Macromolecules 1984, *17*, 2256-2260

Photosensitized Degradation of Polystyrene by Benzophenone in Benzene Solution

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ABSTRACT: Photodegradation of polystyrene in benzene solution sensitized by benzophenone was studied at 60 °C by measuring the rate of benzophenone disappearance and the change in GPC curves of polystyrene during 365-nm irradiation by a high-pressure mercury lamp. Various rate constants for the initiation step were determined by quantum yield and transient lifetime measurements. The quantum yield of benzophenone photoreduction, $\Phi_{(-\mathrm{BP})}$, is 0.0086–0.0035 for [PS] = 0–0.2 unit·M and decreases with increasing polystyrene concentration [PS], showing the influence of quenching of the benzophenone triplet by polystyrene. The photodegradation of polystyrene is supposedly initiated by successive hydrogen abstractions from benzene by triplet benzophenone and from polystyrene by the phenyl radical. The ratio ρ of cross-linking probability to main-chain scission probability for a polystyrene on-chain radical is 0.04–0.13 and increases with increasing benzophenone concentration. A mechanism for the degradation step of polystyrene in solution is proposed.

Introduction

The photodegradation of polystyrene has been studied mainly in film by several researchers over a period of more than 20 years.[1,2] The ultraviolet light or γ-ray irradiation of polystyrene at room temperature results in both corss-linking and chain scission,[3] while thermal degradation of polystyrene at elevated temperatures (250–300 °C) provides main-chain scission.[4,5] This difference has been attributed to the difference in relative rates of β-scission of polystyrene on-chain radical compared to its recombination caused by the higher activation energy for the former process.[6] The investigation in solution provides the possibility of gaining insight into the detailed kinetics of polystyrene degradation, since we can distinguish the intramolecular reaction (β-scission) from the intermolecular one (recombination) by changing the polymer radical concentration.

The photoexcited triplet state of benzophenone is known to abstract hydrogen atom from a suitable hydrogen donor (RH), resulting in the formation of ketyl radical and R radical.[7-10]

$$\mathrm{Ph_2CO} \xrightarrow{h\nu} {}^1\mathrm{Ph_2CO}^* \rightarrow {}^3\mathrm{Ph_2CO}^* \xrightarrow{\mathrm{RH}} \mathrm{Ph_2\dot{C}OH} + \mathrm{R}\cdot \tag{1}$$

The photosensitized degradation of polystyrene by benzophenone in benzene at room temperature has been studied and compared with that of poly(α-methylstyrene) under the same conditions by Yamaoka et al.[11] The much slower rate of main-chain scission of polystyrene in spite of the almost same amount of ketyl radical formation was explained by the greater stability of the polystyrene on-chain radical formed by the hydrogen abstraction compared with that for poly(α-methylstyrene). In the course of the study on polymer photodegradation in solution, we have observed that the rate of benzophenone disappearance in benzene under 365-nm irradiation does not increase but decreases with the addition of polystyrene to the system, though the main-chain scission of polystyrene proceeds during the irradiation. This directed our attention to the initiation mechanism of the sensitized photodegradation of polystyrene in benzene solution.

In the present paper, we report results on the benzophenone-sensitized photodegradation of polystyrene in benzene solution at 60 °C and discuss (1) the influence of the quenching process by the phenyl group in polystyrene on the quantum yield of benzophenone photoreduction in solution, (2) the initiation mechanism consisting of successive hydrogen abstractions by triplet benzophenone from benzene and by phenyl radical from polystyrene, and (3) relative rates of the competing reactions (β-scission and recombination) of polystyrene on-chain radical in solution.

Experimental Section

Materials. Benzophenone was recrystallized twice from ethanol solution. Benzopinacol and biphenyl were also recrystallized from ethanol solution and used for calibration in GPC measurements. Standard polystyrenes with narrow molecular weight distributions ($\bar{M}_n$ = 9.6 × 10^4, 3.4 × 10^5, 4.4 × 10^5, 9.7 × 10^5; $\bar{M}_w/\bar{M}_n$ = 1.1–1.3) were purchased from Toyo Soda Co. Dotite Spectrosol grade benzene was distilled and used as a solvent for photoirradiation and transient phosphorescence measurements.

Photoirradiation Procedures. A 450-W high-pressure mercury lamp (Ushio UM-452) with a combination of two Pyrex glass cylinders and a glass filter (Toshiba UV-D36A) was used as a light source of 365 nm. The sample solution was placed in a rectangular Pyrex cell with a 1.0-cm light path length and was degassed by several freeze–pump–thaw cycles under high vacuum and then sealed off. All photoirradiations were carried out in a thermostat maintained at 60 °C. Actinometry was carried out with an International Light Type IL-411T photoresist photometer calibrated by the potassium ferrioxalate/*o*-phenanthroline system.[12] The incident intensity was about 1.2 × 10^{-8} einstein·cm^{-2}·s^{-1} in the present experiments.

GPC Measurements. The changes in benzophenone concentration and the concentration of benzopinacol and biphenyl formed in the sample solutions after the photoirradiation were measured by a Toyo Soda Type HLC-802UR gel permeation chromatograph (GPC) with a G2000H8 column and a UV (250 nm) detector. The elution volumes for these compounds in tetrahydrofuran at 40 °C with the G2000H8 column were 35.8 mL for benzophenone, 36.7 mL for biphenyl, and 30.4 mL for benzopinacol.

The changes in the molecular weight and molecular weight distribution of polystyrene after the photoirradiation were measured by the same Type HLC-802UR GPC apparatus with a GM1XH6 column and a UV (250 nm) detector in tetrahydrofuran at 40 °C.

Transient Measurements of Quenching Rate Constants. A pulsed nitrogen laser (Avco C950B) as an exciting light at 337 nm, thermostat, monochromator (Jasco CT10), photomultiplier (HTV R1464), and transient time converter (Riken-Denshi TCG 8000) were used for measuring the lifetimes of benzophenone phosphorescence in benzene and its quenching rate constants by polystyrene. The apparatuses are almost the same as those previously used for the triplet probe study of intermacromolecular reactions,[13,14] and details of the measurements have been given elsewhere.[13,15]

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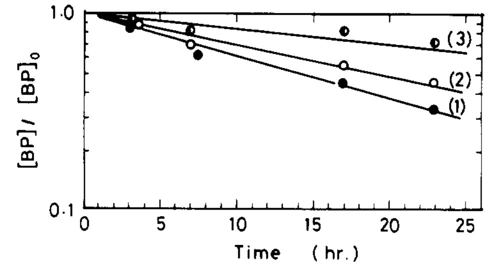


Figure 1. First-order plots of the decrease in benzophenone concentration, [BP], in benzene during 365-nm irradiation at 60 °C. [PS]: (1) 0%; (2) 0.2%; (3) 2.0%. $\bar{M}_n$ of polystyrene = 4.4 × 10^5. $[BP]_0 = 1.9 \times 10^{-3}$ M.

Mechanism of Photoinitiation Step

The disappearance of benzophenone (BP) in benzene during 365-nm irradiation at 60 °C in the absence and presence of polystyrene is shown in Figure 1. The rate of benzophenone disappearance decreases with increasing polystyrene concentration. This suggests that polystyrene (PS) acts in this system as a quencher for benzophenone triplet rather than as a hydrogen donor for it. Benzene (B) is known to act for benzophenone triplet not only as a hydrogen donor[9,16] but also as a quencher.[17]

The primary processes for the decay of benzophenone triplet ($^3BP^*$) in the present system are given in the following:

$$BP \xrightarrow{h\nu} {}^1BP^* \longrightarrow {}^3BP^* \qquad (2)$$

$$^3BP^* \xrightarrow{k_d} BP \qquad \text{deactivation} \qquad (3)$$

$$^3BP^* + B \xrightarrow{k_{qd}^B} BP + B \qquad (4)$$

$$^3BP^* + PS \xrightarrow{k_{qd}^{PS}} BP + PS \qquad (5)$$

physical quenching (4), (5)

$$^3BP^* + B \xrightarrow{k_a^B} BPH\cdot + Ph\cdot \qquad (6)$$

$$^3BP^* + PS \xrightarrow{k_a^{PS}} BPH\cdot + PS\cdot \qquad (7)$$

quenching by H abstraction (6), (7)

The rate of disappearance of benzophenone under the photostationary state is expressed by

$$-d[BP]/dt = (k_a^B[B] + k_a^{PS}[PS])[^3BP^*] = \frac{(k_a^B[B] + k_a^{PS}[PS]) \times 10^3 I_0(1 - 10^{\epsilon[BP]l})/l}{k_d + (k_a^B + k_{qd}^B)[B] + (k_a^{PS} + k_{qd}^{PS})[PS]} \cong \Phi_{(-BP)} \times 2.3 \times 10^3 I_0 \epsilon f[BP] \qquad (8)$$

where the quantum yield of benzophenone disappearance, $\Phi_{(-BP)}$, is given by

$$\Phi_{(-BP)} = \frac{k_a^B[B] + k_a^{PS}[PS]}{k_d + (k_a^B + k_{qd}^B)[B] + (k_a^{PS} + k_{qd}^{PS})[PS]} \qquad (9)$$

I_0 is the intensity of incident light in einstein·cm^{-2}·s^{-1}, ϵ is the molar extinction coefficient of benzophenone in M^{-1}·cm^{-1}, and $f = (1 - 10^{\epsilon[BP]l})/(2.3\epsilon[BP]l)$ is the correction factor for the absorbed dose with optical pass of l cm. Equation 8 can be transformed to eq 10, showing the benzophenone concentration, [BP], at time t

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

where $[BP]_0$ is the initial benzophenone concentration. The change in f during irradiation is negligible compared with the accuracy of the present experimental data, and the value of f for $[BP] = [BP]_0$ and $l = 1$ cm was used in the calculation. The values of $\Phi_{(-BP)}$ calculated from the slopes in Figure 1 with eq 10 are summarized in Table I. The quantum yields for the formation of benzopinacol and biphenyl (Φ_{pin} and Φ_{bip}, respectively) are also given in Table I, which will be discussed later.

Table I
Quantum Yields of Benzophenone Disappearance ($\Phi_{(-BP)}$), Benzopinacol Formation (Φ_{pin}), and Biphenyl Formation (Φ_{bip}) for the Benzophenone-Sensitized Photodegradation of Polystyrene in Benzene at 60 °C

[PS], unit·M	$\Phi_{(-BP)}$	Φ_{pin}	Φ_{bip}
0	$(8.6 \pm 1) \times 10^{-3}$	$(4.3 \pm 1) \times 10^{-3}$	$(2.6 \pm 0.5) \times 10^{-3}$
0.02	$(6.7 \pm 1) \times 10^{-3}$	$(3.7 \pm 1) \times 10^{-3}$	$(2.3 \pm 0.5) \times 10^{-3}$
0.2	$(3.5 \pm 1) \times 10^{-3}$	$(1.6 \pm 0.5) \times 10^{-3}$	

Table II
Lifetime of Benzophenone Triplet in Benzene (τ_0), Its Quenching Rate Constants by Benzene (k_q^B) and by Polystyrene (k_q^{PS}), and Its Rate Constant for Hydrogen Abstraction from Benzene (k_a^B) Together with Their Activation Energies

temp, °C	τ_0, μs	$k_q^B \simeq k_{qd}^B$, M^{-1}·s^{-1}	k_a^B, M^{-1}·s^{-1}	$k_q^{PS} \simeq k_{qd}^{PS}$ M^{-1}·s^{-1}
10	9.4	9.6×10^3		9.3×10^5
20	7.4	1.2×10^4		9.9×10^5
30	6.1	1.5×10^4		1.2×10^6
40	4.8	1.9×10^4		1.4×10^6
60	3.2[a]	2.8×10^4[a]	2.4×10^2	1.7×10^6[a]
act energy, kJ/mol	16.8	16.8		9.5

[a] Extrapolated values.

In order to evaluate k_a^B and k_a^{PS} from eq 9 and Table I, it is necessary to know the lifetime, τ_0, of benzophenone triplet in benzene and its quenching rate constant, $k_q^{PS} = k_{qd}^{PS} + k_a^{PS}$, by polystyrene. The value of k_q^{PS} is related to the lifetime of benzophenone triplet in the presence of polystyrene, τ, by

$$1/\tau = k_d + k_q^B[B] + k_q^{PS}[PS] = 1/\tau_0 + k_q^{PS}[PS] \qquad (11)$$

where $k_q^B = k_{qd}^B + k_a^B$ and τ and τ_0 were obtained from the slopes of the semilogarithmic decay curves of benzophenone phosphorescence excited by the nitrogen laser pulse in the presence and absence of polystyrene, respectively. The quenching rate constant of benzophenone triplet by benzene, k_q^B, was calculated from $1/\tau_0$ by using

$$1/\tau_0 = k_d + k_q^B[B] \cong k_q^B[B] \qquad (12)$$

with [B] = 11.0 M. The approximation is valid, since the rate of spontaneous deactivation, k_d, of benzophenone triplet in nonviscous solution at ambient temperature is supposedly much smaller than $1/\tau_0$. The $1/\tau_0$ is of the order of 10^5 s^{-1} as shown in Table II while $k_d = 1.4 \times 10^3$ s^{-1} in perfluoromethylcyclohexane at 20 °C.[18] The Stern–Volmer plots of $1/\tau$ against polystyrene concentration, [PS], are shown in Figure 2 for the measurements at 10–40 °C, and the values of τ_0, k_q^B, and k_q^{PS} at 10–40 °C and the extrapolated values for 60 °C are listed in Table II. The conditions $k_{qd}^B \gg k_a^B$ and $k_{qd}^{PS} \gg k_a^{PS}$ were used for the presentation in Table II, according to the results given later in this section. Recently k_q^{PS} for benzophenone has been reported to be 1.9×10^6 M^{-1}·s^{-1} at room temperature.[19]

By introducing the values of $\Phi_{(-BP)}$ and τ_0 in the absence of polystyrene into eq 9, we get $k_a^B[B] = 2.6 \times 10^3$ s^{-1}, and hence, $k_a^B = 2.4 \times 10^2$ M^{-1}·s^{-1} at 60 °C, which is also shown in Table II. This value agrees well with that reported in the literature[16] ($k_a^B = 1.6 \times 10^2$ M^{-1}·s^{-1} at room temperature). The comparison of values in Tables I and II in the presence of polystyrene gives small negative values

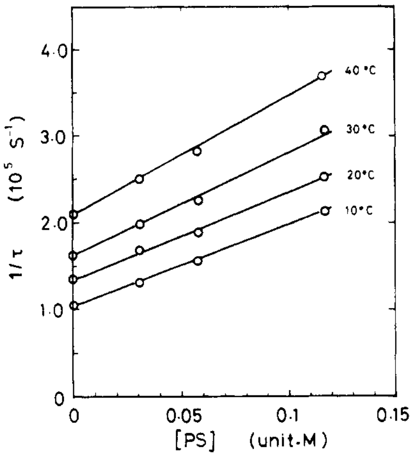


Figure 2. Stern–Volmer plots for the quenching of benzophenone phosphorescence by polystyrene in benzene. Measurement temperatures are shown beside the lines. $\bar{M}_n = 4.4 \times 10^5$, [BP] = 8.7 × 10^{-3} M.

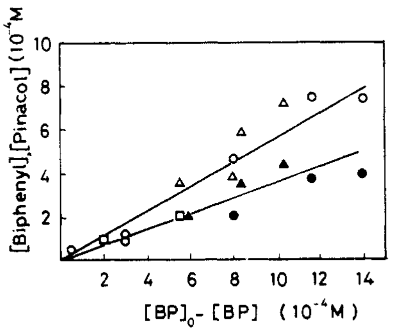


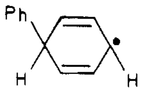
Figure 3. Concentrations of benzopinacol (○, △, □) and biphenyl (●, ▲) formed during the 365-nm irradiation of benzophenone in benzene at 60 °C. $\bar{M}_n = 4.4 \times 10^5$, $[\mathrm{BP}]_0 = 1.9 \times 10^{-3}$ M. [PS] = 0% (○, ●), 0.2% (△, ▲), and 2.0% (□).

(-(0.3–0.4) × 10^3 s^{-1}) for k_a^{PS}[PS]. This may be within the range of error due to the rather scattered values of benzophenone concentration measured by GPC, but we cannot exclude the possibility of the error introduced by disregarding the possible regeneration of benzophenone due to the reaction of BPH· with Ph· (and/or PS·) (reaction 13). The disproportionation between ketyl radicals (eq 14) can be safely disregarded as will be shown later.

The effect of polystyrene addition on $\Phi_{(-BP)}$ can be explained by eq 9 satisfactorily. Though the numerator on the right-hand side of eq 9 does not change much with increasing polystyrene concentration, the denominator of the same term increases much with increasing polystyrene concentrtion due to the approximately hundred-fold larger value of k_q^{PS} in comparison with k_q^{B}. Thus polystyrene plays a role mainly as a quencher for the decay process of excited triplet state of benzophenone in solution.

Equations 13–18 are the main possible reactions of small radicals.

$$\left.\begin{array}{l}\mathrm{BPH\cdot + Ph\cdot\ (or\ PS\cdot) \rightarrow BP + B\ (or\ PS)} \\ \mathrm{BPH\cdot + BPH\cdot \rightarrow BP + PhCH(OH)Ph}\end{array}\right\}\begin{array}{l}\text{dispropor-}\\ \text{tionation}\end{array} \quad \begin{array}{r}(13)\\(14)\end{array}$$

$\mathrm{Ph\cdot + B} \xrightarrow{k_{Ph\cdot}^{B}}$  $\mathrm{(D\cdot) \rightarrow Ph\text{–}Ph}$ phenylation (15)

$$\mathrm{Ph\cdot + PS} \xrightarrow{k_{Ph\cdot}^{PS}} \mathrm{B + PS\cdot} \qquad (16)$$

$$\mathrm{BPH\cdot + BPH\cdot} \longrightarrow \text{benzopinacol} \qquad (17)$$

$$\mathrm{(BPH\cdot, Ph\cdot, D\cdot) + (Ph\cdot, D\cdot)} \longrightarrow \text{other recombination and disproportionation} \qquad (18)$$

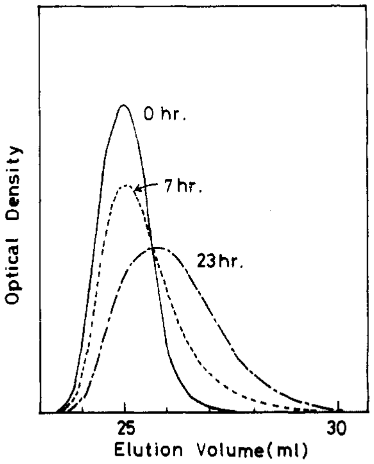


Figure 4. Change in GPC curves for polystyrene during benzophenone-sensitized photodegradation in benzene at 60 °C. [PS] = 2.0%, $[\mathrm{BP}]_0 = 1.9 \times 10^{-3}$ M. $\bar{M}_{n,0} = 4.4 \times 10^5$ and $\bar{M}_{w,0}/\bar{M}_{n,0}$ = 1.3 for t = 0; $\bar{M}_n = 2.7 \times 10^5$ and $\bar{M}_w/\bar{M}_n$ = 1.9 for t = 7 h; $\bar{M}_n = 1.5 \times 10^5$ and $\bar{M}_w/\bar{M}_n$ = 2.2 for t = 23 h.

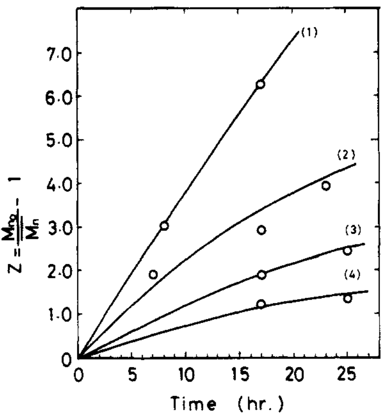


Figure 5. Number of chain scissions per macromolecule, Z, vs. irradiation time at 60 °C. [PS] = 0.2%, $\bar{M}_{n,0} = 4.4 \times 10^5$. $[\mathrm{BP}]_0$ = (1) 2.9 × 10^{-3}, (2) 1.9 × 10^{-3}, (3) 1.2 × 10^{-3}, and (4) 0.6 × 10^{-3} M.

The increase in the concentration of benzopinacol and biphenyl measured by GPC during the photoirradiation of benzophenone in benzene solution at 60 °C is shown in Figure 3 against the concentration of consumed benzophenone. In the case of benzopinacol, a single straight line can be drawn irrespective of the presence or absence of polystyrene, and its slope, representing the ratio of quantum yield for pinacol formation Φ_{pin} to $\Phi_{(-BP)}$, suggests that benzopinacol is formed almost quantitatively by the combination of two ketyl radicals. Consequently reaction 14 and the recombination of ketyl radical with other radicals can be disregarded. The quantum yield for biphenyl formation, Φ_{bip}, is about one-third of $\Phi_{(-BP)}$. In contrast to the ketyl radicals, the phenyl radicals have very high reactivity and can undergo arylation to benzene, resulting in biphenyl formation[9] (eq 15), and if polystyrene is present, they abstract hydrogen from polystyrene, forming the polystyrene on-chain radicals (eq 16). The Φ_{pin} and Φ_{bip} are given in Table I.

Degradation Step of Polystyrene in Solution

The decrease in molecular weight of polystyrene during photoirradiation was followed by GPC. Typical GPC curves over the course of degradation are shown in Figure 4. The increase in the number of main-chain scissions per macromolecule, $Z = (\bar{M}_{n,0}/\bar{M}_n) - 1$, where $\bar{M}_{n,0}$ is the initial value of $\bar{M}_n$, is shown in Figure 5. It is clear that the slope or the rate of chain scission increases with increasing sensitizer (benzophenone) concentration. Z does not increase linearly with time as will be supposed later from eq 30. The possible reactions of polystyrene radicals are summarized as follows:

$$\underset{\mathrm{PS_c\cdot}}{-\mathrm{CH_2\dot{C}(Ph)CH_2C(Ph)H-}} \xrightarrow{k_\beta} -\mathrm{CH_2C(Ph){=}CH_2} + \underset{\mathrm{PS_e\cdot}}{\mathrm{\cdot C(Ph)H-}} \qquad \beta\text{-scission} \quad (19)$$

$$\mathrm{PS_e\cdot} + \mathrm{PS} \xrightarrow{k_f} \mathrm{PS} + \mathrm{PS_c\cdot} \qquad \text{chain transfer} \quad (20)$$

$$\mathrm{PS_e\cdot} \xrightarrow{k_b} \mathrm{PS_c\cdot} \qquad \text{back-biting} \quad (21)$$

$$\mathrm{PS\cdot} + \mathrm{PS\cdot} \xrightarrow{k_t} \mathrm{PS{-}PS} \qquad \text{termination, including cross-linking} \quad (22)$$

$$\mathrm{PS\cdot} + \mathrm{R\cdot}\ (\mathrm{D\cdot}, \mathrm{BPH\cdot}) \xrightarrow{k_t'} \qquad \text{termination with small molecules} \quad (23)$$

In the above equations, $\mathrm{PS_c\cdot}$ and $\mathrm{PS_e\cdot}$ mean the on-chain radical and end radical of polystyrene, respectively, and $\mathrm{PS\cdot}$ covers both ($[\mathrm{PS\cdot}] = [\mathrm{PS_c\cdot}] + [\mathrm{PS_e\cdot}]$).

As we have already shown, neither triplet benzophenone nor ketyl radicals abstract hydrogen from polystyrene appreciably. Therefore the reaction of phenyl radicals with polystyrene is considered to be the only important reaction to produce polystyrene radicals. However, it should be noted that most of the phenyl radicals are consumed by the reaction with benzene. Therefore the amount of phenyl radical $\mathrm{Ph\cdot}$ used to abstract hydrogen from polystyrene is disregarded for the calculation of the stationary-state concentration of $\mathrm{Ph\cdot}$. Then using the stationary state of $[\mathrm{Ph\cdot}]$ and $[\mathrm{BP^*}]$, we obtain the rate of formation of $\mathrm{PS\cdot}$ as

$$\begin{aligned} R_i = k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}[\mathrm{Ph\cdot}][\mathrm{PS}] &= (k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}k_a{}^{\mathrm{B}}/k_{\mathrm{Ph\cdot}}{}^{\mathrm{B}})[\mathrm{BP^*}][\mathrm{PS}] \\ &= (k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}\alpha/k_{\mathrm{Ph\cdot}}{}^{\mathrm{B}})[\mathrm{BP}][\mathrm{PS}]/[\mathrm{B}] \end{aligned} \quad (24)$$

where $\alpha = 2.3 \times 10^3\Phi_{(-\mathrm{BP})}I_0\epsilon f$. R_i is also given by

$$R_i = (k_t'[\mathrm{R\cdot}] + k_t[\mathrm{PS\cdot}])[\mathrm{PS\cdot}] \quad (25)$$

when $\mathrm{R\cdot}$ represents all the small radicals undergoing termination with $\mathrm{PS\cdot}$ and k_t' is their average rate constant. The stationary concentration of the on-chain radical $[\mathrm{PS_c\cdot}]$ is calculated as

$$[\mathrm{PS_c\cdot}] = \frac{k_f[\mathrm{PS}] + k_b + k_t'[\mathrm{R\cdot}] + k_t[\mathrm{PS\cdot}]}{k_f[\mathrm{PS}] + k_b + k_t'[\mathrm{R\cdot}] + k_t[\mathrm{PS\cdot}] + k_\beta}[\mathrm{PS\cdot}] \quad (26)$$

Later in the section on the change of the molecular weight distribution, we will show that $k_\beta > k_t[\mathrm{PS\cdot}]$ under our conditions. The value of k_β at 60 °C may be of the order of 10^{-4} s^{-1},[6] being a little smaller than the rate constant for depropagation of the polystyryl end radicals.[4] The rate constant for chain transfer to a polymer of a growing polystyryl radical in radical polymerization is of the order of 10^{-1} M^{-1}·s^{-1}. Consequently for $[\mathrm{PS}] = 10^{-2}$–10^{-1} unit·M (ca. 0.1–1%), $k_f[\mathrm{PS}] > k_\beta$ holds, and as a first approximation

$$[\mathrm{PS_c\cdot}] \cong [\mathrm{PS\cdot}] \quad (27)$$

The rate of main-chain scission per macromolecule, $\mathrm{d}Z/\mathrm{d}t$, is given by

$$\mathrm{d}Z/\mathrm{d}t = (N/[\mathrm{PS}])(\mathrm{d}[Z]/\mathrm{d}t) = (N/[\mathrm{PS}])k_\beta[\mathrm{PS_c\cdot}] \quad (28)$$

where $[Z]$ is the extent of main-chain scission expressed in mol/L and N is the degree of polymerization of the initial polymer.

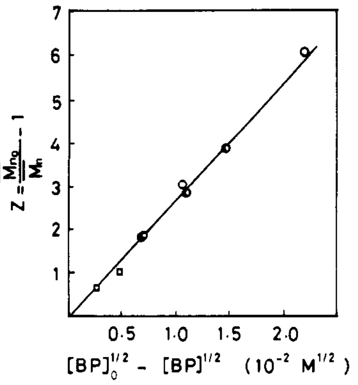


Figure 6. Plots of number of chain scissions per macromolecule, Z, vs. $[\mathrm{BP}]_0{}^{1/2} - [\mathrm{BP}]^{1/2}$ according to eq 30 or 33. $\bar{M}_{n,0} = 4.4 \times 10^5$. (○) [PS] = 0.2%, $[\mathrm{BP}]_0 = 2.9 \times 10^{-3}$ M; (◐) [PS] = 0.2%, $[\mathrm{BP}]_0 = 1.9 \times 10^{-3}$ M; (□) [PS] = 2.0%, $[\mathrm{BP}]_0 = 1.9 \times 10^{-3}$ M.

Now let us consider the case when the termination occurs exclusively between polymer radicals ($k_t'[\mathrm{R\cdot}] \ll k_t[\mathrm{PS\cdot}]$). Substituting the relation

$$[\mathrm{PS\cdot}] = (R_i/k_t)^{1/2} = (k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}\alpha/k_tk_{\mathrm{Ph\cdot}}{}^{\mathrm{B}})^{1/2}([\mathrm{BP}][\mathrm{PS}]/[\mathrm{B}])^{1/2} \quad (29)$$

into eq 27 and 28 and integrating by use of the relation $\mathrm{d}[\mathrm{BP}]/\mathrm{d}t = -\alpha[\mathrm{BP}]$ (eq 8), we get

$$Z = \frac{2Nk_\beta(k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}})^{1/2}}{(2.3 \times 10^3\Phi_{(-\mathrm{BP})}I_0\epsilon fk_tk_{\mathrm{Ph\cdot}}{}^{\mathrm{B}}[\mathrm{PS}][\mathrm{B}])^{1/2}}([\mathrm{BP}]_0{}^{1/2} - [\mathrm{BP}]^{1/2}) \quad (30)$$

Another possibility is the case where the termination takes place between small and polymeric radicals; i.e., $k_t'[\mathrm{R\cdot}] \gg k_t[\mathrm{PS\cdot}]$. As the most small radicals disappear by their own termination (k_t'')

$$k_t''[\mathrm{R\cdot}]^2 = k_a{}^{\mathrm{B}}[\mathrm{BP^*}][\mathrm{B}] = \alpha[\mathrm{BP}] \quad (31)$$

we get

$$[\mathrm{PS\cdot}] = R_i/(k_t'[\mathrm{R\cdot}]) = (k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}[\mathrm{PS}]/k_{\mathrm{Ph\cdot}}{}^{\mathrm{B}}k_t'[\mathrm{B}])(k_t''\alpha[\mathrm{BP}])^{1/2} \quad (32)$$

and

$$Z = (2Nk_\beta k_{\mathrm{Ph\cdot}}{}^{\mathrm{PS}}/k_{\mathrm{Ph\cdot}}{}^{\mathrm{B}}k_t'[\mathrm{B}])(k_t''/\alpha)^{1/2}([\mathrm{BP}]_0{}^{1/2} - [\mathrm{BP}]^{1/2}) \quad (33)$$

In either case, Z should be a linear function of $[\mathrm{BP}]_0{}^{1/2} - [\mathrm{BP}]^{1/2}$ regardless of the initial concentration of benzophenone. Figure 6 shows that this relation holds for our experiments. Figure 6 shows also that Z is almost independent of polystyrene concentration, a fact which fits eq 33 rather then eq 30. This suggests that the termination occurs mainly between $\mathrm{PS\cdot}$ and $\mathrm{R\cdot}$.

To confirm further the validity of eq 33, polymers with different molecular weights were examined, and the results are shown in Figure 7. It is clear that the slope of the plot of Z against $[\mathrm{BP}]_0{}^{1/2} - [\mathrm{BP}]^{1/2}$ is proportional to N. As $[Z]$ ($=[\mathrm{PS}]Z/N$) is the moles of chain broken per liter, the ratio $[Z]/([\mathrm{BP}]_0 - [\mathrm{BP}])$ represents the number of chains broken per benzophenone molecule consumed. The values are about 0.01 for [PS] = 0.02 unit·M (0.2%) and about 0.12 for [PS] = 0.2 unit·M (2%). This shows again that only a very small fraction of small radicals undergoes hydrogen abstraction from polystyrene.

The GPC measurements of polymers irradiated for varying times give information on the change not only of $\bar{M}_n$ but also of molecular weight distribution, $\bar{M}_w/\bar{M}_n$. The

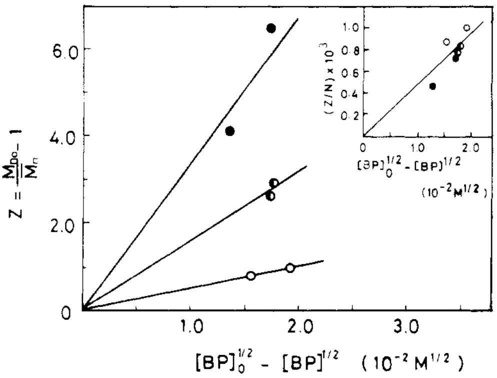


Figure 7. Effect of initial molecular weight $\bar{M}_{n,0}$ on the plots of Z or Z/N (insert) against $[BP]_0^{1/2} - [BP]^{1/2}$. $\bar{M}_{n,0} = 0.96 \times 10^5$ (○), 3.4×10^5 (◐), and 9.5×10^5 (●). $[BP]_0 = 2.9 \times 10^{-3}$ M.

value of $\bar{M}_w/\bar{M}_n$ increases with increasing irradiation time and becomes $\bar{M}_w/\bar{M}_n > 2$ in the present case as shown in Figure 4. This means that cross-linking of polystyrene on-chain radical (eq 22) occurs in parallel with main-chain scission (eq 19) during the benzophenone-sensitized photodegradation of polystyrene in benzene solution at 60 °C. David et al.[3] have formulated the change in $\bar{M}_n$ and $\bar{M}_w$ due to simultaneous cross-linking and chain scission during the irradiation of a polymer with an initial Schultz–Zimm type molecular weight distribution as

$$\bar{M}_n = \bar{M}_{n,0}/(1 + Z_s - Z_x) \tag{34}$$

$$\bar{M}_w = \frac{2\bar{M}_{n,0}\{Z_s - 1 + (1 + Z_s/\sigma)^{-\sigma}\}}{Z_s^2 - 4Z_x\{Z_s - 1 + (1 + Z_s/\sigma)^{-\sigma}\}} \tag{35}$$

where Z_s and Z_x are the number of main-chain scissions and cross-links per initial macromolecule, respectively, and σ is a parameter characterizing the width of the initial distribution:

$$\sigma = \bar{M}_{n,0}/(\bar{M}_{w,0} - \bar{M}_{n,0}) \tag{36}$$

The ratio, ρ, of cross-linking probability to main-chain scission probability is given by

$$\rho = Z_x/Z_s = k_t[PS_c\cdot]/k_\beta \tag{37}$$

The theoretical curves according to eq 34 and 35 relating $\bar{M}_w/\bar{M}_n$ to Z_s during photoirradiation with $\sigma = 3.3$ and $\rho = 0.04$, 0.08, and 0.125 are shown in Figure 8 together with plots of the present experimental results for [PS] = 0.02 M with the approximation $Z \cong Z_s$. Figure 8 shows that ρ lies between 0.04 and 0.13 and increases with increasing benzophenone concentration, a variation consistent with eq 27 and 32. The termination rate constant, k_t, between polymer radicals in free-radical polymerization is known to depend strongly on the mobility of segments of the polymer, i.e., the viscosity of the reaction medium, molecular weight, polymer–solvent interaction, and flexibility of the polymer molecule.[14,20] However, using 10^8 M$^{-1}\cdot$s^{-1} at 60 °C[21] as a mean value of k_t for polymerization of styrene in dilute solution and a value of 10^{-4} s^{-1} for k_β at 60 °C,[6] we may estimate [PS·] to be of the order of 10^{-12} M.

From the results and discussion given above, we can now propose a mechanism for the degradation step of polystyrene in solution. The polystyrene on-chain radicals produced by hydrogen abstraction by phenyl radicals undergo β-scission to give end radicals. However, the former are regenerated immediately by chain-transfer reaction of the latter, and the majority of polymer radicals remain as such in the stationary state. The on-chain radicals recombine with each other to form cross-links at a much slower rate than that of β-scission, and most on-chain radicals disappear by recombination with small radicals.

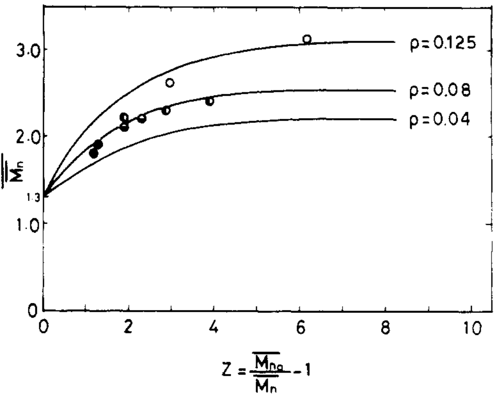


Figure 8. Change in molecular weight distribution, $\bar{M}_w/\bar{M}_n$, of polystyrene against Z during benzophenone-sensitized photodegradation in benzene at 60 °C. $[BP]_0 = 0.6 \times 10^{-3}$ (●), 1.2×10^{-3} (◒), 1.9×10^{-3} (◐), and 2.9×10^{-3} M (○). Solid curves are calculated according to eq 34 and 35 with the ρ values given beside the curves.

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