where L_D = the number of chromophores in the exciton diffusion length, $\bar{r}^2$ = the average of the square of the chromophore separation, and ω = the reciprocal of the average exciton transfer time between chromophores. Once the average polymer length exceeds L_D there should be no further effect of molecular weight. Since our quenching results and previous spectroscopic observations[8] tend to "saturate" for a degree of polymerization of approximately 650–700 and $\tau_T = 2$ s, the value of L_D = 650–700 implies a τ_{trans} of approximately 5×10^{-6} s, much faster than estimated from the quenching formula discussed above (see Table I), but still five to six orders of magnitude smaller than for molecular crystals. Obviously a more direct method for determining triplet exciton transfer rates than quenching experiments is highly desirable.

Our proposed interpretation of our observations is not the only possibility. For example, one could suppose that the rate of triplet exciton transfer systematically increases with higher molecular weight because of some steric effect. Possibly the lower density of a higher molecular weight polymer coil in a 77 K matrix allows an increased number of contacts with quencher molecules per unit length of the polymer chains. The primary reason we propose the above interpretation in terms of an exciton diffusion length is that it seems to be consistent with the molecular weight dependence of triplet–triplet annihilation processes in P2VN.[8] One clear implication of our experimental results is that if triplet excitons were to be exploited to sensitize a photochemical process in matrices then a higher molecular weight polymer would be expected to be more effective. Experiments are planned for the future to study the molecular weight dependence for triplet exciton quenching in fluid solution.

One further observation we have made is quite puzzling. After a period of months samples containing piperylene developed a new "impurity" delayed emission around 400 nm; this impurity did not appear in the unquenched samples. Furthermore the intensity of this impurity emission was much stronger in the solutions containing high molecular weight polymer. These samples were stored in subdued light at room temperature. At present we do not know the origin of this new emission feature.

Acknowledgments. This research was supported by the Robert A. Welch Foundation, whose aid is gratefully acknowledged.

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(9) In ref 4 it was found that the quenching of the DF could be fit to a Perrin model and the phosphorescence to Stern–Volmer kinetics.

(10) Equation 2 is valid for three-dimensional diffusion. Presuming that one-dimensional diffusion is more appropriate to this problem, the relation should be $\omega = 2\lambda/\bar{r}^2$ (see S. Chandrasekhar, *Rev. Mod. Phys.*, **15**, 1 (1943)). We use eq 2 to allow a direct comparison to the values obtained by David et al. (ref 3) and Somersall and Guillet (ref 4).

(11) If the decay of DF were exponential the τ_{DF} would be the lifetime of DF. Since the decay we observe is generally not exponential, τ_{DF} is a relative measure of the extent of signal decay during the 2.4-ms observation time.

(12) This argument can be illustrated by an example. If we compare two polymers of length L and $2L$ the probability of doubly exciting the latter is twice as great as the former. However, for those polymers of length L that do happen to be doubly excited, the average exciton separation is half that of the polymer of length $2L$. A manuscript dealing with exciton densities in one-dimensional lattices is in preparation.

(13) This argument is like the Perrin model: A quenched molecule is quenched so quickly that its lifetime becomes essentially zero; however, the luminescence decays at the rate of an unquenched molecule because those molecules that are quenched make essentially no contribution to the luminescence. Hence for this model a quenching of intensity is possible without changing the luminescence decay rate.

Photo- and Radiation-Induced Degradation of Vinyl Polymers in Solution. 2. Photosensitized Degradation of Poly-α-methylstyrene by Benzophenone

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ABSTRACT: The photosensitized degradation of poly-α-methylstyrene (PMSt) by benzophenone (BP) was studied at 30 °C in benzene solution using 366-nm light. Random scission of the polymer chain was confirmed by GPC measurements. The quantum yield for main-chain scission (ϕ_s) was found to be independent of incident light intensity and greater than that of direct photolysis. On adding a small amount of a triplet quencher (naphthalene), ϕ_s decreased with increasing added quencher concentration. The degradation was found to be initiated by hydrogen abstraction from PMSt main chain by excited triplet BP and the rate constant of this reaction was estimated to be 9×10^3 M^{-1} s^{-1} on the basis of kinetical treatment. The effect of oxygen on the degradation was also discussed.

Extensive studies on photodegradation of polystyrene have been made by many workers.[2] However, little attention has been paid to poly-α-methylstyrene which is well known as a typical degradation-type polymer.

Fox et al. first investigated the photodegradation of PMSt by 253.7-nm light and reported the quantum yield for main-chain scission.[3,4] Their observed values in inert solvents were fairly low compared with those of ketone polymers, e.g., poly(phenyl vinyl ketone),[5] though PMSt itself is a strong absorber of light at the irradiated wavelength.

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They observed the accelerating effect of chlorine-containing compounds such as carbon tetrachloride and chloroform on the degradation. The promoting effect of these compounds has been long known in radiolysis of poly(methyl methacrylate) in solution by γ-ray irradiation.[6] These findings seem to suggest that reactive species formed from such compounds take a large part in main-chain scission of the polymers.

From this viewpoint, we have studied the degradation of PMSt in an inert solvent by using benzophenone as a photosensitizer.[7] Under these conditions the polymer and solvent are transparent and the photoexcited sensitizer is an only chemically active species.

In this paper we wish to report (1) kinetical treatment of BP-sensitized degradation of PMSt involving estimation of the rate constant for the reaction of photoexcited BP with the polymer, (2) a comparison of quantum yields obtained in this work with that by 253.7-nm light, and (3) the effect of oxygen on the degradation of the polymer.

Experimental Section

Materials. α-Methylstyrene was washed with dilute NaOH and with distilled water. It was then dried over anhydrous potassium carbonate and distilled under reduced pressure in an atmosphere of nitrogen, only the middle fraction (bp. 55 °C (15 mmHg)) being retained. The purity of the sample was checked by gas chromatography.

Poly-α-methylstyrene (PMSt) was prepared by cationic polymerization in toluene at −78 °C by boron trifluoride diethyletherate catalyst. It was purified by repeated precipitation from benzene solution with methanol and dried under vacuum at room temperature. The number-average molecular weight of the polymer was determined to be 3.52×10^5 by osmometry.

Benzophenone (BP) was recrystallized three times from ethanol solution in subdued light, dried under vacuum, and then stored in the dark until use. Spectroscopic grade benzene was once distilled over sodium metal. Zone-refined naphthalene was used as commercially obtained.

Photoirradiation Procedures. The light source was a 500W high-pressure mercury lamp (Japan Storage Battery Co., Ltd.). A combination of glass filters, UV-35 and UV-DIA (Toshiba Kasei Ltd.), was employed in order to isolate 366-nm light and a filter solution of potassium chromate was used to obtain 313-nm light.[8] Wire screens were used to vary the incident light intensity.

The irradiation apparatus used for the determination of quantum yields was the same as described previously,[9] that is, consisting of a capillary viscometer and a cylindrical quartz cell of 5-cm diameter and 1.0-cm light path length. The samples were degassed by several freeze–thaw cycles under high vacuum and then sealed off (ca. 1×10^{-5} mmHg). All photoirradiations were carried out in a thermostat maintained at 30 ± 0.2 °C.

When a large amount of irradiated samples were required, an immersion-type photochemical apparatus was used. In this case, 200 mL of the polymer solution containing a definite amount of BP was irradiated through a potassium chromate solution under bubbling of dry nitrogen. The temperature of the solution was kept at 30 ± 3 °C by a cooling jacket during irradiation. After irradiation, the solution was poured into a large excess of methanol and the precipitated polymer was recovered.

Molecular Weight. The progress of the degradation was mainly followed by viscometry. Viscosity measurements were carried out in a thermostat maintained at 30 ± 0.1 °C. Single-point viscosities measured in the irradiation apparatus were converted to intrinsic viscosities through a modification of the Huggins equation:[10,11]

$$[\eta] = (2^{1/2}/C)(\eta_{\mathrm{sp}} - \ln \eta_{\mathrm{rel}})^{1/2} \tag{1}$$

where C is the polymer concentration in grams per deciliter. Intrinsic viscosities thus obtained agreed within the experimental error with those determined by the dilution method. The molecular weight was calculated from the equation[12]

$$[\eta] = 2.49 \times 10^{-4} M_{\mathrm{v}}^{0.647} \tag{2}$$

Number-average molecular weights were determined in toluene solution by using a Hewlett Packard Model 503 high-speed membrane osmometer operating at 37 °C. Additional determinations were made of both the molecular weights and molecular weight distributions using a Toyosoda Model 801A gel-permeation chromatograph calibrated with poly-α-methylstyrene standards in tetrahydrofuran solution.

Actinometry and Quantum Yield. Actinometry was carried out by the ferrioxalate method[13,14] before and after each exposure and the average value was taken as an incident light intensity. In every case, the deviation of each value from the mean value was less than 2% and the good reproducibility of the values of light intensity was observed. The amount of light actually absorbed by BP was determined from the incident light intensity thus measured and the transmitted light intensity measured by a spectrophotometer, being corrected for the absorption of the solvent.

The change of the absorption spectrum of the sample solution was found to be negligible at the irradiated wavelength, i.e., 366 nm, during irradiation and therefore it was confirmed that the amount of quanta absorbed is proportional to the irradiation time.

The quantum yield for the main-chain scission is given by the following equation:[15]

$$\phi_{\mathrm{s}} = \frac{C}{(M_{\mathrm{n}})_0} \frac{\mathrm{d}[(M_{\mathrm{n}})_0/(M_{\mathrm{n}})_t - 1]}{\mathrm{d}(It)} \tag{3}$$

where ϕ_{s} is the quantum yield, which is the number of scissions occurring per quantum absorbed; $(M_{\mathrm{n}})_0$ is the initial number-average molecular weight; $(M_{\mathrm{n}})_t$ is the molecular weight at irradiation time t; I is the intensity of light absorbed by BP; the quantity $[(M_{\mathrm{n}})_0/(M_{\mathrm{n}})_t - 1]$ is the number of scissions per original polymer molecule; and C is the concentration of the polymer.

Ultraviolet spectra were measured with a Shimazu Model MPS-50L spectrophotometer and emission spectra were recorded using a Shimazu RF-501 spectrofluorometer at room temperature.

Except where specified, the polymer concentrations are expressed as moles per liter based on the monomer unit, and therefore all rate constants determined concerning the polymer are based on the monomer unit.

Results and Discussion

Mode of Degradation. Figure 1 shows results of GPC of the original and degraded polymers. Although the peak was shifted to the low molecular weight region after irradiation, the polydispersity indices were estimated to be 2.4, 2.3, and 2.3 for the original polymer and those irradiated for 30 and 300 min, respectively. In other words, the polydispersity of the polymer remains unchanged and retains a most probable distribution approximately throughout the course of degradation. This fact indicates that random scission of the polymer chain occurs in the present system.

Determination of the molecular weights was mainly done by viscometry. When molecular weight is determined by the viscosity method, viscosity-average molecular weight (M_{v}) is obtained and is usually different from number-average molecular weight (M_{n}) except for a monodisperse polymer. To estimate the number of chain scissions, M_{n} is necessary as indicated in eq 3. However, the polymer seems to have a most probable distribution before and after degradation in the

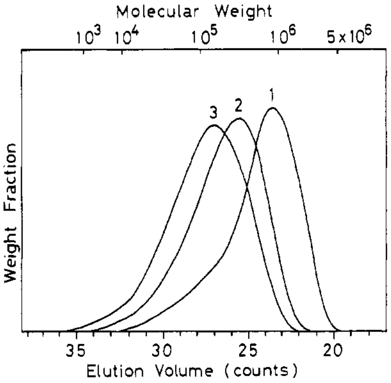


Figure 1. Gel-permeation chromatograms of original PMSt and degraded polymer: (1) before irradiation; (2) after 30 min of irradiation; (3) after 300 min of irradiation.

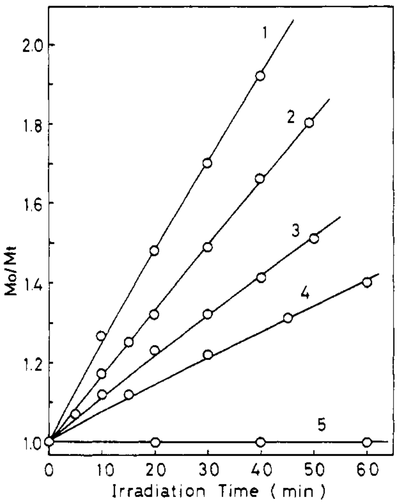


Figure 2. Photosensitized degradation of PMSt by BP under vacuum at various light intensities: (1) 1.56×10^{-4}, (2) 1.01×10^{-4}, (3) 6.78×10^{-5}, (4) 4.37×10^{-5} einstein/L min, (5) in the dark. [PMSt] = 4.2×10^{-2} M; [BP] = 5.1×10^{-3} M.

Table I
Quantum Yield for Main-Chain Scission of PMSt by BP at Various Light Intensities[a]

$I_0 \times 10^5$, einstein/L min	$\phi_s \times 10^3$
4.37	4.3
6.78	4.2
10.1	4.4
15.6	4.4

[a] [PMSt] = 4.2×10^{-2} M; [BP] = 5.1×10^{-3} M.

Table II
Quantum Yield for Main-Chain Scission of PMSt by BP at Various PMSt Concentrations[a]

[PH] $\times 10^2$, M	$\phi_s \times 10^3$
2.64	2.6
3.26	3.0
4.09	4.2
5.01	4.5
6.71	6.6

[a] [BP] = 4.9×10^{-3} M.

present system, and therefore we can assume that the ratio $(M_n)_0/(M_n)_t$ is equal to the ratio $(M_v)_0/(M_v)_t$. This was also confirmed by osmometry.

Light Intensity and Polymer Concentration. Figure 2 shows typical curves for the change in molecular weight of the polymer at various incident light intensities, where M_0/M_t is the ratio of number-average molecular weights before and after irradiation. Chain scission takes place rapidly with increasing light intensity while no degradation occurs in the dark. The polymer and solvent are transparent at 366 nm, and no degradation was observed in the absence of BP for over 300 min of irradiation under vacuum even at the highest light intensity shown in Figure 2. These findings indicate that the degradation of PMSt is initiated by photoexcited BP.

The values of ϕ_s determined at various light intensities are given in Table I. ϕ_s is independent of incident light intensity under these experimental conditions.

Table II shows the variation of ϕ_s with the polymer concentration. ϕ_s increases with increasing polymer concentration over the whole experimental range of polymer concentrations as shown in the table.

Comparison of Quantum Yield for Chain Scission. Fox et al. have reported the photodegradation of PMSt in various solvents by 253.7-nm light.[3] Their system is so-called "direct photolysis", since at the irradiated wavelength the polymer itself shows a strong absorption and the degradation occurs at the excited site of the polymer chain. The quantum yields reported in chlorine-containing solvents such as carbon tetrachloride and chloroform are fairly large compared with that in dioxane. They suggested that reactive solvent radicals produced by light attack the polymer and cause the degradation. On the other hand, dioxane seems to be an inert solvent even if it absorbs a small portion of the incident light. ϕ_s in dioxane is about 5×10^{-4} at the polymer concentration of 1 g/dL. In the present system, ϕ_s is dependent on the polymer concentration and at the highest concentration performed (0.79 g/dL) ϕ_s was 6.6×10^{-3} as given in Table II. This value is about ten times as large as that of direct photolysis in dioxane. It has been clarified that BP is an effective photosensitizer in the degradation of PMSt.

Kinetics. BP which is well-known to be a typical sensitizer in photochemical reactions shows an absorption band in the 310–380 nm region corresponding to an n–π* transition. Many works on this familiar entity have revealed that photoexcited BP reacts with substrates in three different ways: (a) hydrogen abstraction, (b) triplet–triplet energy transfer, and (c) cycloaddition to olefines followed by the formation of oxetane.[16] In these reactions, the triplet state of BP (^{3}BP*) is the chemically active species. ^{3}BP* is also dissipated by first-order processes, such as emission of phosphorescence (eq 6) and radiationless conversion (eq 7). The lifetime of ^{3}BP* has been measured by several authors taking advantage of flash photolysis[17–20] and single photon counting technique.[21] In benzene solution, the lifetime has been estimated to be 1.0×10^{-5} s at room temperature.[22]

The compounds with lower triplet energies than that of BP (68.6 kcal/mol in nonpolar solvents such as benzene[14]) act as energy acceptors in reaction b. Although the triplet energy of PMSt is uncertain, it is undoubtedly higher than that of BP since the compounds with a similar structure to PMSt have much higher triplet energies: toluene has 82.8 kcal/mol and benzene has 84.7 kcal/mol in nonpolar solvents.[14] It is unlikely, therefore, that the degradation of PMSt proceeds via reaction b. The degradation of PMSt is also unlikely to occur through reaction c because PMSt has no "reactive" multiple bonds in its polymer chain.

For hydrogen abstraction by ^{3}BP*, the following scheme has been established:[16]

$$\mathrm{BP} \xrightarrow{h\nu} {}^1\mathrm{BP}^* \rightarrow {}^3\mathrm{BP}^* \qquad (4)$$

$$^3\mathrm{BP}^* + \mathrm{PH} \rightarrow \mathrm{BPH}\cdot + \mathrm{P}\cdot \qquad k_r \qquad (5)$$

$$^3\mathrm{BP}^* \rightarrow \mathrm{BP} + h\nu_p \qquad k_p \qquad (6)$$

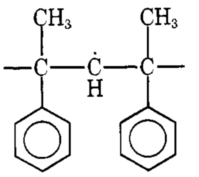
$$^3\mathrm{BP}^* \rightarrow \mathrm{BP} \qquad k_d \qquad (7)$$

$$^3\mathrm{BP}^* + \mathrm{Q} \rightarrow \mathrm{BP} + {}^3\mathrm{Q}^* \qquad k_q \qquad (8)$$

where PH denotes a hydrogen donor and BPH· is a ketyl radical ($\mathrm{Ph_2\dot{C}OH}$). Equation 6 represents the emission of phosphorescence, eq 7 the radiationless conversion, and eq 8 the quenching process when a suitable quencher is present in the system.

In the BP-sensitized degradation of PMSt, the ketyl radical has been detected by flash photolysis experiments[7] and a hydrogen-abstracted polymer radical has also been observed by ESR measurements using the spin trapping technique.[23]

The polymer radical trapped was assigned to that with the following structure:



The chain scission of the polymer would then occur through β scission of the polymer radical in a similar manner to the well-known fragmentation of smaller radicals.

$$\mathrm{P}\cdot \rightarrow \mathrm{P}_m\cdot + \mathrm{P}_n \tag{9}$$

Assuming that the chain scission occurs only in eq 5 (followed by eq 9) and other side reactions are negligible, the following equations can be derived under steady-state conditions of irradiation:[16,24]

$$\frac{1}{\phi_s} = 1 + \frac{1}{\tau}\frac{1}{k_r[\mathrm{PH}]} \tag{10}$$

when a quencher is present,

$$\frac{1}{\phi_s} = 1 + \frac{1}{\tau}\frac{1}{k_r[\mathrm{PH}]} + \frac{k_q}{k_r[\mathrm{PH}]}[\mathrm{Q}] \tag{11}$$

where ϕ_s is the quantum yield for main-chain scission and τ is the lifetime of ^{3}BP* in benzene solution.

Using the values listed in Table II, a plot of $1/\phi_s$ vs. the reciprocal of the polymer concentration (eq 10) is shown in Figure 3. The plot is linear, though the value of intercept is uncertain. This linear relationship seems to indicate the validity of the above assumption. From the slope of the plot, we obtained 9.4×10^3 M^{-1} s^{-1} as k_r using $\tau = 1.0 \times 10^{-5}$ s.

Quenching experiments were carried out in the presence of naphthalene. Naphthalene with triplet energy of 60.9 kcal/mol[14] is one of the typical quenchers of ^{3}BP*. In order to estimate the rate constant for the reaction of ^{3}BP* with PMSt (k_r), the rate constant for triplet quenching by naphthalene in benzene solution (k_q) was determined at first by the measurement of the steady-state phosphorescence intensities of BP in the absence and presence of the quencher, $I_p(0)$ and $I_p(\mathrm{Q})$, respectively:[17]

$$I_p(0)/I_p(\mathrm{Q}) = 1 + \tau k_q[\mathrm{Q}] \tag{12}$$

where τ is the lifetime of ^{3}BP*. The plot of this Stern-Volmer equation is shown in Figure 4. From the slope of the plot, k_q for naphthalene was estimated to be 2.6×10^9 M^{-1} s^{-1}. This value is a little smaller than that obtained by Steel et al.[17,25] but greater than that reported by Bell and Linschitz.[20]

The molecular weight change of the polymer in the presence of naphthalene is shown in Figure 5. In this case, both the polymer concentration and the incident light intensity were kept constant, and the concentration of the added naphthalene was changed. The rate of chain scission decreases with increasing added naphthalene concentration. A plot of $1/\phi_s$ vs. [Q] (eq 11) is again linear as shown in Figure 6. This linear

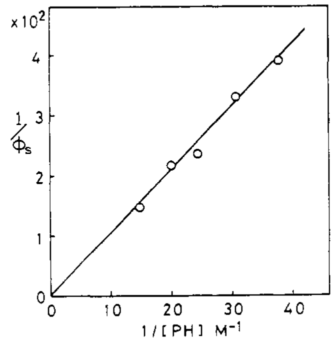


Figure 3. Effect of PMSt concentration on quantum yield for main-chain scission. [BP] = 4.9×10^{-3} M.

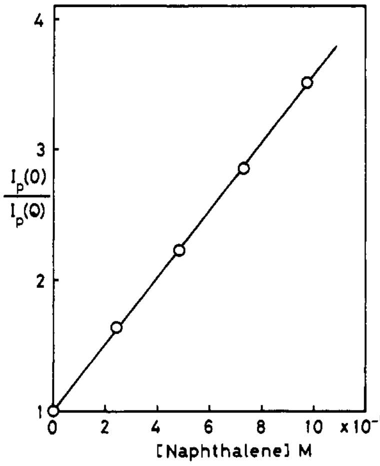


Figure 4. Stern-Volmer plots for naphthalene quenching of BP phosphorescence. [BP] = 9.7×10^{-3} M.

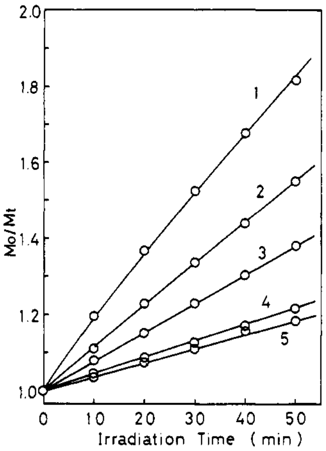


Figure 5. Photosensitized degradation of PMSt by BP in the presence of naphthalene: [naphthalene] = (1) 0, (2) 0.30×10^{-4}, (3) 0.61×10^{-4}, (4) 1.22×10^{-4}, and (5) 1.80×10^{-4} M. [PMSt] = 4.2×10^{-2} M; [BP] = 5.1×10^{-3} M.

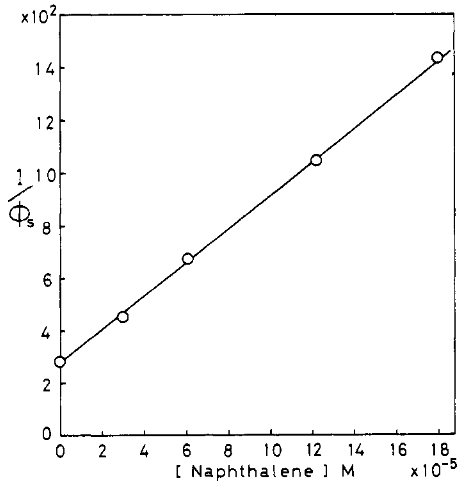


Figure 6. Stern-Volmer plots for naphthalene quenching of main-chain scission of PMSt by BP. [PMSt] = 4.2×10^{-2} M; [BP] = 5.1×10^{-3} M.

relationship of the plot also seems to indicate that the above mechanism is valid for the present system. From the slope of this plot and k_q for naphthalene, k_r was estimated to be 9.3 $\times 10^3$ M^{-1} s^{-1}. This value of k_r agrees well with that estimated from the plot of $1/\phi_s$ vs. $1/[PH]$, though these kinetical methods usually accompany fairly large errors in estimation of rate constants. From the two values obtained independently, k_r is reasonably determined to be 9×10^3 M^{-1} s^{-1} for PMSt.

Effect of Oxygen. Generally, oxygen is said to accelerate the degradation of polymers, and in the case of PMSt the promoting effect of oxygen has been observed.[3,9] In the BP-sensitized degradation, however, oxygen inhibits the main-chain scission significantly as reported previously.[7]

The oxygen molecule acts as a quencher of $^3BP^*$.[26] As oxygen quenches triplet excited acetophenone with a quenching constant of 2.4×10^9 M^{-1} s^{-1},[27] it is expected to quench $^3BP^*$ with k_q of the same order of magnitude as for acetophenone. Preliminary quenching experiments of BP phosphorescence revealed that k_q for the quenching of $^3BP^*$ by oxygen was about an order of 10^9 M^{-1} s^{-1}. Oxygen concentration in nondegassed benzene is 1.9×10^{-3} M at 25 °C,[14] and therefore the deactivation of $^3BP^*$ by oxygen proceeds with a rate ($k_q[O_2]$) of about 10^6 s^{-1} in the presence of air. On the other hand, the rate constant for the reaction of $^3BP^*$ with PMSt (k_r) is 9×10^3 M^{-1} s^{-1} as mentioned above and the polymer concentration employed in this work is around 5×10^{-2} M. Thus the rate of $^3BP^*$ disappearance by PMSt (k_r[PMSt]) is about 5×10^2 s^{-1}. Comparing k_r[PMSt] with $k_q[O_2]$, it is clear that $^3BP^*$ is consumed predominantly by the oxygen molecule and the degradation of PMSt is inhibited in the presence of air.

Singlet oxygen may arise in the course of the quenching process:

$$^3BP^* + {}^3O_2 \rightarrow BP + {}^1O_2^*$$

Recently oxidative degradation initiated by singlet oxygen has received great attention.[28] The results obtained indicate that singlet oxygen has high reactivity toward diene polymers while it is not so effective upon saturated polymers. In our experiments, no evidence has been observed that singlet oxygen thus produced attacks the polymer and causes the degradation. Singlet oxygen is presumably deactivated via the radiationless route even if formed through the quenching process.

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(24) Another assumption is required that the local concentrations of the polymer and quencher in the vicinity of $^3BP^*$ are equal to their macroscopic concentrations. In the present system, this assumption is presumably satisfied for the following two reasons: (1) Since benzene is a good solvent for PMSt, the polymer chains are expected to disperse homogeneously in solution. (2) Spectroscopic results have revealed that there are no specific interactions among the solutes in the ground state.
(25) Assuming that $\tau = 6.5 \times 10^{-6}$ s as reported by Steel et al., we obtained 4.0 $\times 10^9$ M^{-1} s^{-1} as k_q which agrees with their value.
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