

## Photodegradable Polymers. II. Preparation of Styrene Copolymers with Alkyl and Phenyl $\beta$ -Styryl Ketones and Their Photodegradability

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### Synopsis

Photodegradable polymers having pendent carbonyl groups attached directly to the polymer chain were prepared by copolymerization of styrene (St) with alkyl and phenyl  $\beta$ -styryl ketones ( $\text{RCOCH}=\text{CHC}_6\text{H}_5$ ), where  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_5\text{H}_{11}, n\text{-C}_{11}\text{H}_{23}, t\text{-C}_4\text{H}_9, \text{cyclo-C}_6\text{H}_{11}, \text{and C}_6\text{H}_5$ . The photodegradability of these copolymers was traced by viscometric and IR spectroscopic measurements. The degradability of St-benzalacetophenone (BAPh) copolymer is greater than that of St-alkyl styryl ketone copolymers under the irradiation of a high-pressure Hg lamp. The photodecomposition behavior of St-BAPh copolymer was investigated in detail by a spectroirradiation technique. The changes in molecular weight and its distribution by photodegradation were measured by gel permeation chromatography, and the quantum yield for bond scission along the main chains of the copolymer was estimated to be about  $5 \times 10^{-3}$  by 328 nm irradiation in a benzene solution. Examination of the effect of wavelength of the radiation on the bond scission showed that 328-nm light is most effective. The photochemical degradation process was shown to occur chiefly via triplet state of carbonyl groups by the quenching technique using 1,3-cyclohexadiene as a triplet quencher. The quantum yield of decarbonylation process was also estimated to be about  $4.2 \times 10^{-2}$  in benzene.

### INTRODUCTION

Almost all of the currently used plastic materials are very resistant to environmental attack. This property unfortunately results in persistent litter of plastic wastes in our environment. One of the approaches to improve this situation is exploitation of those polymers which will degrade in sunlight to a biodegradable molecular weight in a controllable manner. In recent years, many efforts have been made in the preparation of photodegradable polymers, such as ethylene-carbon monoxide copolymer,<sup>1</sup> copolymers of styrene-vinyl ketones,<sup>2</sup> copolymers of methyl methacrylate-vinyl ketones,<sup>3</sup> and so on. Mechanistic investigation of the photodegradation of copolymers of vinyl ketones has been reported.<sup>4</sup> We also reported the preparation of copolymers of styrene with benzalacetone or benzalacetophenone and a preliminary study of their photodegradation.<sup>5</sup> In this paper, we will describe the preparation of the copolymers of styrene with alkyl  $\beta$ -styryl ketones and their photodegradation behavior in comparison with that of styrene-benzalacetophenone

copolymer. The comonomers selected in this investigation are of 1,2-disubstituted olefin type, which are expected not to have homopolymerizability and therefore not to incorporate more than two comonomer units in sequence in the copolymer chain.

## EXPERIMENTAL

**Materials.** Benzalacetophenone was synthesized from benzaldehyde and acetophenone and purified by recrystallization from ethyl acetate, mp 62°C. Alkyl styryl ketones  $R-CO-CH=CH-C_6H_5$  ( $R = C_2H_5$ ,  $n-C_5H_{11}$ ,  $n-C_{11}H_{23}$ ,  $(CH_3)_3C$ ,  $(C_2H_5)_2CH$ , and cyclo- $C_6H_{10}$ ) were prepared by the reaction of styrene with corresponding aliphatic carboxylic acid chlorides<sup>6</sup> and recrystallized from ethanol. Styrene used for copolymerization was purified by the usual method before use.

**Copolymerization.** Copolymerization was conducted by the procedure of the no-initiator emulsion polymerization process<sup>7</sup> in order to obtain a copolymer of high degree of polymerization. The copolymers obtained by this method are of high molecular weight, and the intrinsic viscosities are in the range of 2.4–7.5. A typical example of the polymerization is as follows: 1 g sodium oleate and 100 ml deionized water were placed in a three-necked flask equipped with a condenser, a dropping funnel, and a nitrogen inlet tube. The mixture was preheated to 80°C under a slow stream of nitrogen gas to remove air from the polymerization system. BAPh, 1 g ( $4.81 \times 10^{-3}$  mole), dissolved in 9.0 g ( $8.64 \times 10^{-2}$  mole) styrene was then added to the mixture and allowed to polymerize for 4 hr with vigorous agitation. The reaction mixture was poured into methanol to precipitate the polymer, which was collected by filtration, washed thoroughly with methanol, and dried at 50°C under reduced pressure. Purification of the polymer was conducted by reprecipitation twice with benzene–methanol.

**Molecular Weight Determination.** The molecular weights of the copolymers prepared and degraded were determined by viscometric or gel permeation chromatographic technique. The gel permeation chromatograph used was Type HLC-807 of Toyo Soda Chemical Co. Ltd. The intrinsic viscosity was measured in benzene solution at 25.0°C.

**Irradiation.** A 100-W high-pressure mercury lamp (USHIO UM-102) or a spectro-irradiation apparatus (JASCO CRM-FA) was used as irradiation apparatus. Irradiation to the copolymers was carried out both in solution and film states. Film for irradiation was cast from benzene solution and dried at 40°C under vacuum.

## RESULTS AND DISCUSSION

As has been reported previously,<sup>5</sup> monomer reactivity ratios of benzalacetone and benzalacetophenone are substantially zero in the radical copolymerization with styrene. Based on their structural similarity, monomer reactivity ratios of the alkyl  $\beta$ -styryl ketones used in this study might also be zero, and their copolymerization with styrene might give copolymers having a structure as in the sequence of styrene monomer units where not more than two inner olefin comonomer units are incorporated in sequence. Characteris-

TABLE I  
Styrene-Alkyl  $\beta$ -Styryl Ketone (ROCH=CHPh) Copolymers

Sample no.	R	St/Styryl ketone ratio in wt.	Ketone monomer		[ $\eta$ ] (25°C) in benzene	$\nu_{CO}$ , $\text{cm}^{-1}$	$n-\pi^*$ $\lambda_{\text{max}}$ in THF, nm
			unit content in copolymer, mole-%	in copolymer, mole-%			
1	CH <sub>3</sub>	90/10	6.4	4.31	4.31	1712	291
2	CH <sub>3</sub>	95/5	4.0	5.20	5.20	1712	291
3	C <sub>2</sub> H <sub>5</sub>	90/10	3.7	4.55	4.55	1712	291
4	C <sub>2</sub> H <sub>5</sub>	95/5	1.5	6.57	6.57	1712	291
5	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	90/10	1.5	3.36	3.36	1696	291
6	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	95/5	1.0	6.10	6.10	1696	291
7	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	90/10	1.8	4.98	4.98	1712	291
8	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	95/5	1.4	5.83	5.83	1712	291
9	cyclo-C <sub>6</sub> H <sub>11</sub>	90/10	3.2	4.00	4.00	1700	291
10	cyclo-C <sub>6</sub> H <sub>11</sub>	95/5	1.5	5.12	5.12	1700	291
11	<i>n</i> -C <sub>11</sub> H <sub>23</sub>	90/10	1.1	6.05	6.05	1712	291
12	<i>n</i> -C <sub>11</sub> H <sub>23</sub>	95/5	0.7	3.40	3.40	1712	291

TABLE II  
Styrene–Benzalacetophenone Copolymers

Sample no.	St/BAPh mole ratio	BAPh unit content in copolymer, mole-%	$[\eta]$ (25°C) in benzene	$\overline{M}_n \times 10^{-4}$
74	20.0	6.8	3.06	120
76	11.7	10.7	1.92	72
78	8.9	14.4	1.59	65
80	5.2	18.2	1.06	49

tics of the copolymers prepared are shown in Tables I and II. The carbonyl  $n-\pi^*$  absorption maxima of the copolymers in tetrahydrofuran (THF) are at around 291 nm.

The changes in intrinsic viscosity ratios of the copolymers prepared by irradiation with the 100-W high-pressure mercury lamp under vacuum at 25°C are shown in Figure 1. The copolymers were rapidly photodegraded in comparison with polystyrene. The features of photodegradation varied with the structure of comonomers incorporated in the copolymers. Alkyl styryl ketone copolymers showed mostly similar degradation patterns, but among them, *t*-butyl styryl ketone copolymer showed a marked decrease in intrinsic viscosity upon irradiation. This might be explained partly by neighboring group repulsion in chain scission of 1,4-diradical intermediates and no participation of side-chain hydrogen abstraction by photoexcited carbonyl. Phenyl  $\beta$ -styryl ketone (i.e., BAPh) copolymer showed most marked degradation due to the most effective light absorption at the irradiated wavelength.

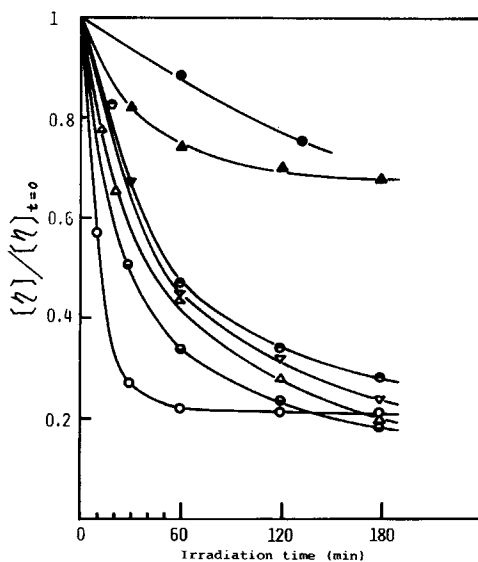


Fig. 1. Changes in intrinsic viscosity ratios of polystyrene (●) and St–RCOCH=CHPh copolymers, where R =  $n$ -C<sub>11</sub>H<sub>23</sub> (no. 11) (▲),  $n$ -C<sub>5</sub>H<sub>11</sub> (no. 7) (●), C<sub>2</sub>H<sub>5</sub> (no. 3) (▽), CH<sub>3</sub> (no. 1) (Δ), *t*-C<sub>4</sub>H<sub>9</sub> (no. 5) (◐), and C<sub>6</sub>H<sub>5</sub> (no. 74) (○). Polymer films (about 40 μm thick) fitted on a Pyrex glass water-cooling jacket were photoirradiated with a 100-W high-pressure Hg lamp under vacuum at 25°C.

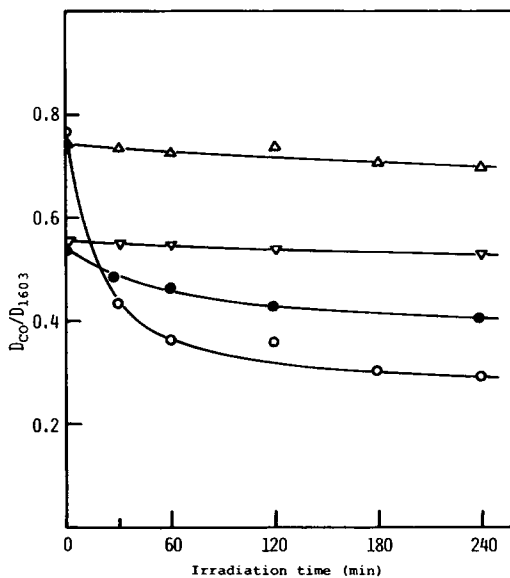


Fig. 2. Changes in absorption ratios  $D_{CO}/D_{1603}$  of IR spectra of St-RCOCH=CHPh copolymers, where R = CH<sub>3</sub> (no. 1) (Δ), C<sub>2</sub>H<sub>5</sub> (no. 3) (▽), cyclo-C<sub>6</sub>H<sub>11</sub> (no. 9) (●), and C<sub>6</sub>H<sub>5</sub> (no. 74) (○). Photoirradiation condition is the same as described in Fig. 1.

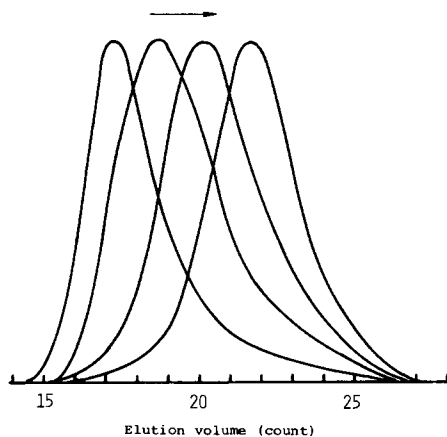
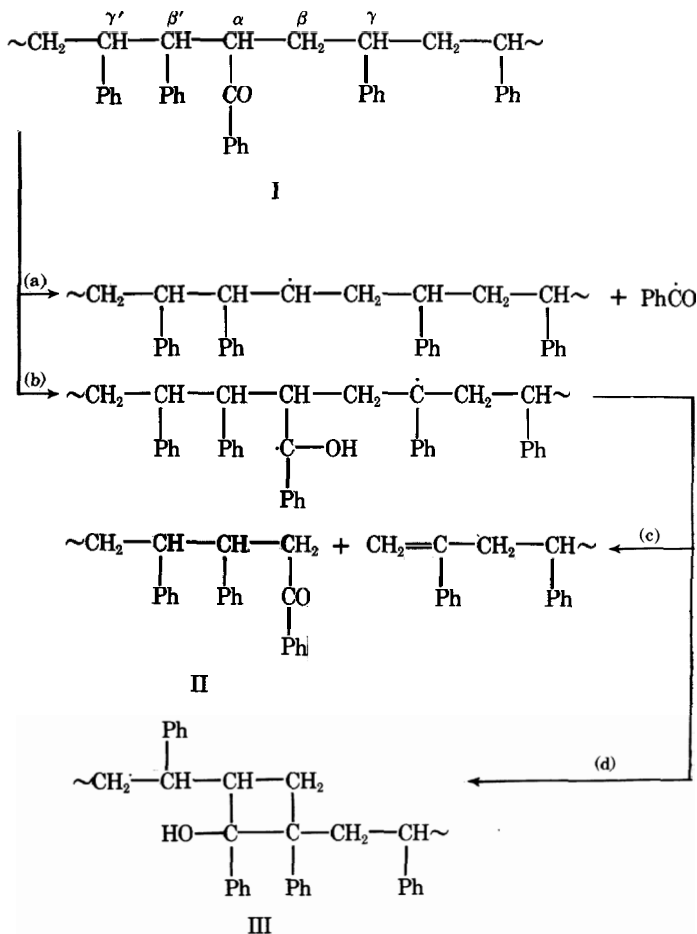


Fig. 3. GPC changes of St-BAPh copolymer (no. 74) upon 328 nm photoirradiation in benzene at room temperature.

The copolymers showed a change in their IR absorption spectra, especially at carbonyl absorption region, upon photoirradiation. The absorbance ratios of  $D_{CO}/D_{1603}$  decreased with irradiation period, as shown in Figure 2. BAPh-St copolymer showed the most rapid decrease in carbonyl content, and the result coincided well with that of the molecular weight degradation.

A detailed study of photodegradation behavior of St-BAPh copolymer was conducted by using a spectro-irradiation apparatus. Light of narrow wavelength range (wavelength indicated  $\pm 7$  nm) was applied to a benzene solution of the copolymer, and the degradation was traced by GPC, UV, and IR techniques. The copolymer chain structure I shown in Scheme I has been sug-

gested from the monomer reactivity ratios,<sup>5</sup> and the degradation of the polymer may be expected to proceed as shown in the scheme. Process (a) is known to be the Norrish type I process and (b), the Norrish type II process. A typical change in gel permeation chromatogram by irradiation is shown in Figure 3, and the changes in number-average ( $\bar{M}_n$ ) and weight-average molecular weight ( $\bar{M}_w$ ) and heterogeneity index  $\bar{M}_w/\bar{M}_n$  are as shown in Figure 4. The results reveal that the average molecular weight decreased very rapidly in the initial stage of the irradiation and that the molecular weight distribution was spread to the low molecular weight side. After the initial stage of the degradation, the distribution became narrow again. The result may imply that initial main-chain scission by the Norrish type II process was followed by photodecomposition of such a terminal carbonyl group as II formed at the initial stage. Considering segmental mobility and steric factors, it is conceivable that terminal carbonyl is incorporated more easily in the degradation than inner-chain carbonyl. In the Norrish type II process,  $\gamma$ -hydrogens are chiefly abstracted.  $\gamma$ -Hydrogen abstraction can be considered zero



or negligible from the fact that UV absorption at around 330 nm decreased with irradiation, as will be described later. If  $\gamma$ -hydrogen abstraction takes place, a stilbene-like terminal must be formed and the absorption must in-

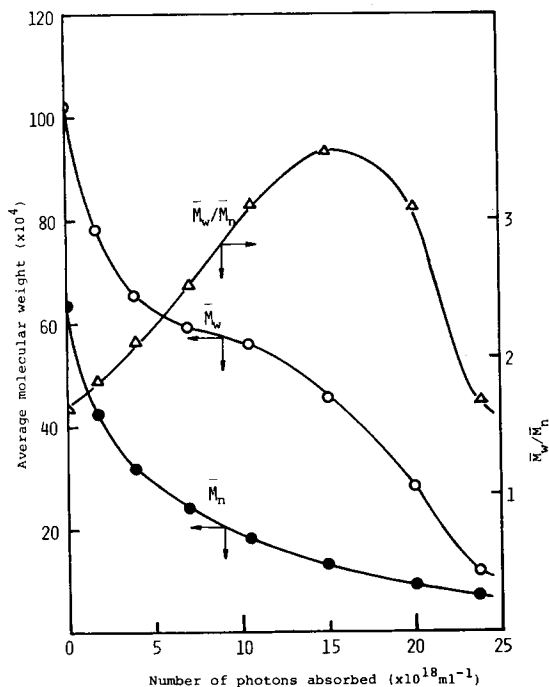


Fig. 4. Changes in  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$  of St-BAPh copolymer (no. 78) upon 328 nm photoirradiation in benzene at room temperature.

crease because of larger molar absorbance of stilbene than the initial ketone by more than two orders. Almost similar results were obtained for the fractionated copolymers having more narrow molecular weight distribution (Table III).

Bond scission was effected most efficiently by irradiation at the absorption maximum. The dependence of the bond scission on the wavelength of the illuminating light was shown in Figure 5. The quantum yield of apparent chain scission  $\Phi_s$  was defined by the following equation:

$$\Phi_s = \frac{\text{total number of chain scission } (s_N)}{\text{total number of photons absorbed } (I)}$$

TABLE III  
Change in Molecular Weight of Fractionated Sample of St-BAPh Copolymer upon Irradiation at 328 nm

No. of absorbed photons, $10^{18}/\text{ml}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	$\bar{M}_w/\bar{M}_n$
0	206	255	1.24
1.5	159	211	1.33
2.9	129	183	1.42
4.4	98.1	146	1.49
5.8	79.0	122	1.54
7.3	67.9	105	1.55

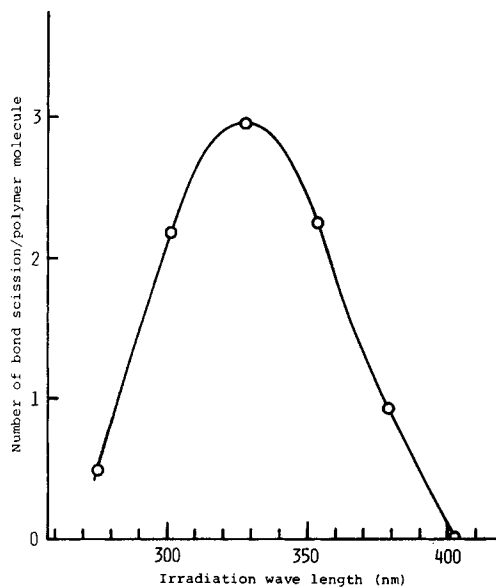


Fig. 5. Effect of wavelength on number of bond scissions per polymer molecule of St-BAPh copolymer (no. 78) in benzene solution. Polymer concentration, 16.9 g/l.; initial number of polymer molecules,  $1.53 \times 10^{16} \text{ ml}^{-1}$ ; number of irradiated photons at each wavelength, about  $1.6 \times 10^{-5}$  einstein/ml.

The average number of chain scission per molecule,  $s$ , was calculated from the following expression:

$$s = (\bar{M}_n^0 / \bar{M}_n^t) - 1$$

where  $\bar{M}_n^0$  and  $\bar{M}_n^t$  are the number-average molecular weights before and after irradiation at time  $t$ . Thus, the total number of chain scissions can be calculated by the equation

$$s_N = s \frac{w}{\bar{M}_n^0} N_A$$

where  $w$  and  $N_A$  are the weight of the polymer in the solution irradiated and the Avogadro number, respectively.

The quantum yield was not dependent on the wavelength of the irradiation. The value of BAPh copolymer at 328 nm was about  $5 \times 10^{-3}$  and not

TABLE IV  
Quantum Yield of Chain Scission of St-BAPh Copolymers (Irradiated at 328 nm in Benzene)

Sample no.	$\bar{M}_n \times 10^{-4}$	Concn. of polymer, g/l.	Quantum yield $\Phi_s \times 10^3$
74	120	18.9 - 25.1	5.2
76	72	19.7	4.8
		14.4	4.7
		9.7	4.7
78	65	15.9	4.8
80	49	11.4	5.2



TABLE V  
Change in Quantum Yield of Chain Scission by Addition of 1,3-Cyclohexadiene as Quencher (Sample No. 78, Irradiated at 328 nm in Benzene)

Concn. of polymer g/l.	Concn. of quencher, $10^{-2}$ mole/l.	$\Phi_s \times 10^3$	$\Phi_s^\circ / \Phi_s$
15.9	0	4.8	1
17.0	1.55	3.8	1.3
15.8	3.17	3.1	1.5
16.8	4.06	2.7	1.8
17.1	5.81	2.4	2.0
16.8	7.61	2.2	2.2
17.2	10.2	2.0	2.4

dependent on the concentration of the polymer solution, the molecular weight of the polymer, nor the carbonyl content in the polymer (Table IV). The value is much smaller than that for small molecules<sup>8</sup> and other ketone polymers.<sup>3,10</sup> Wagner,<sup>11</sup> Stermitz,<sup>12</sup> and Whitten<sup>13</sup> have reported independently unusual deactivation of excited ketones by  $\beta$ -phenyl substituents. The polymers prepared in this work all have  $\beta$ -substituents as shown in the aforementioned scheme. The rapid quenching reported by these authors may also occur here, but according to Wagner's report  $\beta, \gamma$ -diphenyl substituents do not deactivate excited ketones as efficiently as  $\beta$ -phenyl ones. Another reason for the unusually low quantum yield may be due to the neglect of terminal fragmentation or reabstraction of 1,4-biradical to give ground-state ketone.

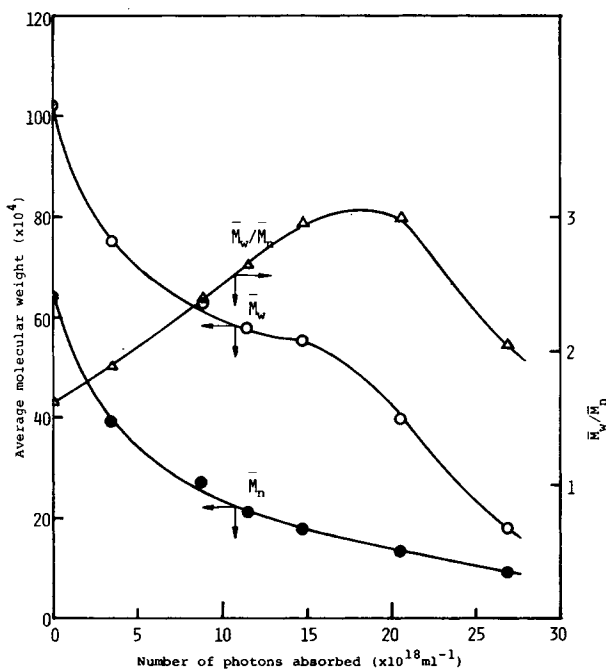


Fig. 6. Quencher effect on changes in  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$  of St-BAPh copolymer (no. 78). Polymer solution in benzene (16.8 g/l.) was irradiated in the presence of 1,3-cyclohexadiene ( $4.06 \times 10^{-2}$  mole/l.) as triplet quencher.

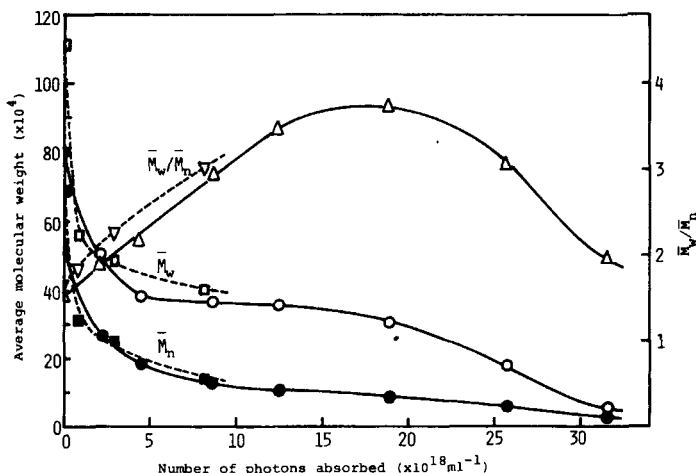


Fig. 7. Changes in  $M_w$ ,  $M_n$ , and  $M_w/M_n$  of St-BAPh copolymer by photoirradiation in THF (---) and dioxane (—). The polymer irradiated in THF was sample no. 78, and that in dioxane had a number average-molecular weight of  $52 \times 10^4$  and a carbonyl content of 13.8 mole-%.

The result of the quenching using 1,3-cyclohexadiene as a triplet quencher is shown in Table V and Figure 6. The degradation pattern in molecular weight change is similar to that shown in Figure 4, but retarded by quenching. The Stern-Volmer equation holds well to give a value of  $k_q\tau = 18$  l./mole, which is lower than that for triplet small ketones.<sup>8,9</sup> The triplet lifetime was calculated to be  $3.6 \times 10^{-9}$  sec on the assumption that  $k_q = 5 \times 10^9$  l./mole/sec for benzene.\* The lifetime obtained is in good agreement with that reported by Wagner<sup>11</sup> and is in the same order of the singlet lifetime of 4-methyl-4-phenyl-2-pentanone.<sup>13</sup> This result may imply that the bond scission occurs via excited triplet and partly singlet states of carbonyl groups in the copolymer, in accordance with the Norrish type II process.

The solvent effect of the photodegradation was examined. Irradiation in THF and dioxane gave a similar degradation pattern to that in benzene, as shown in Figure 7. In all cases, heterogeneity indices increased at first and then decreased. This reflects a slower decrease in  $\bar{M}_w$  than in  $\bar{M}_n$  at the in-

TABLE VI  
Dependence of Quantum Yield of Chain Scission on the Solvent Used

Solvent	Irradiation wavelength, <sup>a</sup> nm	Quantum yield $\Phi_s \times 10^3$
Benzene	328	$4.9 \pm 0.4$
Dioxane	330	$6.0 \pm 0.2$
Tetrahydrofuran	330	$9.8 \pm 0.7$

<sup>a</sup> The irradiation wavelength is the  $n-\pi^*$  absorption maximum in each solvent.

\* The apparent viscosity of the polymer solution is about 4 cp, but the diffusion rate of small molecules may not be affected by the apparent solution viscosity in such a low polymer concentration range. This consideration can be rationalized as autocatalytic effect or gel effect in the radical polymerization.

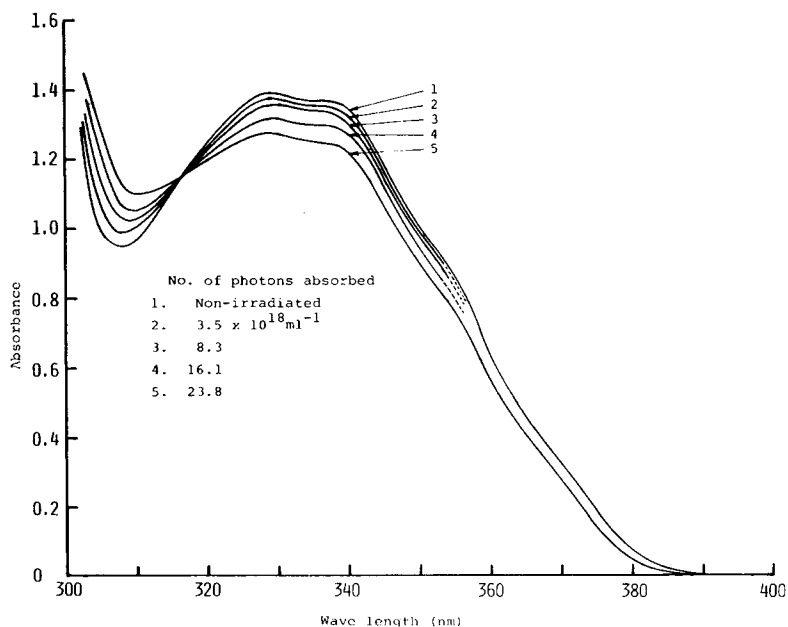


Fig. 8. Changes in UV spectrum ( $n-\pi^*$  absorption) of St-BAPh copolymer (no. 78) upon 328 nm photoirradiation in benzene (16.82 g/l.).

intermediate stage of photodegradation. The apparent quantum yields in various solvents at the wavelength cited are listed in Table VI. The value in THF is somewhat larger than the others. This phenomenon of larger quantum yield in a more polar solvent is consistent with that of small ketones.

As described before, photoirradiation decreased carbonyl content in the polymer. The ketone carbonyl-diminishing process was followed by UV analysis, giving the change shown in Figure 8, which has an isosbestic point at 317 nm. The carbonyl content in the polymer can be estimated from the absorbance at 328 nm by using the calibration equation  $A_{328} = 82.8[\text{CO}]$ , which was obtained from the UV spectra of copolymers of different carbonyl contents. From the UV spectrum change, the quantum yield of the carbonyl content decrease was calculated to give a value of  $(4.2 \pm 0.2) \times 10^{-2}$ . The quantum yield of this process also depends on the solvent used, as shown in Table VII. The tendency is almost similar to the chain scission process. The decrease of carbonyl content may be due to process (a) (Norrish type I) or process (d) (cyclization), but there is no evidence of cyclobutanol formation. No increase in IR absorption was observed in the OH stretching ab-

TABLE VII  
Dependence of Quantum Yield of Decarbonylation on the Solvent Used (at 25 °C)

Solvent	Quantum yield $\times 10^2$
Benzene	$4.2 \pm 0.2$
Dioxane	$8.1 \pm 0.4$
Benzene containing 10 wt-% <i>t</i> -BuOH	7.7

sorption region. Therefore, the decrease may be tentatively attributed to the type I decarbonylation process. According to Lewis and co-workers, however, type I cleavage of phenyl ketones is quite inefficient.<sup>14,15</sup> Furthermore, from the result of unusual triplet deactivation by  $\beta$ -phenyl substituents discussed before, the decarbonylation may be considered to occur mainly via singlet state. Anyway, more detailed investigation is necessary with regard to the decarbonylation process.

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