Polymer Effect on the Photochemical Reaction of Benzophenone with Tetrahydrofuran and with Diphenylamine in Benzene

Mikiharu KAMACHI, Yoshio KIKUTA, and Shun-ichi NOZAKURA

*Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan.*

ABSTRACT: The rate constant of hydrogen abstraction by the n, π^* triplet state of poly(4-vinylbenzophenone) (PVBP) from tetrahydrofuran was compared with that of benzophenone (BP) in benzene solution at 25°C, the former being about twice as large as the latter.   The electronic behavior of the triplet BP group in the polymer was investigated by T—T absorption and phosphorescence, being the same as that of BP.   A well-resolved ESR spectrum of the diphenylamino radical was detected upon UV irradiation of a benzene solution of PVBP and diphenylamine (DPA) and its concentration was compared with that of the poly(vinylbenzophenone-*co*-methyl methacrylate)—DPA or BP—DPA system.   The concentration decreased in the order: PVBP>copolymer>BP.   The polymer effect on the rate constant and the radical formation was explained in terms of the increase in the reaction efficiency on account of energy migration along the side chain of the polymer.
    KEY WORDS   Polymer Effect / Poly(4-vinylbenzophenone) / Hydrogen Abstraction / Triplet State / Lifetime / Laser Photolysis / Phosphorescence / ESR Study / Diphenylamino Radical /

The polymer molecule which has chromophores within its side chain can be thought of as a one-dimensional crystal where photoexcited energy migrates randomly along the chain.[1-8]   If the distance between the chromophores is close enough for photoexcited energy to migrate the polymeric photosensitizer is expected to be more effective than a monomeric one because of the rapid energy migration through the chromophores attached to the polymer chain.   Although several attempts have been made to use polymer sensitizers for isomerization reaction, no remarkable advantage of polymer has been obtained yet.[5,9-11]   We found that poly(4-vinylbenzophenone) (PVBP) was a more effective photosensitizer than benzophenone (BP) in the hydrogen abstraction reaction from tetrahydrofuran (THF) and in the polymerization of methyl methacrylate (MMA) by the THF radical thus obtained.[12]   In this report, the polymer effect on the rate constant for the abstraction is shown.   Mention will also be made regarding the polymer effect on the hydrogen abstraction reaction of triplet BP from diphenyl-amine.

EXPERIMENTAL

Materials

4-Vinylbenzophenone was prepared from the reaction of ethylmagnesium chloride and benzonitrile in THF.[13]   The crude monomer was purified by repeated recrystallization from ligroin.   Yield was 68%, mp 50—50.5°C.[13] (lit. 50.5°C).

BP was purified by recrystallization from petroleum ether followed by repeated sublimation, mp 49.5°C.

MMA was washed with an aqueous 5-% NaOH solution and water, dried over $CaCl_2$ and distilled through a Vigreux column under reduced pressure. THF and 2-methyltetrahydrofuran were refluxed with $LiAlH_4$, distilled through a Vigreux column, dried over sodium wire and distilled again.

Naphthalene was purified by recrystallization from methanol followed by repeated sublimation. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol.   Benzene was purified

by usual procedure.[14] Diphenylamine was recrystallized from H_2O–ethanol.

Polymerization

Polymerization of 4-vinylbenzophenone and its copolymerization with MMA were carried out using AIBN at 60°C in benzene solutions. The polymer was precipitated with methanol and purified by the reprecipitation from the benzene solution with methanol. The content of 4-vinylbenzophenone in the copolymers was determined by optical density at 342 nm of the UV spectrum.

Laser Photolysis

The laser photolysis was carried out using a Ruby laser with an output of *ca.* 1.5 J.[15] All samples were dissolved in benzene and were adjusted to such concentrations thta the optical density was 0.5—0.8 and were prepared in a vacuum at less than 10^{-5} mmHg. The transient species generated by exciting in the n, π^* band of BP with 347-nm laser pulse was monitored by a Xe lamp. The 100-% transmission line was corrected by the blank test.
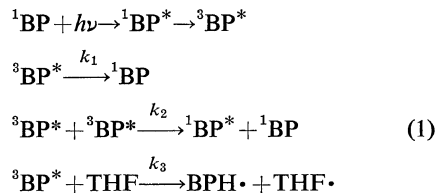
Measurement

The phosphorescence spectra were obtained at -196°C by a Shimadzu RF-502 spectroflurophotometer with a phosphorescence attachment in MTHF. Samples were prepared in duplicate in 5-mm pyrex tubes using solutions of 2.4×10^{-3} M as BP unit and were degassed by three freeze-pump-thaw cycles at less than 10^{-5} mmHg. Relative fluorescence yields were determined from the peak height. UV spectra were determined in THF on a Hitachi-124 spectrophotometer. ^{1}H NMR spectra were recorded on a Varian HL-100 spectrometer. The viscosity of the polymer was measured by an Ostwald viscometer at 30°C. ESR measurements were made by using a Japan Electron Optics Modes JES-FE3X ESR spectrometer with 100 kc/s modulations.

RESULTS AND DISCUSSION

It is well known that an n, π^* triplet BP abstracts a hydrogen atom from tetrahydrofuran.[16,17] The sequence of photophysical processes and photochemical reactions of the BP group is given in Scheme 1, where BPH· is the corresponding benzhydrol radical.

$$^1BP + h\nu \rightarrow {}^1BP^* \rightarrow {}^3BP^*$$

$$^3BP^* \xrightarrow{k_1} {}^1BP$$

$$^3BP^* + {}^3BP^* \xrightarrow{k_2} {}^1BP^* + {}^1BP \qquad (1)$$

$$^3BP^* + THF \xrightarrow{k_3} BPH\cdot + THF\cdot$$

The transient spectra obtained from PVBP just after laser photolysis have an absorption at around 535 nm, the position being consistent with the triplet—triplet absorption of BP.[18] (Figure 1). Thus, the transient species was assigned to the n, π^* triplet state of the BP unit of the polymer. The rise and decay curve at 535 nm was observed, following, apparently, first order kinetics (Figure 2). The lifetimes of the transient
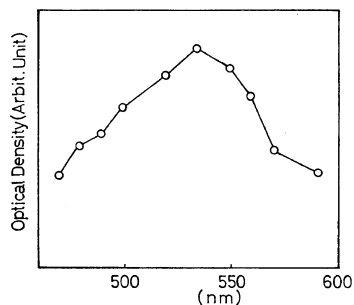

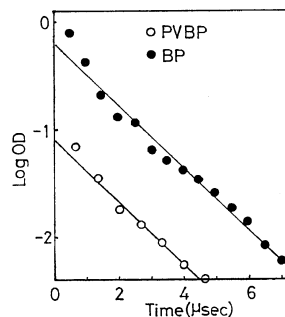**Figure 1.** Transient absorption spectrum observed immediately after the flash in a benzene solution of PVBP; [PVBP]=5.0×10^{-3} base mol/l.

Figure 2. First-order plot of optical density of T—T absorption of PVBP and BP (535 nm); [PVBP]= 5.0×10^{-3} base mol/l and [BP]=5.0×10^{-3} mol/l in benzene.

Table I. Dependence of lifetimes of the triplet PVBP and the triplet BP on the concentration of THF in benzene at room temperature[a]

THF, M	τ_{PVBP}, μs	τ_{BP}, μs
0	2.27	3.57
0.1	0.92	1.12
0.3	0.33	0.82
0.6	0.28	0.46

[a] [PBVP]$=5.0 \times 10^{-3}$ base mol/l; [BP]$=5.0 \times 10^{-3}$ mol/l; transient absorption for the lifetime, 535 nm.

Table II. Values of the rate constant k_3 of the hydrogen abstraction from THF at room temperature[a]

| Sensitizer	$k_3 \times 10^{-6}$, $M^{-1} s^{-1}$
BP	3 ± 1
PVBP	7 ± 2

[a] Solvent, benzene.

species in several THF concentrations were estimated by the first order kinetics as shown in Table I. The fact that the lifetime of the triplet BP is larger than that of the triplet BP unit in the polymer might be ascribed to the intramolecular hydrogen abstraction in the polymer chain.

The k_3 values were obtained from a plot of reciprocal lifetime of triplet state versus concentrations of THF by eq 2 (Figure 3 and Table II)

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_3 [\text{THF}] \qquad (2)$$

where τ is the lifetime of the triplet BP unit in the presence of THF and τ_0 that in absence of THF. The k_3 value for the triplet BP is in accordance with that determined by Kuhlman and Schnabel
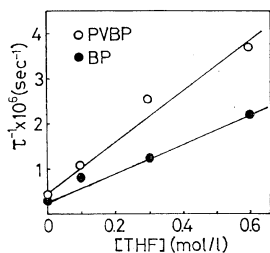
Figure 3. Reciprocal lifetime of triplet BP or BP unit in polymer *vs.* the concentration of THF in benzene solutions.

$(k_3 = 3 \times 10^6 \ M^{-1} s^{-1})$.[19] The k_3 value for PVBP is twice as large as that for BP.

In order to investigate the nature of the n, π^* triplet state of PVBP, the phosphorescence of PVBP and BP was recorded at $-196°C$ in a 2-methyltetrahydrofuran solution (Figure 4). The phosphorescence as well as the T—T absorption of PVBP are the same as those of BP. Accordingly, the rate of the hydrogen abstraction (k_3) of PVBP does not seem to be larger than that for BP because of the steric effect of the polymer chain on the reaction and/or difficulty of the diffusion of the substrate in polymer. However, the fact that the k_3 value for PVBP is larger than that for BP suggests the following possibilities: 1. The local concentration of THF near the polymer chain. 2. The increase in the effective collision radius through energy migration along the chain. In order to investigate the possibility of the latter, relative phosphorescence yields were determined as a function of the concentration of naphthalene which was a quencher for triplet
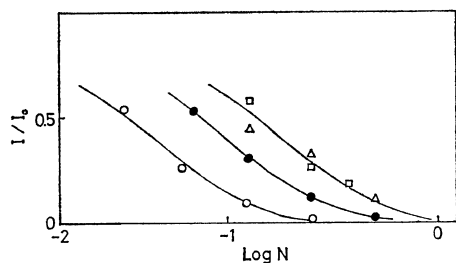
Table III. Values of critical transfer distance (R_0) for various sensitizers

Sensitizer	R_0, Å	$[\eta]$[a]
PVBP	19.7	0.38
Copolymer-1 (BP: MMA$=0.43$: 1)	15.1	0.44
Copolymer-2 (BP: MMA$=0.10$: 1)	12.3	0.62
BP	12.4	—

[a] Benzene, 30°C.
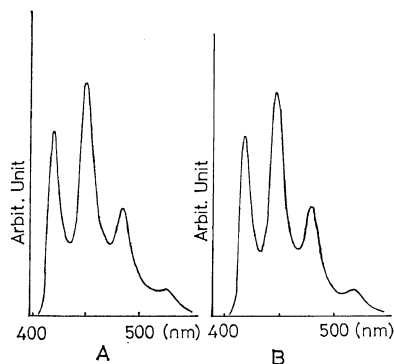
Figure 4. Phosphorescence spectra of PVBP and BP in MTHF at $-196°C$. Excitation at 366 nm: A, [BP]$=2.4 \times 10^{-3}$ mol/l; B, [PBVP]$=2.4 \times 10^{-3}$ base mol/l.

Figure 5. Transfer efficiency of benzophenone to naphthalene as a function of naphthalene concentration (N): ———, theoretical curve according to Hirayama's theory; [BP unit]$=2.4\times10^{-3}$ mol/l; ○, PVBP; ●, copolymer 1; △, copolymer 2; □, BP.

benzophenone (Figure 5). From this figure, the efficiency of the energy transfer was estimated as a critical transfer distance by using Hirayama's theory[20] (Table III). The migration distance is considerably enhanced in the PVBP, indicating that energy migration is more liable to occur in PVBP than in poly(benzophenone-*co*-methyl methacrylate) and BP.

If the energy migration through the chromophore of the side chain is important in the efficiency of the reaction, PVBP will also be effective in other hydrogen abstractions. It is well known that the diphenylamino radical is formed at room temperature by the reaction of triplet BP with diphenylamine.[21] So, an ESR study of the reaction was carried out in a benzene solution of PVBP, (BP—MMA)copolymers or BP. The same spectra were observed in all systems except for their intensity, being assigned to the diphenylamino radical[21] (Figure 6). The concentration of the radical became stationary in 2 min after irradiation. The stationary concentration of diphenylamino radical depends on both the rate of its formation and that of its decay which is caused by radical reactions.[21] The decay rate of the radical in the reactions is considered to be diffusion-controlled, being likely to decrease by increasing the viscosity in the reaction system.[22,23] When the copolymer systems have the same concentration of BP unit as PVBP system, the viscosity of the former ones is larger than that of the latter one. Therefore, if the formation rate of the radical is the same in all systems, the stationary concentration of the radical in copolymerization system would be larger than that of PVBP. This is not the case, since the stationery concentration of the radical
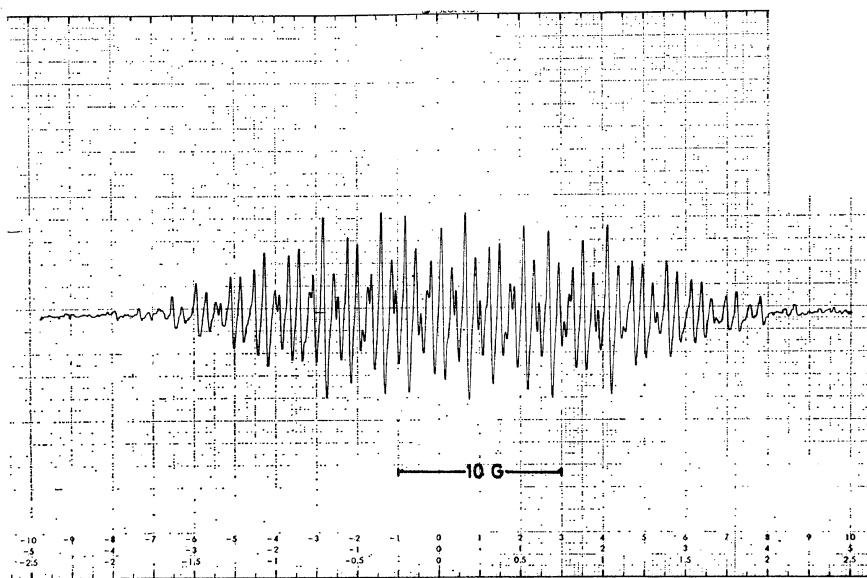
Figure 6. ESR spectrum of the radical obtained by 365-nm irradiation of benzene solution of PVBP and DPA; [PVBP]$=1.0\times10^{-2}$ base mol/l; [DPA]$=3.3\times10^{-2}$ mol/l. Irradiation source was a 500-W high pressure mercury lamp (Filter, Toshiba UV-1C).

Table IV. Stationary concentration of diphenyl-amino radical (DPA) in the reaction of PVBP or BP with DPA in benzene[a]

Sensitizer	[DPA] $\times 10^{18}$, spin	[DPA] $\times 10^{6}$, M
PVBP	33.0	1.0
Copolymer-1	17.0	0.5
Copolymer-2	9.0	0.3
BP	7.0	0.2

[a] [BP unit]$=1.0\times10^{-2}$ M; [DPA]$=3.34\times10^{-2}$ M.

is in the order: PVBP > copolymer-1 > copolymer-2 $\approx$ BP (Table IV). The decrease of the radical concentration in copolymer systems might be caused by MMA units in the polymer chain. The concentration of diphenylamino radical in the reaction of ^{3}BP with DPA in benzene was compared with that in the presence of PMMA. The presence of PMMA $(2.0\times10^{-2}$ base mol/l) increased a little the stationary concentration. Thus, the presence of MMA unit in copolymer is not considered to decrease the concentration. The experimental fact that the stationary concentration of the radical increased with the sequence length of BP in the polymer chain seems to support that energy migration along the BP unit in the polymer is an important factor for the reaction efficiency.

Table V. [η] and Huggins constant (k') of PVBP in benzene and THF at 30°C

	[η]	k'
Benzene	0.38	0.34
THF	0.39	0.34

The increase of the local concentration of THF near polymer chain might be contained in the polymer effect. However, since intrinsic viscosity and Huggins constant of PVBP in benzene solution were almost the same as those in THF solution (Table V), THF is not considered to interact predominantly with PVBP in its benzene solution. Therefore, the polymer effect cannot be explained by the local concentration of THF near the polymer.

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