^{-1}	$\Phi_{(-\mathrm{BP})}$	f_a
0	2.6×10^{-8}	0.018	0.85
30	1.9×10^{-8}	0.042	0.95
	1.4×10^{-8}	0.056	
	8.1×10^{-9}	0.049	
	8.0×10^{-9}	0.052	
60	2.6×10^{-8}	0.075	0.99
100	1.9×10^{-8}	0.32	1.0
140	1.9×10^{-8}	0.49	1.0

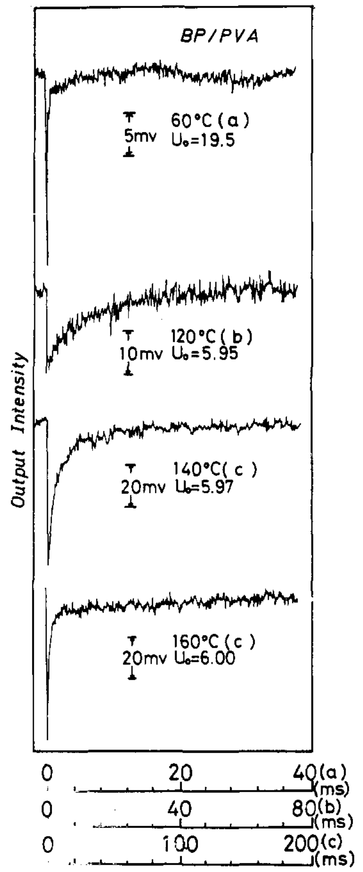

Figure 7. Transient absorption for benzophenone ketyl radical in poly(vinyl alcohol) at 545 nm.

$$f_a = k_a[\mathrm{PVA}]/(k_0 + k_a[\mathrm{PVA}]) = 1 - \tau_0^{-1}\int_0^\infty I_p(t)\,\mathrm{d}t \quad (14)$$

which can be calculated from integration of phosphorescence decay curves. Values of f_a are also given in Table I. The very small value of $\Phi_{(-\mathrm{BP})}$ compared to f_a for $T < T_g$ suggests that most of the ketyl radicals formed by hydrogen abstraction disproportionate with the geminate PVA radicals inside the cage of the matrix, reproducing benzophenone molecules. The extent of this backward reaction inside the cage becomes less pronounced for $T > T_g$, where $\Phi_{(-\mathrm{BP})}$ amounts to more than 30% due to the liberation of micro-Brownian motion of the polymer main chain. Thus, the quantum yield, $\Phi_{(-\mathrm{BP})}$, is expressed by eq 15, where k_b is the rate coefficient for disproportionation

$$\Phi_{(-\mathrm{BP})} = \frac{k_a[\mathrm{PVA}]}{k_0 + k_a[\mathrm{PVA}]}\,\frac{k_r}{K_r + k_b} = f_a k_r/(k_r + k_b) \quad (15)$$

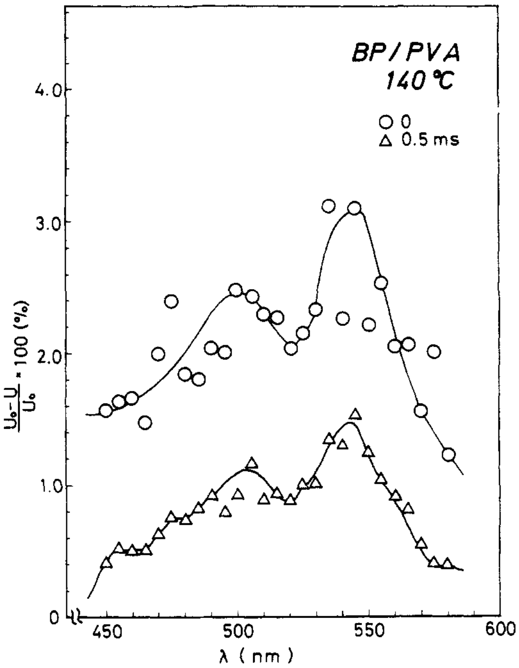

Figure 8. Transient spectra for benzophenone ketyl radical in poly(vinyl alcohol).

inside the cage and k_r is the rate coefficient for escape from the cage resulting in the irreversible reaction product. The reaction scheme is summarized in Figure 6.

Transient Measurements of Benzophenone Ketyl Radicals. Transient spectra and decay lifetime were measured for poly(vinyl alcohol) film containing benzophenone after 337-nm laser pulse irradiation. The transient absorption at 545 nm observed from −120 to +30 °C showed the same decay profile and lifetime as the phosphorescence decay at the same temperature, and so it was attributed to the triplet–triplet absorption of ^{3}BP*. A new transient absorption at 545 nm appeared in the millisecond region for $T > T_g$ (Figure 7). The transient spectrum of this absorption, shown in Figure 8 has peaks at 500 and 545 nm and has been assigned to benzophenone ketyl radical.[16] The concentration of this absorbed species increases with increasing temperature, and its lifetime decreases from 18 ms at 120 °C to 10 ms at 140 °C to 3.0 ms at 160 °C. Thus, the observed absorption at $T > T_g$ is supposed to be due to the benzophenone ketyl radical escaping from the cage in the matrix. The ketyl radical inside the cage for $T > T_g$ could not be observed in the present experiments probably due to its very rapid decay by the backward disproportionation reaction inside the cage.

In conclusion, the phosphorescence decay of benzophenone in poly(vinyl alcohol) shows deviation from a single-exponential type for the temperature range $T_\gamma < T < T_g$ and is attributed to diffusion-controlled hydrogen abstraction by benzophenone triplet from the poly(vinyl alcohol) matrix. Measurements of quantum yield for benzophenone disappearance under continous irradiation as well as transient absorption revealed the existence of a predominant backward disproportionation reaction of ketyl radicals inside the cage of the matrix.

Acknowledgment. This work was supported in part by a Grant-in-Aid on Special Project Research for "Organic Thin Films for Information Conversion" from the Ministry of Education of Japan.

Registry No. BP, 119-61-9; PVA, 9002-89-5.

References and Notes

(1) Horie, K.; Mita, I. *Chem. Phys. Lett.* **1982**, *93*, 61.
(2) Horie, K.; Morishita, K.; Mita, I. *Macromolecules* **1984**, *17*, 1746.
(3) Horie, K.; Mita, I. *Eur. Polym. J.* **1984**, *20*, 1037.
(4) Horie, K.; Tsukamoto, M.; Morishita, K.; Mita, I. *Polym. J.* (Tokyo) **1985**, *17*, 517.
(5) Horie, K.; Tsukamoto, M.; Mita, I. *Eur. Polym. J.* **1985**, *21*, 805.
(6) Horie, K.; Hirao, K.; Mita, I.; Takubo, Y.; Okamoto, T.; Washio, M.; Tagawa, S.; Tabata, Y. *Chem. Phys. Lett.* **1985**, *119*, 499.
(7) Salmassi, A.; Schnabel, W. *Polym. Photochem.* **1984**, *5*, 215.
(8) Fraser, I. M.; MacCallum, J. R.; Moran, K. T. *Eur. Polym. J.* **1984**, *20*, 425.
(9) Horie, K.; Ando, H.; Morishita, K.; Mita, I. *J. Photogr. Soc. Jpn.* **1984**, *47*, 345.
(10) Burland, D. M.; Haarer, D. *IBM J. Res. Dev.* **1979**, *23*, 534.
(11) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; p 119.
(12) Turro, N. J. *Modern Molecular Photochemistry*; W. A. Benjamin: Menlo Park, CA, 1978; p 237.
(13) Brauchle, D.; Burland, D. M.; Bjorklund, G. C. *J. Phys. Chem.* **1981**, *85*, 123.
(14) Dedinas, J. *J. Phys. Chem.* **1971**, *75*, 181.
(15) Mita, I.; Takagi, T.; Horie, K.; Shindo, Y. *Macromolecules* **1984**, *17*, 2256.
(16) Buettner, A. V.; Dedinas, J. *J. Phys. Chem.* **1971**, *75*, 187.

Conformational Control of Benzylic Radical Bromination in Polymers from Methylstyrenes

Dario Pini, Roberta Settambolo, Andrea Raffaelli, and Piero Salvadori*

Centro di Studio CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, 56100 Pisa, Italy.

Received February 26, 1986

ABSTRACT: Atactic and isotactic poly(3,4-dimethylstyrenes) (poly(3,4-DMSt)) have been subjected to benzylic radical bromination using either the *N*-bromosuccinimide–benzoyl peroxide (NBS–BPO) or the Br_2–K_2CO_3–light systems. Brominated and unbrominated polymers were studied by ^{13}C NMR spectroscopy. A remarkable difference in the chemical reactivity of the methyl groups in positions 3 and 4 of the benzene ring between atactic poly(3,4-DMSt) and isotactic poly(3,4-DMSt) was observed. These results suggest a conformational control of the polymer main chain on the chemical reactivity of the two methyl groups on the benzene ring toward the bromine substitution reaction.

Introduction

In order to prepare a macromolecular ligand having a diphosphino group system anchored to a stereoregular polymeric matrix and to study the influence of an ordered macromolecular structure on the selectivity in reactions catalyzed by transition-metal complexes bound to the