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Photodegradation of Poly(phenyl vinyl ketones) Containing β-Phenylpropiophenone Moieties[1a]

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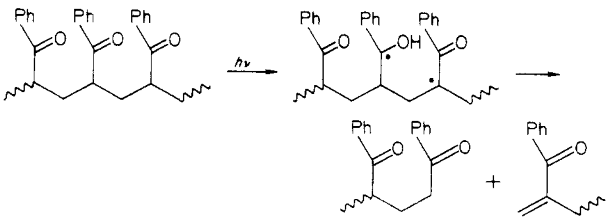
ABSTRACT: The photodegradation of poly(phenyl vinyl ketone) and its copolymers with the methacrylate esters of two para-hydroxy-substituted derivatives of β-phenylpropiophenone (1) was investigated in chlorobenzene solution at 30 °C. Only modest decreases in the photodegradation quantum yields are observed for the copolymers relative to that for poly(phenyl vinyl ketone), and this is rationalized in terms of structural constraints on the energy-transfer process. These result from the fact that the β-phenylpropiophenone moieties are held at considerable distances from their nearest-neighbor benzoyl groups on the polymer backbone, distances that are too large for efficient triplet energy transfer to take place. The relative effectiveness with which the isomeric methacrylate esters stabilize the polymer is consistent with the predominance of an intracoil quenching mechanism. The parent substrate, 1, quenches phenylalkyl ketone triplets with a rate constant of $k_q = 1.7 \times 10^9$ M^{-1} s^{-1} in benzene solution at room temperature.

Introduction

The photodegradation of aromatic ketone-based polymers, e.g., poly(phenyl vinyl ketone) (pPVK, eq 1), has been the subject of numerous investigations.[3-9] These polymers are known to undergo photodegradation primarily via the Norrish II reaction from the triplet manifold.[5,6a]



(1)

The initial quantum yield for photodegradation of pPVK is ca. 0.24;[5,6a,8d,9b] the efficiency of this process decreases rapidly as photodegradation proceeds as a result of the accumulation of α,β-unsaturated ketone end groups, which act as efficient triplet quenchers.[8b]

Laser flash photolysis studies have unraveled many of the mechanistic details pertaining to the photodegradation of polymers of this type. The triplet lifetime in carefully purified samples (τ = 55 ns)[9c,10] is a factor of ca. 20 longer than that of monomeric phenylalkyl ketones capable of intramolecular γ-hydrogen abstraction, such as γ-methylvalerophenone,[11] which may reflect the decreased mobility of the benzoyl group with respect to γ-hydrogens in the polymer. Furthermore, since energy migration in these polymers has been shown to reduce their rate of

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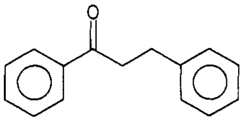
interaction with other substrates,[12] it would not be surprising if the same reduction applied to intramacromolecular processes such as hydrogen abstraction. The decrease in the triplet lifetime with the extent of degradation parallels the decrease in the quantum yield for photodegradation.[9c] A variety of studies have allowed the conclusion that triplet energy migration (i.e., "triplet energy hopping") occurs rather efficiently in pPVK;[6d,9bc,11] the calculated hopping frequency of $k = 10^{12}$ s^{-1} corresponds to an estimate of ca. 700 for the number of benzoyl groups that are visited by the excitation during the lifetime of the triplet state.[9b]

As the photodegradative behavior of partially degraded samples of pPVK would suggest, it is possible to improve the photostability of these polymers considerably by incorporating small amounts of triplet quenchers in the polymer chains. Our approach to this has involved doping the polymers with carbonyl substrates whose triplet states are both short-lived and nonreactive (in a degradative sense) but otherwise identical with the reactive chromophores that comprise the bulk of the polymer. One example of this approach has utilized *o*-methylbenzoyl groups;[9c,13] in this case, photoenolization efficiently deactivates the carbonyl n,π^* triplet state and thus provides a triplet energy "sink". The effectiveness with which these substrates stabilize polymers of pPVK is due in large part to the "energy-hopping" phenomenon described earlier.

β-Phenylpropiophenone (1) is another phenylalkyl ketone that, although its absorption spectrum and n,π^* triplet energy are identical with those of other phenylalkyl ketones, possesses an unusually short-lived, nonreactive triplet state.[14] This is known to be the result of deactivating interactions between the localized carbonyl n,π^* triplet and the β-phenyl ring,[14-16] presumably via the intermediacy of an intramolecular exciplex.[17] Unlike (*o*-methylphenyl)alkyl ketones, the short triplet lifetime of β-phenylpropiophenone is the result of nonreactive decay.[14-16]



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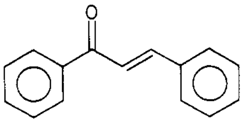
In order to be useful as a polymer photostabilizer, one obvious requirement is that there be a convenient method for incorporating β-phenylpropiophenone moieties into pPVK polymers. Since chalcone (2) is a rather poor monomer (while it copolymerizes readily with styrene,[18,19] it does not do so with either PVK or methyl methacrylate),[19] it is necessary to employ as comonomers derivatives of β-phenylpropiophenone that contain readily polymerizable substituents.



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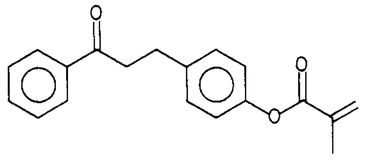
We have shown that the presence of substituents on the β-phenyl ring has an almost negligible effect on the triplet lifetime of β-phenylpropiophenone.[16] Similar behavior is found for derivatives with ring substituents on the benzoyl group, provided that the substituent does not alter the n,π^* character of the lowest triplet state. Thus, the methacrylate esters of para-hydroxy-substituted derivatives (3 and 4) should provide polymerizable β-phenylpropiophenones with triplet states almost identical in character with that of the parent molecule. Indeed, laser flash photolysis studies of copolymers of 3 and 4 with methyl methacrylate have shown that the character of the lowest triplet states of these moieties is unaffected by their incorporation in a polymer matrix.[16]



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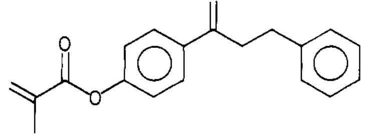

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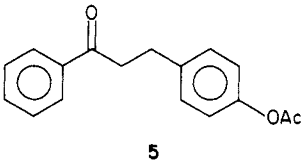
In this report, we examine the suitability of these monomers as polymer photostabilizers by investigating the photodegradation of copolymers of 3 and 4 with phenyl vinyl ketone (PVK). The degradation measurements were carried out with an automatic viscometer based on an earlier design[20] but considerably improved to achieve full automation. This instrument is described in some detail in the Experimental Section.

Results

The methacrylate esters 3 and 4 were synthesized by condensation of methacryloyl chloride with the appropriate para-hydroxy-substituted β-phenylpropiophenone[16,21] and were purified by rapid column chromatography immediately prior to their copolymerization with PVK.

All polymer samples were prepared by free radical polymerization in benzene solution at 50 °C with azobis(isobutyronitrile) as the initiator. In all cases, the polymerizations were allowed to proceed to less than ca. 15% conversion.

The compositions of the copolymer samples were estimated from the relative intensities of the esteric (1740 cm^{-1}) and ketonic (1680 cm^{-1}) carbonyl stretching bands in the infrared spectra of the copolymers in chloroform solution. The extinction coefficient ratio of these two bands in the copolymer samples was assumed to be the same as those for β-(4-acetoxyphenyl)propiophenone (5) and β-phenyl-4-acetoxypropiophenone (6), which were found to be identical under conditions employed for the measurements.



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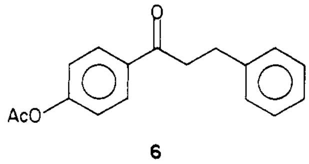

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Several attempts were made to prepare copolymers of 4-acetoxychalcone (7) and PVK with variously proportioned mixtures of the two monomers under the conditions described above. The infrared spectra of the purified polymers (see Experimental Section) that were obtained showed that in no case did incorporation of the chalcone

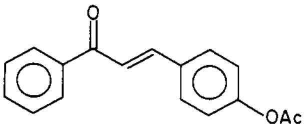

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Table I
Quenching of Monomeric Phenylalkyl Ketone Triplets by β-Phenylpropiophenone (1) and γ-Methylvalerophenone (8)[a]

sensitizer	concn, M	quencher[b]	$10^{-9}k_q$[c]
propiophenone[d]	0.01[e]	**1**	1.69 ± 0.17
	0.05[e]	**1**	1.32 ± 0.16
	f	**8**	1.3
4-methoxyacetophenone[g]	0.01[e]	**1**	1.11 ± 0.13
	0.05[e]	**1**	0.98 ± 0.11
	h	**8**	1.3

[a] In deoxygenated solution at 27 °C. [b] Introduced as aliquots of standard benzene solutions. [c] In units of $M^{-1}\ s^{-1}$. Errors are reported as $\pm 2\sigma$. [d] Triplet decay monitored at 360 nm. [e] In benzene. [f] In heptane; from ref 27. [g] Triplet decay monitored at 380 nm. [h] In heptane: Encinas, M. V.; Scaiano, J. C., unpublished results.

derivative reach a detectable level, even when equimolar mixtures of **7** and PVK were employed in the polymerization.

The rate constants for the quenching of propiophenone and 4-methoxyacetophenone triplets by β-phenylpropiophenone in benzene solution at 27 °C were measured by laser flash photolysis, employing the pulses (337.1 nm, ~10 mJ/pulse, ~8 ns) of a nitrogen laser for excitation and using the computerized facility described in detail elsewhere.[22] Figure 1 shows the plot of k_{decay} vs. [Q] that was obtained for one of these systems; the insert shows a typical decay trace. The quenching rate constants were found to vary only slightly with the concentration of the sensitizer. Thus, while the triplet states of these ketones are approximately isoenergetic,[14,16] reversible triplet energy transfer is essentially precluded by the exceedingly short triplet lifetime of the excited quencher. Table I contains the measured rate constants for quenching of propiophenone (PPP) and 4-methoxyacetophenone (MAP) triplets by β-phenylpropiophenone. For comparison, the table also contains the rates of triplet quenching of the same sensitizers by γ-methylvalerophenone;[23] the short triplet lifetime for this ketone is the result of its efficient Norrish Type II reaction.[11]

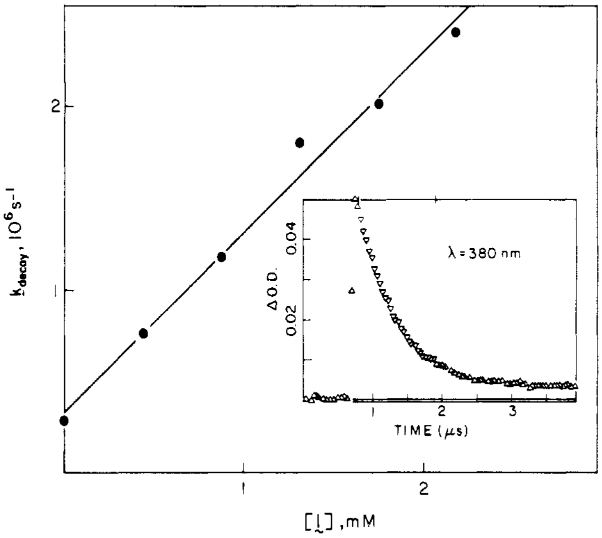


Figure 1. Quenching of *p*-methoxyacetophenone triplets by β-phenylpropiophenone (**1**) in 0.05 M benzene solution at 27 °C: k_{decay} vs. [**1**]. Insert: Typical decay trace, monitored at 380 nm for [**1**] = 1.31 mM.

Photodegradation (340-nm irradiation) of these polymers was carried out in chlorobenzene solution at 30 °C. The extent of degradation was monitored by following the change in viscosity of the solutions (at 30 °C) with time. The samples were contained in an apparatus that consists of a thermostated Ubbelohde viscometer connected to a similarly thermostated quartz irradiation cell. Intrinsic viscosities $[\eta]$ were calculated according to eq 2, where η_{sp}

$$\eta_{\mathrm{sp}}/c = [\eta] + Kc[\eta] \qquad (2)$$

is the specific viscosity, *c* the solution concentration in g/100 mL, and *K* the Huggins constant. A value of *K* = 0.47 (that for pPVK in benzene solution)[5,9c] was employed throughout. A series of preliminary measurements of *K* (using irradiated samples) in chlorobenzene confirmed that the value is within experimental error the same as for benzene. The value of the number of bonds cleaved per initial macromolecule, *S*, was calculated according to eq 3, where $[\eta]_0$ is the intrinsic viscosity of the unirradiated

$$S = ([\eta]_0/[\eta])^{1/\alpha} - 1 \qquad (3)$$

polymer sample. A value of $\alpha = 0.82$ was determined for pPVK in chlorobenzene solution and was employed throughout.[24] Viscosity-average molecular weights, *w*, were estimated according to eq 4. We have employed a value

$$[\eta] = K'W^{\alpha} \qquad (4)$$

of $K' = 2.82 \times 10^{-5}$ (the value for pPVK in benzene)[5] in our calculations, since the intrinsic viscosities calculated for samples of this polymer in chlorobenzene solution according to eq 2 are essentially the same as the values obtained for benzene solutions, for which the constants α, *K*, and *K′* are accurately known.[5,9c]

Our results are summarized in Table II. All these experiments were carried out with solutions whose concentrations were high enough to absorb >99.5% of the incident light. Figure 2 shows the plots of *S* vs. *t* that were obtained from these data.

Quantum yields of chain scission, Φ_{cs}, were calculated with the initial slopes of these plots (first five points)

Table II
Photodegradation of pPVK and Copolymers with 3 and 4[a]

	pPVK[b]			p(**3**-*co*-PVK)[c]		p(**4**-*co*-PVK)[d]	
t, min	$[\eta]$	*S*	*t*, min	$[\eta]$	*S*	$[\eta]$	*S*
0	1.107	0	0	1.048	0	1.098	0
3	0.752	0.613	5	0.634	0.858	0.767	0.558
6	0.568	1.278	10	0.458	1.780	0.590	1.152
9	0.466	1.908	15	0.365	2.677	0.489	1.715
12	0.395	2.567	20	0.311	3.483	0.418	2.293
15	0.352	3.119	25	0.270	4.330	0.370	2.824
18	0.315	3.720	30	0.243	5.071	0.333	3.355
21	0.286	4.316	35	0.223	5.745	0.305	3.853
24	0.262	4.921	40	0.205	6.492	0.282	4.355
27	0.243	5.501	45	0.192	7.115	0.263	4.825
30	0.233	5.837	50	0.181	7.771	0.248	5.281

[a] Irradiated at 340 nm in deoxygenated chlorobenzene solution, 30 °C. [b] *c* = 0.942 g/100 mL; $W = 4.7 \times 10^5$. [c] *c* = 0.768 g/100 mL; $W = 4.4 \times 10^5$. [d] *c* = 0.908 g/100 mL; $W = 4.6 \times 10^5$.

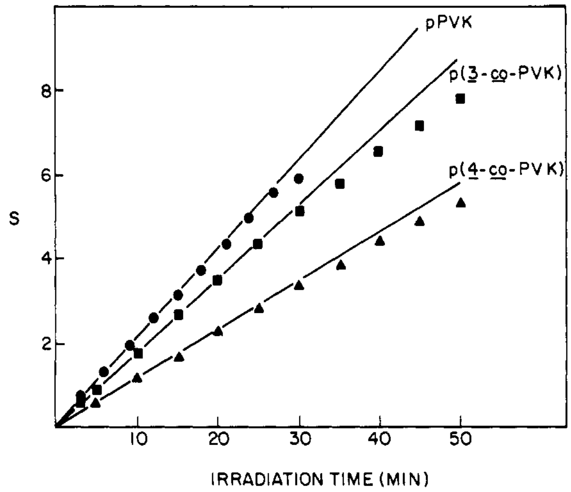


Figure 2. Plot of number of bonds cleaved/initial macromolecule (S) vs. irradiation time for photolysis (340 nm) of pPVK (●), p(3-*co*-PVK) (■), and p(4-*co*-PVK) (▲) in chlorobenzene solution at 30 °C. The solid lines correspond to the initial slopes of the curves, calculated with the first five points in each plot.

Table III
Quantum Yields of Chain Scission (Φ_{cs}) for Photolysis of pPVK and Copolymers with 3 and 4 in Chlorobenzene Solution at 30 °C

polymer	comp[a]	$10^{-5}W$[b]	S/t[c]	$10^7 I_a$[d]	Φ_{cs}[e]
pPVK		4.7	0.210 ± 0.010	2.5 ± 0.2	0.31
p(**3**-*co*-PVK)	15% **3**	4.4	0.170 ± 0.010	3.0 ± 0.2	0.22
p(**4**-*co*-PVK)	6% **4**	4.6	0.109 ± 0.006	3.0 ± 0.2	0.10

[a] Estimated from the infrared spectrum in chloroform solution. [b] Initial viscosity-average molecular weight (eq 4). [c] Initial slope of S vs. t plot in Figure 2; errors as $\pm 2\sigma$. [d] Determined by valerophenone actinometry. [e] Calculated with eq 5; error is ca. 10%.

according to eq 5, where V is the volume of solution irradiated and I_a is the incident light flux (einsteins/min) that

$$\Phi_{cs} = (c/WV)(S/t)/I_a \tag{5}$$

was measured at frequent intervals during the course of the study by valerophenone actinometry, taking the quantum yield for acetophenone formation in benzene as 0.30.[25] The quantum yield of chain scission so obtained for pPVK in chlorobenzene (Φ_{cs} = 0.31) compares favorably with reported values for this polymer in benzene solution.[5,6a,8d,9b] The quantum yields obtained for the three polymers are summarized in Table III.

We wish to comment on our use of viscosity measurements to monitor the photodegradation of these polymers, as opposed to other methods such as gel permeation chromatography. GPC analyses were in fact carried out for each of the polymers studied, both prior to and at the end of the total irradiation period. These analyses (representative GPC traces are available as supplementary material) indicated that extensive photodegradation had indeed occurred, with calculated changes in molecular weight that were in agreement with those obtained from the viscosity measurements. However, several considerations make the use of viscosity measurements a much more sensitive (particularly to monitor low-conversion changes), and certainly more convenient, method of monitoring polymer photodegradation. First, the molecular weight distributions of the polymers, as measured by GPC, were rather broad. Thus, determination of the weight-average molecular weights from the GPC traces is subject to substantially greater error than is interent in the viscosity measurements. Second, for a typical polymer sample examined before and after irradiation for 30 min, the GPC retention time (relative to chlorobenzene) changes by roughly a factor of 2, compared to a fivefold change in the specific viscosity of the solution. Third, analysis of the polymers by GPC to obtain the same number of points as using viscosities would increase substantially the time required for each experiment. For these specific studies viscosimetry is more sensitive and less time-consuming than GPC.

Discussion

The photostability of β-phenylpropiophenone derivatives is well recognized in polymeric[18] as well as in monomeric systems.[14-17] Thus, while the photoreactivity of PVK/styrene copolymers toward Norrish II degradation is similar to that of pPVK itself, copolymers of chalcone (**2**) and styrene show a markedly reduced tendency for photodegradation.[18] The photodegradation quantum yields have been reported to be Φ_{cs} = 0.14 and 0.004 for PVK/styrene and chalcone/styrene copolymers, respectively, in benzene solution.[18a] The triplet lifetime for the chalcone/styrene copolymer was determined by Stern–Volmer quenching studies to be a factor of ca. 15 less than that of the PVK/styrene copolymer. This is consistent with the value of τ = 2 ns determined for p(**2**-*co*-styrene) by laser flash photolysis.[16]

The measured rate constants for quenching of propiophenone (PPP) and 4-methoxyacetophenone (MAP) triplets by β-phenylpropiophenone (Table I) demonstrate that β-phenylpropiophenone is a reasonably efficient quencher of phenylalkyl ketone triplets. The measured rates are a factor of 5 or so less than those generally observed for exothermic triplet energy transfer in solution at room temperature; for example, the rate of quenching of MAP triplets by 1-methylnaphthalene is $k_q = 7 \times 10^9$ M^{-1} s^{-1}.[23] This is presumably due to the fact that in the present case, donor and acceptor triplet states are approximately isoenergetic. In such cases, triplet energy transfer rates are normally significantly less than those for exothermic transfers, as a result of the rather severe entropic requirements for isoenergetic quenching.[23] Energy transfer to **1** from MAP is slightly slower than that from PPP; this is reasonable, since MAP has a somewhat lower triplet energy than PPP.[26] For comparison, Table I also contains rate constants for quenching of the same ketone triplets by γ-methylvalerophenone.[23,27]

Reversibility of triplet energy transfer depends on the donor–acceptor triplet energy difference, the lifetime of the acceptor triplet state, the donor concentration, and the viscosity of the medium.[28] The absence of any appreciable dependence of the triplet quenching rates on donor concentration demonstrates that reversible energy transfer is relatively unimportant in the systems listed in Table I. This is the result of the short triplet lifetimes of the two acceptors. In the case of **1** τ = 1 ns at 27 °C.[15] This is known to be due to deactivating interactions between the localized carbonyl n,π^* triplet and the β-phenyl ring;[15] for γ-methylvalerophenone (τ = 2 ns at 27 °C)[11] the short triplet lifetime is the result of efficient deactivation via the Norrish Type II reaction.

In the case of **1** and substituted derivatives, it is known that the efficiency of the intramolecular deactivation depends directly on the flexibility of the system, i.e., whether or not the excited species can readily achieve the conformation required for deactivation within its lifetime.[15] Our previous study[16] has shown that there is essentially no difference between the triplet lifetimes of poly(methyl methacrylate) copolymers of **3** and **4** and their corresponding monomeric analogues (i.e., **5** and **6**). The above results all suggest that **3** and **4** have the potential to act as efficient photostabilizers when incorporated in PVK copolymers if energy migration efficiently funnels the excitation energy toward these locations.

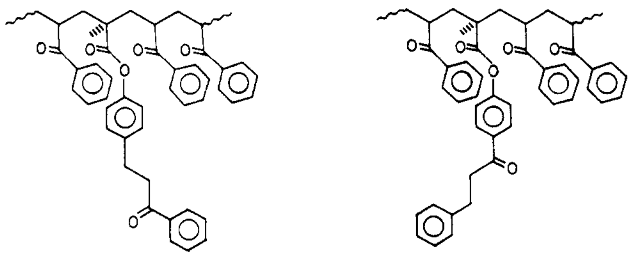
The photodegradation results provide a sensitive measure of the ability of **3** and **4** to alter the photoreactivity of pPVK in this way. The plots of S vs. t (Figure 2) obtained by monitoring the change in viscosity as a function of irradiation time show curvature. This has been noted previously for pPVK[9b] and is believed to be the result of the production of α,β-unsaturated ketone end groups in the polymer as a result of Norrish Type II photodegradation. Since these moieties are reasonably efficient quenchers of phenylalkyl ketone triplets, their growth in abundance as photodegradation proceeds is accompanied by a corresponding decrease in the quantum yield for Norrish Type II degradation.[9c] The fact that the curvature in the S vs. t plots in the present instance is similar for all three polymers presumably indicates that the Norrish Type II process remains the dominant degradative pathway in the copolymers of **3** and **4**.

Since the three polymer samples illustrated in Figure 2 were of similar molecular weight and incident light intensities were reasonably constant, the relative slopes of these plots are proportional to the relative degradation quantum yields. It is clear that some stabilization of the polymers is effected by incorporation of the β-phenylpropiophenone moieties **3** and **4** and, furthermore, that **4** is more effective than **3** in this regard. The quantum yields of chain scission, calculated according to eq 5 (Table III), indicate that **4** is in fact at least 3 times more effective than its isomer (**3**), taking into account that a greater effect is achieved with a lower degree of incorporation in the copolymer. Considering the rather high concentration of β-phenylpropiophenone moieties in the two copolymers, however, the quantum yield data indicate that **3** and **4** are rather ineffective photostabilizers of pPVK. This is in sharp contrast to reported results for *o*-methylacrylophenone (TVK/PVK copolymers, for which decreases in Φ_{cs} of a similar magnitude to those found in the present instance were observed in copolymers containing as little as 1% TVK.[9c,13]

Triplet excitation transfer occurs via the exchange mechanism, which requires close proximity of donor and acceptor moieties in order for efficient transfer to take place.[29] In a polymer, triplet quenching can take place via two mechanisms:[30] intracoil quenching, in which the quencher moiety interacts with excited nearest neighbors, and intercoil quenching, in which the quencher interacts with a donor moiety that is located either on a remote segment of the same polymer chain or on another chain. Since the latter mechanism requires diffusion together of two relatively immobile fragments, it is known to be a markedly slower process than intracoil quenching.[31]

We attribute the relative inefficiency with which **3** and **4** stabilize pPVK to structural constraints on the quenching process; this is illustrated in Chart I with the structures of the two copolymers. In both cases, the β-phenylpropiophenone moieties are rather far removed from the polymer backbone. To the extent that the optimum configuration for intracoil quenching is one that enables overlap between the donor and acceptor benzoyl groups, Chart I further indicates that **4** should be a somewhat more effective quencher than **3**, in agreement with the observed results. It should be noted that our results are not compatible with an intercoil quenching mechanism, since in this case the opposite behavior would be expected for the relative quenching efficiencies of **3** and **4**. In other words, approach by a foreign molecule will be facilitated when the moiety in question extends outside of the main polymer backbone.

Chart I



p(3-co-PVK) p(4-co-PVK)

The high efficiency with which TVK stabilizes pPVK is in sharp contrast to the behavior of **3** and **4**, although this difference is understandable within the framework of the structural arguments presented above. TVK is ideally suited as a photostabilizer of pPVK since in the copolymer the TVK moieties reside in the optimum configuration for intracoil quenching.

Clearly, analogues of **1** cannot be expected to be reasonable photostabilizers of pPVK unless β-phenyl rings can be attached directly to the polymer backbone. It is interesting to note that this situation will be obtained in samples of pPVK synthesized with phenyl radical precursors, such as benzoyl peroxide or phenyllithium, as the initiators, where β-phenyl groups will be present as end groups. The stability of such polymers will, of course, depend substantially on the molecular weight of the polymer.

Conclusions

β-Phenylpropiophenone is an efficient isoenergetic quencher of phenylalkyl ketone triplets, as a result of its short triplet lifetime. In spite of this, incorporation of this moiety in PVK polymers via the methacrylate esters of para-hydroxy-substituted derivatives **3** and **4** provides copolymers with only slightly improved photostability relative to pPVK itself. This is attributed to steric constraints on intracoil triplet quenching, since the β-phenylpropiophenone moieties are held in positions that are rather far removed from the polymer backbone. The somewhat higher photostability of p(4-*co*-PVK) can be explained within the framework of an intracoil quenching mechanism, since the benzoyl group in **4** is in a more favorable position for overlap with nearest-neighbor benzoyl groups on the polymer backbone.

Experimental Section

Benzene and chlorobenzene were both Fisher Reagent grade and were purified by repeated washings with concentrated sulfuric acid, followed by water and saturated aqueous bicarbonate. The solvents were then refluxed over calcium hydride for 24 h and distilled.

The methacrylate esters **3** and **4** were prepared as described previously[16] and were purified by column chromatography (silica gel, dichloromethane) immediately prior to their copolymerization with PVK.

Phenyl vinyl ketone (PVK) was prepared and purified as described previously.[9b] Polymers were prepared in sealed, evacuated tubes by free radical polymerization at 50 °C using azobis(isobutyronitrile) as initiator in degassed benzene solution. The polymerizations were not allowed to proceed past ca. 15% conversion, as qualitatively judged by the viscosities of the reaction mixtures, and were quenched by the addition of spectroscopic grade methanol. The polymers were purified by eight dissolution/precipitation cycles using benzene and methanol and were finally freeze-dried from benzene. All preparations and subsequent handling of the polymers were performed in the dark.

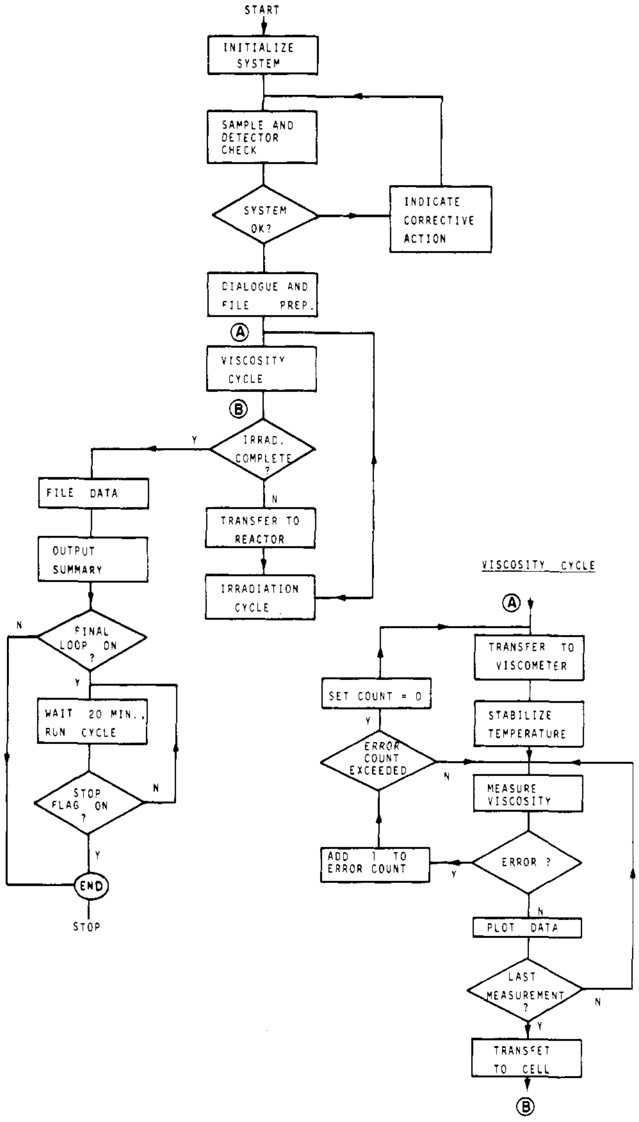


Figure 3. Flow chart showing the sequence used for experiment control and raw data acquisition.

The compositions of the copolymers were determined by infrared spectroscopy. Spectra were recorded on a Perkin-Elmer Model 1330 infrared spectrometer, using chloroform solutions in 1-mm sodium chloride solution cells. Polymer compositions were estimated from the relative intensities of the esteric (1740 cm^{-1}) and ketonic (1680 cm^{-1}) carbonyl stretching bands, using the extinction coefficient ratio $\epsilon_{1740}/\epsilon_{1680} = 1.43$, which was obtained from the spectra of **5** and **6** measured under the same conditions.

Laser flash photolysis experiments employed the pulses (337 nm, ~10 mJ/pulse, 8 ns) of a Molectron UV24 nitrogen laser for excitation and the computerized facility that has been described in detail previously.[22] Samples were contained in 7 × 7 mm^2 cells made of Suprasil quartz (Vitro Dynamics) and were deoxygenated with dry nitrogen prior to the laser flash experiments. The optical densities of the solutions were ca. 0.3 at the laser wavelength, and quenchers were added as aliquots of standard solutions.

Polymer photodegradation studies were carried out in a computer-controlled automatic viscometer system. A similar system, on which some of our components are based, was reported by Guillet et al.[20b] Our system has been interfaced with an Apple II+ microcomputer via a DI09 interface (from Interactive Structures Inc.). The system has been programmed so that it controls completely the experiment, including aspects such as solution degassing and transfers, flow time measurements, irradiation control (timing, temperature stabilization, and stirring), and provides data storage and processing capabilities. The design of the viscosimeter and separate reaction cell, as well as the use of solenoid valves to control flow patterns, was based on the design mentioned before[20b] and, while different in appearance, performed in much the same manner. Our approach to the flow detectors was somewhat different from that published and deserves some comment. Three detectors (as opposed to two in earlier reports)[20b] were used; these monitored the top and bottom levels of the viscometer itself, while the third one monitored flow in either direction between the viscometer and the irradiation cell. The units used are Photon Coupled Interrupter Modules Type H13A2 (General Electric). We have found that these detectors perform quite well under water, after the external contacts have been sealed with epoxy resin. These detectors are held around a capillary tube (~1–2-mm i.d.), the exterior walls of which had been ground to a rectangular shape (3 × 7 mm^2) in the case of the viscometer or a 5 × 2 mm^2 in the case of the liquid-transfer detector. The tubing for the latter was obtained from Vitro Dynamics.

The control module that takes care of timing, stirring, shutters, and the various transfers was entirely redesigned, largely as a matter of convenience, but performs operations similar to those already described in the literature.[20] A block diagram of this unit and schematics are available as supplementary material.

A library of BASIC programs handles the experiment, as well as all calculations and displays. The central one controls the experiment and acquires the raw data. Figure 3 shows a flow chart that effectively describes the experimental sequence. Essentially it consists of four parts: (i) preliminary preparation, which includes detector checks and sample preparation (i.e., degassing), and the initial dialogue with the operator; (ii) the actual experiment, consisting of viscosity and irradiation cycles, along with appropriate stabilization times and transfers; (iii) a final dialogue, file creation, and output; and (iv) what we have called "final loop". This consists of a cycle that moves the liquid up and down the viscometer every 20 min, thus preventing any solid polymer from depositing in the delicate capillary tubes in the viscometer module, and allows the system to sit unattended for long periods of time (e.g., during overnight experiments) after the experiment has ended. Figure 3 also shows a detail of the viscosity cycle (bottom right), which illustrates the sequence of events, along with the error-logging part of it. Errors are usually caused by bubbles; sometimes this reflects an incomplete transfer from the reaction cell. In this case the system automatically attempts to repeat the transfer.

Flow times used for the calculation of solution viscosities are the average of 5–7 measurements and are reproducible to ±0.002 s. The solutions (20 mL; 0.7–1.0 g/100 mL; $OD_{340nm} > 2$) were contained in the thermostated Suprasil quartz cell (2 × 2 × 7 cm^3; connected via Teflon tubing to the Ubbelohde viscometer) and were irradiated with the filtered output from a 150-W Oriel high-pressure xenon arc lamp (340-nm interference filter). Sample irradiation and flow time measurements were both carried out at 30.0 ± 0.01 °C.

Lamp intensities were checked frequently by valerophenone actinometry, using 0.024 M solutions of valerophenone in benzene and the same apparatus and conditions as employed for the polymer irradiations. The yield of acetophenone was measured by gas chromatography (Varian Model 1400 gas chromatograph, fitted with a flame ionization detector and a 6 ft × $^1/_8$ in. 15% OV-101/Chromosorb stainless steel column). Incident-light fluxes were calculated with a value of $\Phi = 0.30$ for the quantum yield of acetophenone from valerophenone.[25]

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Registry No. 1, 1083-30-3; pPVK (homopolymer), 26742-84-7; p(3-*co*-PVK) (copolymer), 98395-67-6; p(4-*co*-PVK) (copolymer), 98395-68-7; propiophenone, 93-55-0; 4-methoxyacetophenone, 100-06-1; γ-methylvalerophenone, 2050-07-9.

Supplementary Material Available: Figures 4 and 5, giving details of the control system used in these experiments (block diagram and schematics), and Figure 6, illustrating GPC measurements for one sample (6 pages). Ordering information is given on any current masthead page.

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Determination of the Tacticity and Analysis of the pH Titration of Poly(acrylic acid) by ^{1}H and ^{13}C NMR

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ABSTRACT: The tacticity, to triad and partial pentad resolution, of a commercial sample of poly(acrylic acid) was determined by ^{1}H and ^{13}C NMR. Curve deconvolution of the ^{13}C NMR spectrum for the methine resonances gave relative areas of 27, 50, and 23% for the rr, mr, and mm sequence, respectively, based on Schaefer's peak assignments. The use of Bernoullian statistics gave the corresponding probabilities of r and m configuration as 52% and 48%, respectively, establishing the atactic character of the polymer. This was confirmed by the ^{1}H NMR spectrum of the methylene protons. The simulated pentad spectrum was constructed on the basis of these probabilities and the experimental spectrum. The changes in chemical shift of the methine resonance for each tacticity and for the carbonyl resonance with changing pH were treated as typical polyelectrolyte titrations and analyzed by the extended Henderson–Hasselbalch and Mandel's equations. We found a small tacticity effect on the acid dissociation behavior of poly(acrylic acid).

Introduction

^{13}C NMR has been extensively used for elucidating the stereochemical sequence of vinyl polymers, such as poly(methyl methacrylate),[1] poly(vinyl acetate),[2] and polyacrylonitrile.[3] By comparison, there have been only a few studies[4-8] of poly(acrylic acid) (PAA), and these are incomplete. Schaefer[5] has reported on the triad sequence of the methine carbon for PAA by ^{13}C NMR. Comparing the spectrum of isotactic PAA with that of the atactic polymer, he found that the upfield portion of both the methine and methylene carbon resonances may be attributed to the meso (m) configuration and, by default, the downfield region to the racemic (r) configuration. Furthermore, it was shown that the tacticity of the methine and methylene carbons was observed only at high pH. At low pH the resonance for each carbon nucleus was a single peak, shifted upfield. Interestingly, the carbonyl peak was insensitive to tacticity at both high and low pH. Watts,[7] in contrast, ascribed the downfield component of the methylene carbon resonances to the m configuration and the upfield component as a mixture of both m and r configurations. His assignments, however, were made on an unjustified extrapolation of the ^{1}H NMR results. In the first part of this paper, we will provide a quantitative solution to the tacticity of PAA by ^{13}C NMR at the triad level and propose a pentad analysis as well.

The acid dissociation constant (pK_a) of a polyelectrolyte generally depends on the mole fraction of charged sites (α).

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