Edwards' mean-field theory[9] is inadequate for this system owing to the lack of the term including B_2. The value of B_1 can be determined from intrinsic viscosity or light scattering observed in dilute solutions, though some ambiguity remains depending on individual theoretical formulations used for analyzing experimental data. Yamakawa[15] estimated $B_1 = 2.11 \times 10^{-27}$ cm^3 from intrinsic viscosity[26] and $B_1 = 2.19 \times 10^{-27}$ cm^3 from light scattering[27] measured on dilute solutions of polystyrene in toluene. The result obtained in the present work is in good agreement with these values.

From these results, we conclude that the observed values of ξ and g_m are consistent with the scaling predictions and with the concentration blob concept when the molecular weight of the polymer is higher than 1.1×10^5 and ξ is not very small ($\gtrsim$20 Å). For lower molecular weights and smaller values of ξ, on the contrary, experimental results deviate from the scaling prediction, and the mean-field theory becomes more appropriate.

Registry No. Polystyrene (homopolymer), 9003-53-6; toluene, 108-88-3.

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Photochemistry of Ketone Polymers. 18. Effects of Solvent, Ketone Content, and Ketone Structure on the Photolysis of Styrene–Vinyl Aromatic Ketone Copolymers

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ABSTRACT: Studies of the kinetics and mechanisms of the type II photoelimination reaction of some styrene–vinyl aromatic ketone copolymers in solution are reported. Effects of solvent, ketone content, and ketone structure on the lifetime of the chromophores and the quantum yield of polymer chain scission were investigated. Solvent polarity has a pronounced effect on the chain scission quantum yield (Φ_s) of poly(styrene-*co*-phenyl vinyl ketone) (pS–PVK). This solvent effect can be interpreted as a compromise between two opposing effects. In polar solvents H-bond formation enhances the quantum yield of scission, while the polar solvent exerts a polymer coil contracting effect, which leads ultimately to reduction in the rate of polymer chain scission. Dependence of Φ_s on PVK content in pS–PVK originates in the large chemical reactivity difference in the two comonomers, which leads to an inhomogeneous distribution of ketone in the copolymer at high conversion.

Study of the kinetics and mechanisms of photochemical reactions of small-molecule carbonyl compounds in the gas phase[1] and in solution[2,3] is highly advanced and extensive. While it is found that the photochemical behavior of the carbonyl chromophore in long-chain polymers often does not deviate much from that in their small-molecule analogues, significant differences sometimes occur.[4] These differences often reflect the characteristic long-chain nature of the polymer and the restriction of the environment on the dynamics of the polymer chains. Thus, studies of photochemistry of ketone polymers have provided a great deal of information for the understanding of polymer structure and the dynamics of polymer reactions.

The major photochemical reactions originating from the carbonyl n–π^* excited state in the photolysis of polymers containing pendant carbonyl chromophores will be the Norrish type I α-cleavage, giving free radicals, and the type II photoelimination to form an olefin and a lower ketone. The type II reaction leads to polymer main-chain scission

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Table I
Characteristics of Polymers

polymer	ketone content,[a] mol %	$\bar{M}_n$[b]	polydispersity[c]
poly(styrene-*co*-phenyl vinyl ketone)	7.6	348 000	2.6
	7.5	476 000	1.9
	3.6	513 000	2.2[d]
	1.1	489 000	2.1[d]
	0.8	395 000	
poly(styrene-*co*-phenyl isopropenyl ketone)	3.1	80 000	2.5
	9.1	51 000	1.9
	12.1	53 000	2.2

[a] Determined by UV absorption. [b] By osmometry, in toluene at 25 °C. [c] By GPC, in toluene at 25 °C. [d] Assuming $\bar{M}_w \simeq \bar{M}_v$.

and hence a decrease in the polymer molecular weight. The type I reaction is important only when a tertiary radical is generated and the environment permits a diffusional separation of the product radical pairs.[4a]

This paper reports studies of the kinetics and mechanisms of the type II photoelimination reaction of some styrene–vinyl aromatic ketone copolymers in solution. Effects of solvent, ketone content, and ketone structure on the lifetime of the chromophores and the quantum yield of polymer chain scission were investigated.

Experimental Section

Polymers. A list of the polymers used is given in Table I. The samples were synthesized and characterized in the authors' laboratory. Copolymers of styrene and phenyl vinyl ketone (pS–PVK) and styrene and phenyl isopropenyl ketone (pS–PIPK) were made by emulsion polymerization.[5,6] Phenyl isopropenyl ketone (PIPK) was prepared from propiophenone by a modified Mannich reaction, followed by steam distillation. The copolymer pS–PIPK was prepared by emulsion polymerization at 75 °C for 16 h with the use of 0.2 wt % ammonium persulfate and 0.8 wt % Ultra-Wet K an alkylaryl sulfate) as initiator and emulsifier, respectively.[6] The polymers were dried first in a vacuum oven and then on a high-vacuum line for several days to constant weight. The ketone mole ratio of the copolymers was determined by UV spectroscopy.[7] Extinction coefficients for the ketone chromophores were taken from the literature values for the homopolymer of phenyl vinyl ketone (PVK)[8] and PIPK.[6] Polymer characterization and sample preparation procedures were reported in previous papers.[7] Mark–Houwink coefficients in various solvents for polystyrene are available in the literature.[9]

Chemicals. All solvents used were either spectroscopic or reagent grade (Fisher). They were freshly distilled before use.

Apparatus and Procedure. The arrangement of the apparatus and procedures for polymer solution photolysis have been described previously.[7] Isolation of the 364- and 313-nm bands from the medium-pressure mercury light source was achieved with Jena-Schott narrow-band interference filters.

The kinetics of polymer chain scission was followed by measuring the solution viscosity after different periods of photolysis. If, during a random degradation process, a polymer with initial number-average molecular weight $\bar{M}_n{}^0$ undergoes an average of s scissions per chain, the total number of molecular species at the conclusion of the degradation will be $(1 + s) \sum_i n_i$, where n_i is defined from $\bar{M}_n{}^0$ as follows:

$$\bar{M}_n{}^0 = \sum_i n_i M_i / \sum_i n_i \tag{1}$$

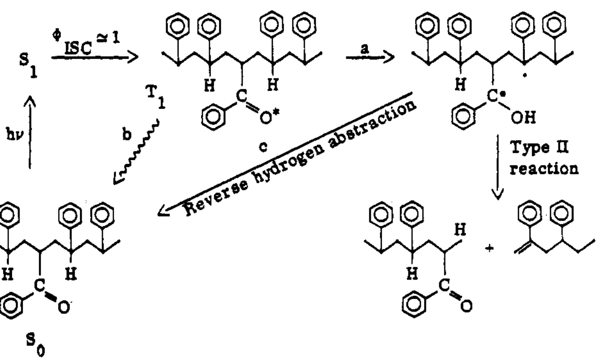
The number-average molecular weight for the polymer after degradtion will then be

$$\bar{M}_n = \sum_i n_i M_i / (1 + s) \sum_i n_i \tag{2}$$

so that the average number of scissions per chain is

$$s = (\bar{M}_n{}^0 / \bar{M}_n) - 1 \tag{3}$$

Scheme I



As shown by Amerik and Guillet,[10a] eq 3 can be approximated with minimal error by

$$s = (\bar{M}_v{}^0 / \bar{M}_v) - 1 \tag{4}$$

The total number of moles X of polymer chain breaks will then be given by

$$X = \frac{w}{\bar{M}_n{}^0}\left(\frac{\bar{M}_n{}^0}{\bar{M}_n} - 1\right) \simeq \frac{w}{\bar{M}_n{}^0}\left(\frac{\bar{M}_v{}^0}{\bar{M}_v} - 1\right) \tag{5}$$

where w is the weight in grams of the polymer undergoing degradation.

Nemzek and Guillet[10b] have applied computer simulation techniques to polymer systems of various initial molecular weight distributions and concluded that if the initial polydispersity γ_0 falls in the range $1.5 < \gamma_0 < 2.5$, a deviation smaller than 10% can be expected through the use of eq 5.

In the case of photodegradation, the quantum yield of polymer chain scission is defined by

$$\Phi_s = \frac{X}{I_A t} \simeq \frac{w[(\bar{M}_v{}^0/\bar{M}_v) - 1]}{\bar{M}_n{}^0 I_A t} \tag{6}$$

where I_A is the number of einsteins of photons absorbed by the polymer per unit time, obtained by absorbance measurements and actinometry, and t is the period of irradiation. $\bar{M}_v{}^0$ and $\bar{M}_v$ are determined by measurement of the intrinsic viscosity of the solution and application of the Mark–Houwink equation.

In practice, quantum yields of chain scission are determined by plotting the number of chain scissions per molecule against irradiation time. The initial slope $\Delta s/\Delta t$ of the plot is then used for quantum yield calculations

$$\Phi_s = \frac{w}{\bar{M}_n{}^0} \frac{\Delta s/\Delta t}{I_A} \tag{7}$$

The extrapolation of the chain scission quantum yield to zero conversion minimizes errors that might arise from internal filtering and quenching of excited reactants by photoproducts. The use of automatic viscometry makes it possible to monitor polymer chain scission at the earliest stages of the photodegradation process, so that $\Delta s/\Delta t$ in eq 7 can be determined with high accuracy. Temperature of the solution for photolysis was controlled by a Tamson thermobath with a temperature variation of ±0.1 °C.

Values of Mark–Houwink constants, K and a, for polystyrene in different solvents were found in the literature.[9] Correction of the flow time for solvent evaporation during photolysis was performed in the quantum yield calculations.

Results and Discussion

Kinetics of Type II Photoelimination. Upon excitation to an n–π* state, aromatic ketones proceed to the triplet with unit quantum yield of intersystem crossing. In the presence of a γ-hydrogen atom, two major processes deplete the excited triplet chromophore: intramolecular hydrogen abstraction followed by the type II elimination, and radiationless decay of the triplet to the ground state. This is illustrated by Scheme I with pS–PVK as an ex-

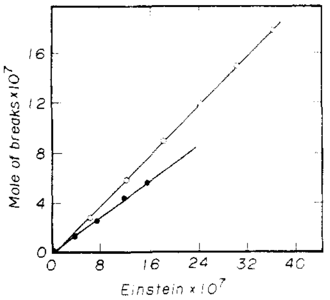
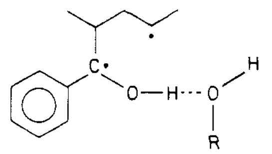


Figure 1. Photolysis of poly(styrene-co-phenyl vinyl ketone) (7.6%) in benzene solution: (○) at 36.5 °C; (●) at 25.2 °C.

ample. For the pS–PVK copolymer, the type II reaction results in polymer chain scission, as shown experimentally in Figure 1. The quantum yield for main-chain scission (Φ_s) of pS–PVK (7.6%) was 0.42 ± 0.02 in benzene at 25.2 °C. This is in good agreement with literature values reported for small-molecule model compounds (0.43 for butyrophenone[11] and 0.50 for γ-phenylbutyrophenone[12]).

At 25.2 °C the Stern–Volmer quenching constant $k_q\tau_T$, determined with naphthalene as triplet quencher, is 212 ± 5 M^{-1}, from which the triplet lifetime τ_T can be estimated at 42 ns. This $k_q\tau_T$ is in good agreement with the literature value for the same copolymer determined at 30 °C ($k_q\tau$ = 183 M^{-1})[7] and is higher than that reported for the PVK homopolymer (PPVK; $k_q\tau$ = 82 M^{-1}), which corresponds to a triplet lifetime of 7.5 ns.[13] This low value is presumably due to the occurrence of triplet migration in the homopolymer, resulting in a sixfold reduction in the lifetime of the PVK triplet.

As shown in Scheme I, the type II process proceeds via a 1-hyroxy-1,4-biradical. Wagner[14] has demonstrated that addition of a Lewis base such as alcohol (ROH) leads to hydrogen bond formation between the alcohol and the biradical, as shown:



This would suppress the reverse hydrogen abstraction path (c) and would cause an increase in the type II elimination quantum yield. Indeed, it has been shown that at a sufficiently high alcohol concentration, the quantum yield for type II reaction approaches unity.[14] This implies that the formation of the biradical (path a) occurs with a quantum efficiency close to unity and that direct radiationless decay (b) from the triplet does not compete significantly with γ-hydrogen abstraction (a). In fact, Lewis[15] has shown that k_b, the rate constant for radiationless decay directly from triplet, is smaller than 10^6 s^{-1} for small-molecule aryl ketones in benzene solution, which is much smaller than the known values of k_a (ca. 10^8).[12] Thus the triplet species returns to ground state radiationlessly via a combination of paths a and c.

Solvent Effects. As mentioned previously, in polar solvents the quantum yields for the type II reactions of triplet ketones are enhanced, presumably because hydrogen bonding from the hydroxy biradical to the solvent inhibits the biradical disproportionation to ground-state reactant but leaves the cleavage reaction unaffected.[14,16] In a polymer solution, solvent polarity exerts a pronounced effect on the conformation of the polymer chain.[17] In a good solvent, the polymer coil expands either because of a favorable solvation of the chain or because the weak solvent–polymer interaction is overcome by the stronger intrachain repulsion. On the other hand, in a poor solvent the solvent–polymer repulsive interaction is strong and the polymer coil contracts. This property of polymer solution is usually reflected in the value of the Mark–Houwink coefficient α. In a good solvent an expanded polymer coil generally is associated with a high α value.

Table II
Effect of Solvent on pS–PVK Chain Scission Quantum Yield[a]

solvent	Φ_s[b]	ϵ[c]	α[d]
benzene	0.39 (0.42)[e]	2.28	0.73
chlorobenzene	0.36	5.62	0.749
dichlorobenzene	0.36	9.93	0.677
1-chlorobutane	0.49	7.39	0.659
1,2-dichloroethane	0.51	10.36	0.66
toluene	0.38		0.75
90% toluene–10% methanol	0.38		0.715
80% toluene–20% methanol	0.52		0.612

[a] pS–PVK (7.5%), 25 °C, irradiated at 313 nm. [b] Estimated error <±5%. [c] Dielectric constant of solvent. [d] Mark–Houwink α parameter (ref 9). [e] pS–PVK (7.6%).

Table III
Dependence of Φ_s on Ketone Content in pS–PVK[a]

PVK, mol %	Φ_s	PVK, mol %	Φ_s
0.8	0.06	7.5	0.39
1.1	0.13	7.6	0.42
3.6	0.15		

[a] In benzene, at 25 °C, irradiated at 313 nm.

Variations of chain scission quantum yield with solvent in polymeric ketones such as pS–PVK show the effects summarized in Table II. Methanol is a nonsolvent for ordinary nonpolar polymers so that a high concentration of methanol will lead to polymer precipitation. However, alcohols are capable of hydrogen bond formation, as demonstrated by Wagner,[14] who showed that 10% *tert*-butyl alcohol caused a 93% increase in the photoscission quantum yield of valerophenone in hexane. It would seem, therefore, that the value of 0.38 for Φ_s of pS–PVK in 90% toluene–10% methanol shown in Table II, which is the same as the Φ_s value in neat toluene, indicates that the biradical stabilization effect of the alcohol is compensated by the coil-contracting effect of the nonsolvent. The latter effect leads to a compact polymer coil in which access to a conformation favorable for the type II reaction is more difficult. As the concentration of the methanol is increased, the hydrogen-bonding stabilization effect predominates, and the Φ_s value increased to 0.52 in a 80% toluene–20% methanol mixture.

As shown in Table II, the effects of aromatic and aliphatic chlorinated hydrocarbon solvents are not as pronounced as that of the alcohol. Φ_s values in aromatic solvents fail to correlate with either solvent polarity or polymer coil compactness. In chlorinated aliphatic solvents, higher solvent polarity leads to an increase in quantum yield of main-chain scission, illustrating the solvation effect of the polar solvent on the biradical intermediate.

Effect of Ketone Content. An increase in quantum yield of main-chain scission with increasing ketone content was first observed on the study of the methyl methacrylate–methacrylophenone copolymer system,[18] although the cause for this increase was unknown. This dependence of main-chain scission quantum yield on ketone content was also observed in pS–PVK copolymer systems. The results are listed in Table III.

The sequential structure of a copolymer depends on two factors, namely the monomer feed ratio and the monomer

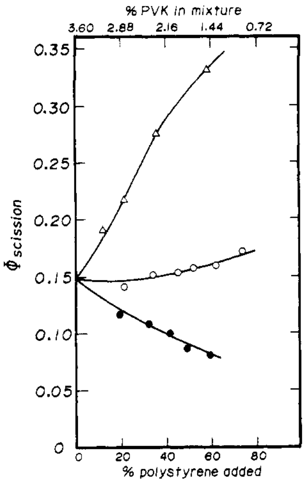


Figure 2. Dependence of Φ on amount of "inert" polystyrene ($\bar{M}_{n_1}$ = photoactive polymer polystyrene, $\bar{M}_{n_2}$ = photoinactive): (△) $\bar{M}_{n_1} = 513000$, $\bar{M}_{n_2} = 171000$; (○) $\bar{M}_{n_1} = 513000$, $\bar{M}_{n_2} = 388000$; (●) $\bar{M}_{n_1} = 513000$, $\bar{M}_{n_2} = 748000$.

reactivity ratios. Feed ratios may be varied to change the copolymer composition. The monomer reactivity ratios, r_1 and r_2, which are properties of the monomers themselves, are defined as ratios of the rate constant for addition of a given radical to its own monomer to that for addition to the other monomer.[19] For the copolymerization of styrene and phenyl vinyl ketone, styrene has an r_1 value of 0.107 and PVK has an r_2 of 1.10.[20] This shows that the PVK is much more reactive than the styrene monomer and hence the first polymer formed contains a disporportionate amount of PVK. Later in the copolymerization the PVK monomer is largely consumed and the polymer formed is essentially a homopolymer of styrene. Hence, if polymerization is allowed to proceed to high conversion, considerable variations will occur in the actual PVK content of individual polymer chains.

The decrease of Φ_s values of pS–PVK at low PVK content can be readily explained by this reactivity ratio difference of the monomers. Since these copolymers were prepared with a low ketone feed ratio (<5%) and carried to high conversion (>50%), nearly all of the more reactive PVK monomer was consumed in the early stages of the copolymerization, resulting in a high ketone content in a few chains and a large number of polymer chains that contained only styrene. Polystyrene does not undergo photodegradation when irradiated in the near-UV range in the absence of oxygen. The inclusion of large numbers of nearly inactive polystyrene chains will result in quantum yield variation for chain scission, which is dependent on the $\bar{M}_n$ of the inactive polystyrene chain. As the ketone content in the monomer mixture increases, there is more likelihood of incorporation of PVK monomer into all the polystyrene chains, and the number of the photoinactive chains is reduced. This would give an observed increase in Φ_s at higher PVK mol % in the copolymer. However, it is worth pointing out that the assumption of random scission, which is inherent in the quantum yield calculation and in the viscometric molecular weight determination, is not valid for polymers with nonuniform distributions of chromophores. Hence great care is necessary in preparing copolymers with comonomers of widely different reactivity.

Photolysis of Blends of PS and pS–PVK. In order to test this postulate, systems containing the styrene–PVK copolymer and a controlled amount of polystyrene standards were photolyzed. The observed chain scission quantum yield variations are shown in Figure 2. These results demonstrate that the presence of pure, photochemically inactive polystyrene molecules will alter the accuracy of the photoscission quantum yield measurements as determined by solution viscometry.

The results shown in Figure 2 illustrate the difficulties of obtaining accurate quantum yield data on copolymer samples that are not of uniform composition. The quantum yield was calculated from eq 6. The effect of adding photoinactive polystyrene depends on its molecular weight. If the molecular weight is lower than that of the copolymer, then a higher quantum yield is given by this relation, whereas the addition of high molecular weight polymer causes a significant reduction in the calculated quantum yield. This is presumably because of the influence of $\bar{M}_n^0$ in the denominator of eq 6. This makes Φ_s inversely proportional to the measured viscosity (or molecular weight) of the starting polymer mixture. Since in a copolymerizing system such as styrene–PVK it would be expected that the inert styrene polymer made after the PVK was used up would be of higher molecular weight than the copolymer, these experiments support our contention that the low quantum yields observed for pS–PVK copolymers with less than 7% PVK are not inherent but are artifacts resulting from heterogeneous composition distributions. We would therefore expect that a uniform copolymer of styrene–PVK containing 1% or less of PVK would have a Φ value approaching 0.4.

The effect of ketone content on the triplet lifetime in the pS–PVK system is shown in Table IV. In view of the heterogeneity of the copolymers only the value for the 7.6% PVK copolymer can be considered to be reliable.

Table IV
Effect of Ketone Content on Triplet Lifetime of pS-PVK in Benzene at 25 °C

PVK, mol % in polymer	Φ_s	$k_q\tau_T$,[a] M^{-1}	τ_T,[b] ns
1.1	0.13	130	26.0
3.6	0.15	89	17.8
7.6	0.42	212	42.4

[a] Irradiated at 364 nm, naphthalene as quencher, $k_q\tau_T$ from Stern–Volmer plot. [a] Assuming $k_q = 5.0 \times 10^9$ M^{-1} s^{-1}.

Table V
Dependence of Φ_s on Ketone Content in pS-PIPK[a]

PIPK, mol %	Φ_s
3.1	0.37
9.1	0.36
12.1	0.36

[a] In benzene, at 25 °C, irradiated at 313 nm.

Poly(styrene-*co*-phenyl isopropenyl ketone) Copolymers. In the pS–PIPK system, Table V shows that Φ_s values are independent of the ketone content. In this case the values of the monomer reactivity ratios for the styrene–phenyl isopropenyl ketone system are not available in the literature. However, PIPK monomer does not homopolymerize,[21a] so that the value of the reactivity ratio for PIPK monomer in the compolymerization must be zero. The reactivity ratio for styrene in the styrene–methyl isopropenyl ketone copolymerization has been determined to be 0.44.[21b] By analogy, the copolymer pS–PIPK would therefore be expected to have a random distribution of isolated PIPK units in a polymer in which styrene units predominate. There should always be some active chromophores (PIPK) present in each polystyrene chain, and the homogeneity of the ketone chromophore distribution results in the observed constancy of Φ_s with ketone content.

Competition between Type I and Type II Processes. Competitive type I and type II photoreactions have long been known to occur, in both small-molecule[22] and poly-

Table VI
Effect of Temperature on Triplet Lifetime and Quantum Yield of Chain Scission of pS–PIPK (9.1%)[a]

temp, °C	Φ_s[b]	$k_q\tau_T$,[c] M^{-1}
8.2	0.29	89
15.8	0.33	69
25.2	0.36	57
36.5	0.39	46
55.0	0.40	42

[a] In benzene. [b] Irradiated at 313 nm. [c] Irradiated at 364 nm, naphthalene quencher, from Stern–Volmer plot.

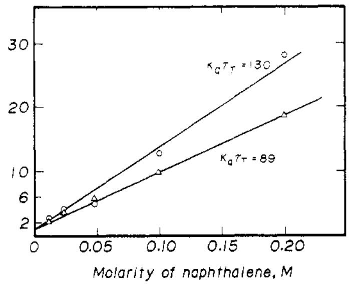


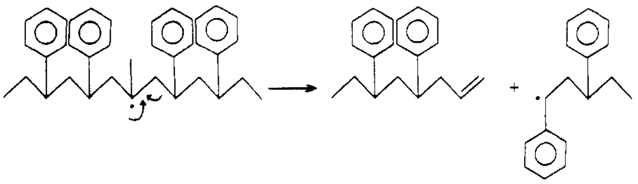
Figure 3. Stern–Volmer plot of naphthalene quenching pS–PVK scission in benzene at 25 °C (irradiation at 364 nm): (△) 3.6% PVK; (○) 1.07% PVK.

meric dialkyl ketones.[23] The type I α-cleavage has also been observed in benzyl phenyl ketones[24] and in *tert*-alkyl phenyl ketones[25] in which the α-cleavage generates relatively stable free radicals. The rate constants of α-cleavage for *tert*-alkyl phenyl ketones are usually 2 orders of magnitude lower than those for dialkyl ketones,[22,25] possibly because the lower triplet energies of phenyl ketones make α-cleavage less exothermic.[3,25] As a result it would be interesting to see whether the type I reaction competes in a polymeric *tert*-alkyl phenyl ketone system such as pS–PIPK.

The quantum yield and quenching data for pS–PIPK (9.1%) are given in Table VI. The value of 0.36 for Φ_s in benzene at 25.2 °C is somewhat higher than the value determined in dichloroethane (0.26).[6] The Stern–Volmer constant for pS–PIPK at 25.2 °C, i.e., 57 M^{-1}, is close to literature values of 44[25b] or 48 M^{-1}[26] determined for the model compound α,α-dimethylvalerophenone.

The smaller Stern–Volmer constants indicate that the triplet lifetime of the PIPK $n-\pi^*$ chromophore is considerably shorter than that of PVK (see Figure 3). The shorter lifetime in pS–PIPK could reasonably be attributed to the presence of a competing type I α-cleavage reaction, which in addition significantly depletes the triplet excited state. The primary radicals formed may recombine in the solvent cage or undergo further radical reactions.[25,26] The chemistry of the macromolecular radicals generated from the type I cleavage is not well characterized at the present time.

The quantum yields of main-chain scission for pS–PIPK are quite high (Table VI). Since the intrinsic reactivity of the carbonyl $n-\pi^*$ toward hydrogen abstraction is relatively insensitive to the effect of α-substituents, the rate constants of type II reactions for pS–PVK, i.e., k_a, k_c and k_{II} as shown in Scheme I, might be expected to be similar to those for pS–PIPK copolymer. On the basis of this assumption and applying the τ_T value for pS–PIPK, the quantum yield of type II photoelimination for pS–PIPK was estimated to be 0.11 at 25.2 °C, lower than the value given in Table V. This suggests that some of the macromolecular radicals generated from type I cleavage may undergo chemical reactions that also lead to polymer main-chain scission. One possibility is the following disproportionation reaction:



Further investigations to confirm this speculation are now in progress. In conclusion, this study showed that the solvent effects are more complex than in simple model compounds, presumably because the increased stability of the biradical caused by addition of the hydrogen-bonding alcohols is counteracted by unfavorable conformations induced by contraction of the polymer chain in poorer solvents. Whereas the quantum yields for chain scission in pS–PIPK copolymers are independent of the ketone concentration in the polymer chain, as predicted from theory, that of pS–PVK is not. It is suggested that this is because the reactivity ratios of styrene and phenyl vinyl ketone are such that wide variations in copolymer composition are obtained between the beginning and the end of the polymerization. This compositional heterogeneity leads to artificially low quantum yields for polymers with low PVK content.

From consideration of the triplet lifetimes and quantum yields for pS–PIPK there is some evidence for the possibility that up to two-thirds of the observed chain scission could come from β-scission of the tertiary radicals produced by a Norrish type I process.

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Photochemistry of Ketone Polymers. 19. Temperature and Solvent Effects in the Quenching of Ketone n–π^* States by Hydroperoxy and Peroxy Groups

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ABSTRACT: Studies of the photolysis of ketone-containing polymers such as poly(styrene-*co*-phenyl vinyl ketone) and poly(styrene-*co*-methyl isopropenyl ketone) in the presence of *tert*-butyl hydroperoxide show that both the singlet and triplet n–π^* states of the ketones are quenched by the peroxide at diffusion-controlled rates. Temperature and solvent effects in the quenching process were studied. The quenching constants and Arrhenius parameters for the triplet quenching are indicative of a bimolecular collisional process. The inverse dependence on temperature of the singlet quenching constant indicates a possibility of reversible exciplex formation in the quenching process. The observed solvent effects and the correlation of quenching constants with oxidation–reduction potential also seem to indicate a polar exciplex is a possible intermediate in the ketone–peroxide quenching process.

Photochemical or thermal homolysis of hydroperoxides and peroxides generates free radicals that initiate autooxidation chain reactions in lipid peroxidation[1] and in polymer oxidation.[2] This leads to the destruction of the biological membrane systems and a deterioration of polymer physical properties. Since aliphatic hydroperoxides and peroxides are only weakly absorbing in the near-ultraviolet and visible region, more efficient initiation of the free radical chain reactions could involve energy transfer from the excited states of more strongly absorbing chromophores to peroxy systems, causing cleavage of the –O–O– linkage.[3a] Both aromatic and aliphatic ketones and aldehydes, for example, have much higher extinction coefficients than do hydroperoxides[3b] in the near-UV, in which the carbonyl compounds are promoted to the n–π^* excited state. Photosensitized decomposition of small-molecule peroxides by different aromatic ketones has been demonstrated experimentally.[4a,b] In a previous paper it was shown that the quenching of the aliphatic and aromatic carbonyl n–π^* state by hydroperoxides and peroxides is an efficient process.[3b] Quantitative quenching measurements revealed that the rate constant of energy transfer is of the order of 10^9, i.e., close to the diffusion-controlled limit. It is known that ketonic carbonyl groups, along with other carbonyls such as ester and acid, accumulate in hydrocarbon polymer systems as the oxidation process continues,[2] while the hydroperoxide and the peroxy groups quickly reach a stationary state, usually at a relatively low concentration. Energy transfer from the photoexcited carbonyl to the peroxy groups thus may be an essential step in maintaining or accelerating the rate of degradation. Similar proposals have more recently been made by Geuskens et al. to explain certain features in the photooxidation of solid polystyrene.[4c]

Stewart et al. have shown that in the case of triplet benzophenone quenching by *tert*-butyl hydroperoxide, around 65% of the quenching events involve hydrogen abstraction from the O–H group.[5] They also showed that the behavior of polymer-bound chromophores is similar to that of small molecules.

Table I
Structure and Molar Absorptivity (313 nm) of Polymers and Reagents

compd	ϵ_{313},[a] M^{-1} cm^{-1}	compd	ϵ_{313},[a] M^{-1} cm^{-1}
pS–PVK (7.6%)	87[b]	decanoyl peroxide	1.45[c]
pS–MIPK (6%)	19[b]	Luperox 2.5, 2.5	0.36[c]
t-BOOH	0.27[c]	acetone	4[c]
di-*tert*-butyl peroxide	0.93	3,3-dimethyl-2-butanone	10[c]

[a] Molarity in ketone units. [b] In benzene. [c] In 1,2-dichloroethane.

A study of the temperature and solvent effects in the hydroperoxide quenching of aliphatic and aromatic ketone n–π^* states in polymers is reported in this paper. Thus study may provide information about the nature of the interactions involved in the energy-transfer step.

Experimental Section

Materials. Polymers. Poly(styrene-*co*-phenyl vinyl ketone) (7%) (pS–PVK (7%)) and poly(styrene-*co*-methy isopropenyl ketone) (6%) (pS–MIPK (6%)) copolymers were identical with those employed in the previous studies.[3b] The number-average molecular weights are 348 000 and 71 400, respectively. The polydispersity of these polymers is 1.9 and 2.9 for pS–PVK (7%) and pS–MIPK (6%), respectively, and both lie in a suitable range for viscometric determination of polymer chain scission kinetics.

Chemicals. Purification of *tert*-butyl hydroperoxide (*t*-BOOH) and di-*tert*-butyl peroxide was described in a previous paper.[3b] Hydrogen peroxide was obtained by fractional distillation of a commercial 30% solution at reduced pressure, followed by extraction in anhydrous ether. Separation of concentrated H_2O_2 was achieved by evaporation of the ether solution. A stock solution of H_2O_2 in benzene was prepared. The molarity of the H_2O_2 was determined by iodometry. The molar absorptivities of the ketone copolymers and the small molecules determined with a Cary 14 UV spectrometer at 313 nm are shown in Table I. Quantum yields

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