by X-ray analysis of several isotactic polymers with branched side chains.[11,16] The crystal structure proposed by Petraccone et al.[11] for poly[(S)-3M1P] shows two equiprobable conformations of the side-chain end (methyl C_5 only). In this case flippings from one conformation to the other in neighboring chains are interrelated; however, ^{13}C CP–MAS NMR analysis of this polymer[5,6] shows unique resonances, indicating that the exchange rate between the two conformations at room temperature is fast with respect to the NMR time scale. In the present case of poly[(S)-3,7DM1O] the disorder should involve a much larger part of the side groups. It is conceivable that low-temperature ^{13}C CP–MAS NMR measurements may help one to further elucidate the structure of this polymer.

Experimental Section

(S)-3,7-Dimethyl-1-octene was synthesized in three steps from (S)-citronellol according to the literature.[12] Purified (S)-3,7DM1O (5 mL) in 10 mL of anhydrous toluene was polymerized at 80 °C in the presence of δ-$TiCl_3$ (3.2 mmol) and $Al(CH_3)_3$ (1.7 mmol). After 4 days the polymerization was stopped by adding HCl-acidified methanol; then the polymer was collected, washed, and dried under vacuum. Yield: 1.06 g. The crude polymer was then fractioned with boiling solvents.[8] An annealed sample of the boiling diisopropyl ether soluble, diethyl ether insoluble fraction, obtained by heating at 250 °C for 2 h and slow cooling (1 °C/5 min) showed a highly crystalline X-ray pattern.

The ^{13}C CP–MAS NMR spectrum of annealed poly[(S)-3,7DM1O] was obtained on a Bruker CXP-300 spectrometer operating at 75.46 MHz, with a magic-angle rotation speed of 4.3 kHz. Free induction decays were generated by cross polarization using a single contact pulse of 1 ms per ^1H spin locking and a recycle of 5 s. The chemical shifts were referred to external Me_4Si.

The ^{13}C NMR spectrum of the diethyl ether soluble, diisopropyl ether insoluble fraction of the same polymer was obtained at 94 °C on a Bruker AM-270 spectrometer operating at 67.9 MHz in the PFT mode. The sequence τ_1–90°–τ_2–180°, 90°–τ_2–135°, 180°–τ_2–BB–acquire was used for the DEPT experiment[13] with a delay τ_2 of 3.6 ms and 90° pulse widths of 7.3 and 1.9 μs for ^{13}C and ^1H, respectively. A sweep width of 3600 Hz was used with 16K of computer memory for the interferogram. The sample was prepared by dissolving the polymer in 1,2,4-trichlorobenzene and by adding 1% hexamethyldisiloxane (HMDS) as an internal standard. The chemical shifts were converted to the Me_4Si scale.

Registry No. Isotactic poly[(S)-3,7-dimethyl-1-octene], 29407-49-6; 2,6-dimethylheptane, 1072-05-5.

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Transient Spectroscopy and Kinetics of Poly(1-(4-substituted-phenyl)-2-propen-1-ones)†

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ABSTRACT: The transient absorption spectra of 1-(4-substituted-phenyl)-2-propen-1-one chromophores in model compounds, homopolymers, and copolymers with styrene and methyl methacrylate were examined in chloroform at room temperature using laser flash photolysis techniques. Most triplets showed maxima in the 350-nm region with the exception of methoxy-substituted derivatives, where the maxima at ~390 nm, characteristic of the π,π* triplet, were observed. Spectra are quite similar for the model compounds and homopolymers. When the polymers can undergo the Norrish type II reaction we observe a drastic decrease in triplet lifetime as compared with the model compounds, where this is not possible. Quenching rate constants for small molecules (e.g., conjugated dienes) normally follow the order k_q(model) > k_q(copolymer) ≥k_q(homopolymer). Polymer-bound quenchers show similar efficiency to free ones, when local concentration effects are taken into consideration.

Introduction

Carbonyl chromophores in polymer systems continue to attract attention even though their photochemical behavior has been extensively studied during the last decade.[1a] Poly(1-phenyl-2-propen-1-one), also known as poly(phenyl vinyl ketone) or poly(acrylophenone), and its derivatives have been investigated rather thoroughly.[2] Not surprisingly, many aspects of the photochemistry and photophysics of carbonyl groups in polymers in solution parallel closely the behavior of their monomeric analogues. There are, however, specific effects, related either to the polymeric structure and/or to the ability of the excitation energy to migrate along the chain of chromophores.

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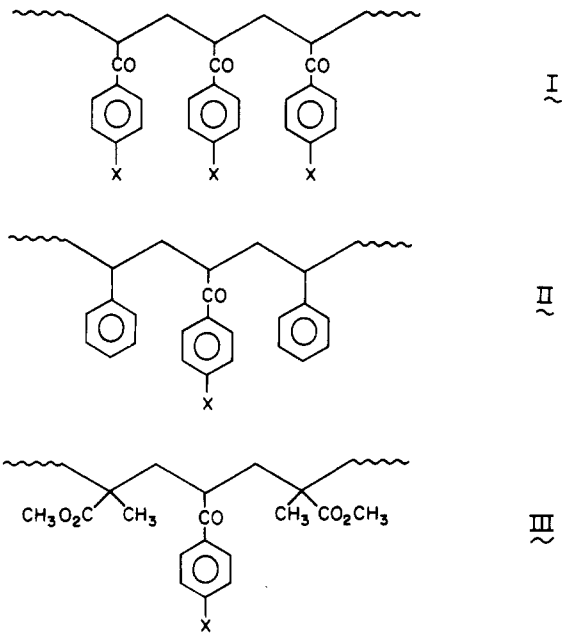
Chart I



Photochemical studies in polyketones, in particular in the case of the Norrish type II reaction, lead to quantum yields of photofragmentation comparable to those observed in low molecular weight analogues. This suggests that arylcarbonyl groups behave largely as isolated chromophores.[2] On the other hand, inter- or intramolecular studies of triplet quenching in macromolecules suggest that isoenergetic triplet energy transfer along the polymer chain plays an important role in determining macromolecular behavior.[3-6]

Extensive studies of the quenching of triplet macromolecules and model compounds by low molecular weight quenchers have been recently reported.[6] Quenching rate constants, k_q, were systematically lower for the polymers as compared with the model compounds.[6] This is usually attributed to negligible diffusion of the center of mass of the polymer.[7] Others[8-11] have also observed that polymeric triplet sensitizers are equal to or less effective than the low molecular weight models. A rather unusual result was recently reported by Urruti and Kilp,[12] who observed that energy transfer to 1-methylnaphthalene was more rapid for the polymeric benzophenone than for benzophenone itself.

The photochemistry and photophysics of poly(1-(4-substituted-phenyl)-2-propen-1-one) was systematically studied during the last decade.[2] These studies showed that substitution by electron-donating groups tends to prolong the triplet lifetime; this is expected to lead to readily observable T–T absorption for poly(*p*-methoxyacrylophenone).[13,14] In the case of the unsubstituted polymer the transient absorption signals due to the triplet state and the Norrish type II 1,4-biradical overlap extensively in wavelength and time. Early reports of the triplet lifetime at room temperature ranged from 7[15] to 70 ns[16] in benzene. More recent measurements in chloroform led to a value of 74 ns.[17]

In this paper we report on the transient spectra and lifetimes of triplet poly(1-(4-substituted-phenyl)-2-propen-1-ones) in chloroform at room temperature and their quenching by 2,5-dimethyl-2,4-hexadiene, nitroxyl radicals, and polymer-bound quenchers. Solvent effects were also examined.

Experimental Section

Preparation and Characterization of Monomers. 1-(4-Substituted-phenyl)-2-propen-1-one has been described previously.[18-24] Homopolymers (I) and copolymers (with styrene (II) and methyl methacrylate (III) were prepared by radical polymerization at high conversion (see Chart I). They were purified by several precipitation–redissolution cycles and characterized by viscometry and GPC. Copolymers of 1-(4-methoxyphenyl)-2-propen-1-one with functionalized triplet quenchers (2-naphthyl methacrylate, *p*-diphenyl methacrylate, and 2-hydroxy-4-(2-(methacroyloxy)ethoxy)benzophenone) were the same as in earlier papers.[25,26]

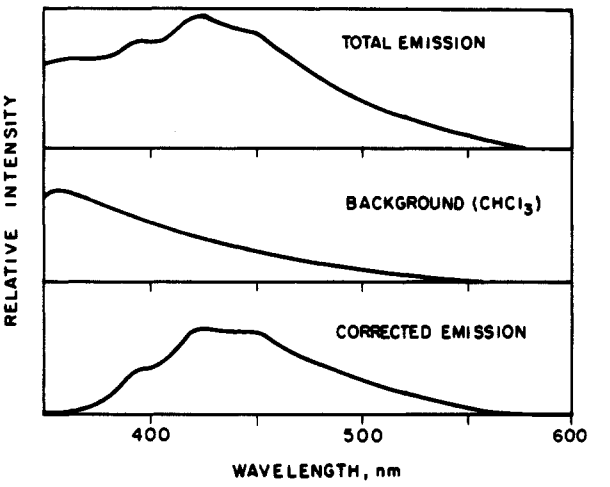


Figure 1. Emission spectrum of an aerated solution of 1-(4-fluorophenyl)-3-chloropropan-1-one in chloroform at room temperature: (1) total emission; (2) solvent background; (3) difference of spectra 1 and 2.

Materials. Spectrophotometric grade solvents (Fisher or Aldrich) were used throughout. Fresh stock solutions of 2,5-dimethyl-2,4-hexadiene (Aldrich) in chloroform were prepared immediately before each measurement. 4-(Acetyloxy)-2,2,6,6-tetramethylpiperidine-*N*-oxyl was prepared as described earlier.[27]

Luminescence. Emission spectra were recorded in an LS-5 Perkin-Elmer spectrofluorimeter equipped with a PE-3600 data station and printer. The excitation source was a pulsed-xenon lamp (10 μs at 60 Hz). Typical bandwidths were in the 2–5-nm range. Samples were deaerated by bubbling with oxygen-free nitrogen.

Laser Flash Photolysis. A Molectron UV-24 nitrogen laser (337.1 nm, ~8 ns, up to 10 mJ/pulse) was used for excitation. The data, initially acquired by a Tektronix R-7912 digitizer, was transferred to a PDP 11/23 computer that controlled the experiment and provided suitable storage, hard copy, and processing facilities. The system has been described in detail elsewhere.[28,29] The samples were contained in cells made of 3 × 7 or 7 × 7 mm^2 Suprasil tubing and were deaerated by bubbling with oxygen-free nitrogen. The concentration of material was normally selected to achieve optical densities between 0.3 and 0.7 in the laser cell at 337.1 nm.

Results and Discussion

Emission Spectra. Model compounds led to readily detectable luminescence, even in aerated solutions. For example, Figure 1 shows the luminescence of 1-(4-fluorophenyl)-3-chloropropanone in aerated chloroform. Much stronger and better resolved spectra are obtained in deaerated solution. An example for the same compound is shown in Figure 2. The luminescence corresponds to ketone phosphorescence, which is usually easily observable in halogenated solvents.[30] The lifetime of the compounds that do not undergo fast intramolecular reactions is frequently determined by impurities or by traces of oxygen and was typically about 10 μs. When there are hydrogens in the γ-position with respect to the reactive carbonyl, the emission is quenched by intramolecular photochemical reaction (in solution at room temperature).[1] Thus, no emission (phosphorescence) is observable from homo-

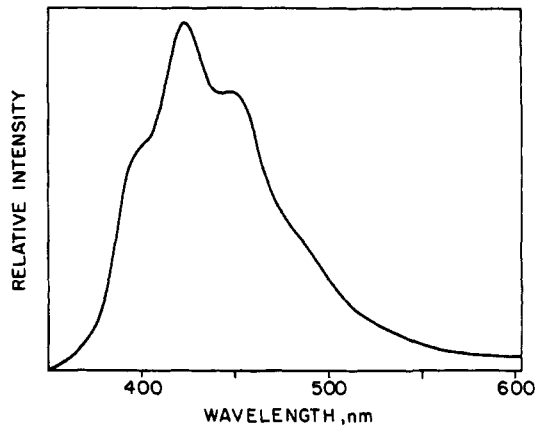


Figure 2. Emission spectrum of 1-(4-fluorophenyl)-3-chloropropan-1-one in deaerated chloroform at room temperature.

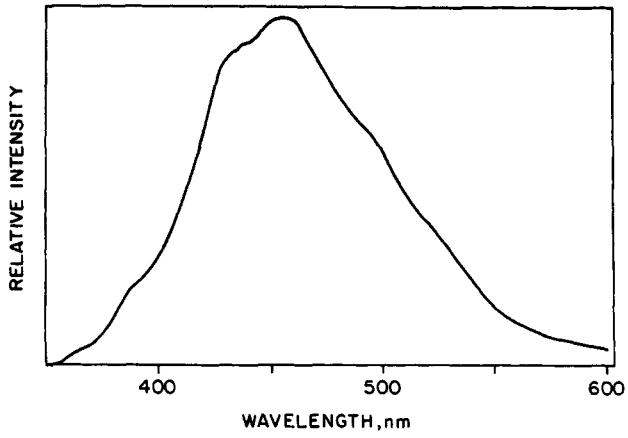


Figure 3. Emission spectrum of copolymer 1-(4-acetylphenyl)-2-propen-1-one/methyl methacrylate in deaerated chloroform at room temperature.

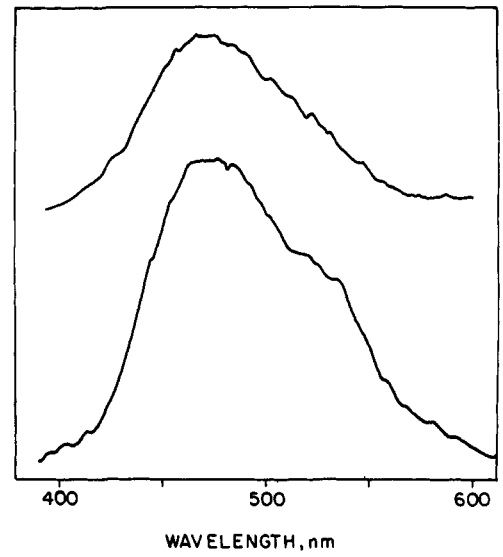


Figure 4. Top: emission spectrum of the model compound 1-(3,4-dimethoxyphenyl)-3-chloropropan-1-one in deaerated chloroform at room temperature. Bottom: emission spectrum of poly(1-(3,4-dimethoxyphenyl)-2-propen-1-one) under the same conditions.

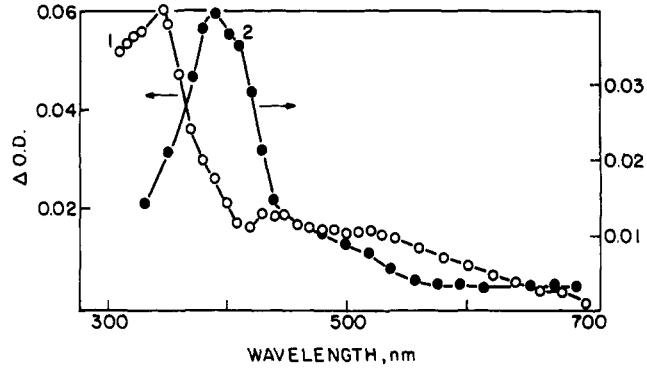


Figure 5. Transient spectra of 1-poly(1-(4-fluorophenyl)-2-propen-1-one) (1) and 2-poly(1-(3,4-dimethoxyphenyl)-2-propen-1-one) (2) in chloroform at 300 K.

polymers and copolymers with styrene. For copolymers with methyl methacrylate, the emission is observed if the carbonyl chromophore content is low (Figure 3). Methoxy substitution at the 3 and 4 position of the aromatic ring decreases the carbonyl reactivity. Weak phosphorescence emission was observed from the model compound and from poly(1-(3,4-dimethoxyphenyl)-2-propen-1-one); see Figure 4. The earlier failure to detect this luminescence[31] was probably due to insufficient instrument sensitivity. The emission in Figure 4 is similar to that observed at 77 K,[21] showing poor vibrational resolution.

Transient Spectroscopy. Typical transient spectra obtained for poly(1-(4-fluorophenyl)-2-propen-1-one) and poly(1-(3,4-dimethoxyphenyl)-2-propen-1-one) are shown in Figure 5. The former has a very reactive triplet, while the later does not (vide infra).

The methoxy derivatives have low-lying, relatively unreactive π,π^* triplets.[32,33] As a result, monitoring their triplet T–T spectra is straightforward. However, for some of the shorter lived triplets one can expect considerable overlap of the triplet and biradical signals.[17] In order to minimize these complications the signals were typically monitored in the 350–360-nm range, which tends to reduce this problem because of lower biradical absorptions in this spectral region. The basic characteristics of the transient spectra have been summarized in Table I; the position of the maxima was always determined by monitoring the spectra in a time window substantially shorter than the triplet lifetime. It should be noted that the model compounds usually differ from the corresponding polymers in that the former cannot undergo the Norrish type II reaction. This is the main factor that determines the differences in lifetimes, in particular for those systems with low-lying n,π^* states. Comparison of the transient spectra of model compounds and homopolymers leads to the conclusion that there is no great difference in the position of the maxima. Strong electron-donating substituents in position 4 of the benzene ring cause a bathochromic shift. Some model compounds and polymers exhibited additional weak absorbances at wavelengths longer than 400 nm that decayed with slower kinetics than the main absorption. The data are given in Table I in parenthesis. In most cases the decay curves did not return to the original (preexcitation) value of absorption. A weak residual absorption is observed for all model compounds and polymers. At short time scales part of this absorption may be due to the biradical, while at long times (microseconds) they are probably due to ketone enols produced in the type II reaction.

In the case of the nonreactive 3,4-dimethoxy derivatives the triplet lifetime was longer for the polymer than the model compound. Substitution at the 4 position in the polymers systematically increases the triplet lifetime with the only exception of fluorine. Methoxy substitution leads to long lifetimes, as expected from the π,π^* nature of the low-lying triplet state. It has been suggested that the 3,4-dimethoxy derivative exhibits efficient self-quenching;[34] this characteristic was not evident from our results.

Table I
Transient Spectra Obtained for Poly(1-(4-phenyl)-2-propen-1-ones) in Chloroform at Room Temperature

substrate	λ_{max}, nm	τ_T, ns	k_q, M^{-1} s^{-1}	R^a	K_{SV},[b] M^{-1} naph	biphenyl	diene	ref
			X = F					
model[c]	347 (436)	2576	5.30×10^9					
homopolymer	345 (449)	75	1.14×10^9	4.6	62	30		23
copolymer/(styrene)	325	72	1.60×10^9	3.3	190	43		23
model[c]	350	7820	3.90×10^9					
			X = Cl					
model[c]	350	7820	3.90×10^9					
homopolymer	350	200	1.26×10^9	3.1	260	48		23
			X = Br					
model[c]	381	60	5.72×10^9					
homopolymer	380	107	1.77×10^9	3.2	110	30		23
copolymer/(styrene)		34	1.59×10^9	3.6	47	17		23
			X = I[d]					
			$X = CH_3CO$					
model[g]		456	4.54×10^9					
homopolymer	361	489	1.52×10^9	3.0	381[h]	4.4[h]		20
copolymer/(styrene) (43.2%)		459	1.47×10^9	3.1	770	3.2	620	20
copolymer/(MMA) (41.8%)	352	6894	1.96×10^9	2.3	9670	65	2400	20
copolymer/(MMA) (6.0%)	352	19583	1.82×10^9	2.5				
			$X = COOC_2H_5$					
homopolymer	349	126.5	5.57×10^8	170				24
			$X = CH_3$					
homopolymer	347	288	9.72×10^8		436	133		22
			$X = C_2H_5$					
homopolymer	349	293	8.9×10^8		345	78		22
			$X = (CH_3)_3C$					
homopolymer	350	307	5.7×10^8		336	96		22
			$X = CH_3O$					
model[c]	393	5800[f]	4.25×10^9					
homopolymer	389 (640)[e]	4600[f]	7.64×10^8	5.6	1700[i]	530[i]		18
copolymer/(styrene) (22.2%)	391	4400[f]	1.33×10^9	3.2	1000[i]	350[i]		18
copolymer/(MMA) (22.3%)	398	9800[f]	1.15×10^9	3.7	7100[i]			18
			$X = 3,4\text{-}(CH_3O)_2$					
model[c]	393	12300[f]	2.60×10^9					
homopolymer	392	28300[f]	2.56×10^8	10.1				
copolymer/(styrene)	380	20400[f]	7.16×10^8	3.6				
copolymer/(MMA)	390	29900	6.71×10^8	3.9				

[a] Ratio of rate constant (model/polymer). [b] Benzene. [c] Model is (1-4-X-phenyl)-3-chloropropan-1-one. [d] Iodine derivatives were examined (model, homopolymer, and copolymer with styrene), but the signals were too weak to allow a detailed study. [e] Weak additional absorption. [f] Extrapolated to zero laser dose. [g] Model is 1,4-diacetylbenzene. [h] Dioxane. [i] Chlorobenzene.

Table II
Influence of the Solvent on Transient Spectra of 1-(3,4-Dimethoxyphenyl)-2-propen-1-one Chromophores

substrate	λ_{max},[a] nm	$HCCl_3$ k_0, s^{-1} (r)[b]	τ_0, μs	$HCCl_3$/hexane (1:1) k_0, s^{-1} (r)[b]	τ_0, μs
model[c]	393	8.16×10^4 (0.987)	12.3	3.73×10^4 (0.9982)	26.7
homopolymer	392	8.54×10^4 (0.9773)	28.3	76.2×10^4 (0.9773)	1.3
copolymer/Styrene	380	4.91×10^4 (0.9757)	20.4	6.13×10^4 (0.9997)	16.3
copolymer/MMA	390	3.34×10^4 (0.9969)	29.9	3.99×10^4 (0.9354)	25.1

[a] Maximum of transient spectra. [b] Correlation coefficient of the plot of k vs. OD. [c] 1-(3,4-Dimethoxyphenyl)-3-chloropropan-1-one.

Since the chromophore in 1-(3,4-dimethoxyphenyl)-2-propen-1-one) yields a strongly absorbing long-lived transient, we have investigated the effect of nonsolvent addition on the kinetics of the decay for this chromophore in a macromolecule. Hexane was selected as nonsolvent, instead of a polar one, such as methanol. Methanol can, besides influencng the size of macromolecules, exhibit certain polar effects on the chromophore. Addition of hexane (Table II) slightly shortens the lifetime of copolymers but significantly shortens the lifetime of the homopolymer and extends the lifetime of the model compound. This means that addition of the nonsolvent leads to compression of the macromolecular coil and self-quenching presumably starts to play a role. This effect is less pronounced for copolymers. Addition of hexane had essentially no effect on the transient absorbance measured immediately after laser excitation. A more pronounced effect of the nonsolvent on the transient absorption had been observed in the case of poly(1-(4-biphenyl)-2-propen-1-one).[31] Efficient self-quenching of 2-naphthylcarbonyl chromophores has been suggested to prevent detection (in the microsecond time scale) in the case of homopolymers and copolymers with styrene and methyl methacrylate.[31] For poly(1-(3,4-dimethoxyphenyl)-2-

Table III
Quenching of 1-(3,4-Dimethoxyphenyl)-2-propen-1-one Chromophores

substrate	k_q, M^{-1} s^{-1} 2,5-dimethyl-2,4-hexadiene: $HCCl_3$	$HCCl_3$/hexane (1:1)	$HCCl_3$/CH_3OH (25%)	k_q, M^{-1} s^{-1} *N*-oxyl radical[a]: $HCCl_3$	$HCCl_3$/CH_3OH (25%)
model[b]	2.60×10^9	3.65×10^9	3.34×10^9	8.12×10^8	4.38×10^8
homopolymer	2.56×10^8	4.76×10^8	3.43×10^8	3.22×10^7	3.68×10^7
copolymer/(styrene)	7.16×10^8	7.04×10^8	1.04×10^9	9.65×10^7	1.05×10^8
copolymer/(MMA)	6.71×10^8	4.85×10^8	8.54×10^8	7.63×10^7	8.98×10^7

[a] 4-(Acetyloxy)-2,2,6,6-tetramethylpiperidine-*N*-oxyl. [b] 1-(3,4-Dimethoxyphenyl)-3-chloropropan-1-one.

propen-1-one), only the shortening of the lifetime is observed. More quantitative studies are required to find out whether the mechanism of deactivation of these chromophores is similar.

Triplet Quenching Experiments. All aryl ketone triplets were readily quenched by conjugated dienes, in particular, 2,5-dimethyl-2,4-hexadiene. Naphthalenes are known to be more efficient quenchers,[2] but in this case dienes are more convenient because their triplets do not present strong absorptions in the region of interest. The quenching rate constants (k_q) have been summarized in Table I; analysis of these data leads to the following conclusions:

1. All k_q values are lower than the $\sim 1 \times 10^{10}$ M^{-1} s^{-1} limit expected for diffusion-controlled processes in benzene or chloroform at room temperature.

2. All k_q for model compounds are higher than k_q for polymeric substrates, as expected.[6] Table I contains the Stern–Volmer slope (K_{SV}) values based on the inhibition of degradation. Naphthalene, biphenyl, and less frequently dienes were used as quenchers. The products of the triplet lifetime and k_q are of the same order of magnitude as K_{SV} for naphthalene. The agreement is only approximate. The values of K_{SV} reflect the same basic features as τ, since, for substrates with the longer lifetimes, the values of K_{SV} are higher. Figure 6 illustrates the parallel observed between K_{SV} and the triplet lifetimes.

In general we find the rates of quenching for the homopolymers to be slower than for the model compounds. The largest difference is observed for the case of the 1-(3,4-dimethoxyphenyl)-2-propen-1-one chromophore. These results contrast with a recent report by Urruti and Kilp,[12] which indicated that 1-methylnaphthalene quenched poly(4-vinylbenzophenone) faster than benzophenone itself. For the latter they reported a value of $k_q = 9.4 \times 10^8$ M^{-1} s^{-1} in benzene at room temperature. This is too slow for an exothermic triplet energy transfer process; we have measured this rate constant again under identical experimental conditions with those used by Urruti and Kilp but monitoring the decay of benzophenone triplets at 600 nm (which makes the determination straightforward) and obtained $k_q = (7.0 \pm 0.6) \times 10^9$ M^{-1} s^{-1} (errors as $\pm 2\sigma$). If this value is used, all the other quenching results reported by Urruti and Kilp[12] fit well with the expected trends in reactivity.

For copolymers the quenching rates are usually a factor of 3 less than for the model compounds. Table I includes the value of $R = k_q(\text{model})/k_q(\text{polymer})$. As pointed out by Guillet,[1b] quenching studies on a variety of isolated chromophores in polymer chains usually show a value of $R \sim 3$. In this work the average value for eight copolymers is 3.2 (excluding the value for the fluorine derivative, which appears to be anomalous). Most of the homopolymers in this work also show a value very close to 3. This reduced efficiency is often attributed to the lower rate of self-diffusion of the polymer-bound chromophore. However, even

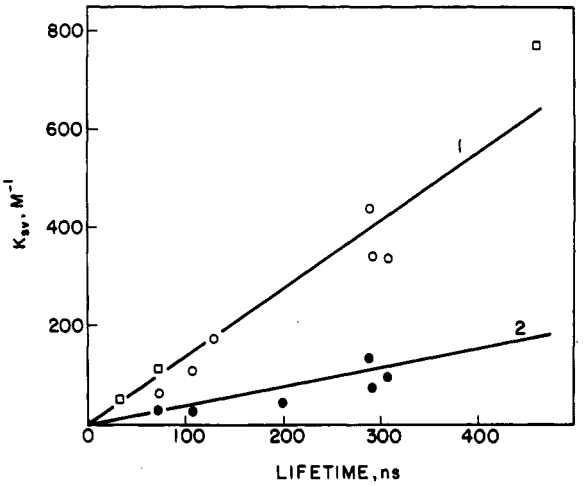


Figure 6. Plots of K_{SV} vs. τ with K_{SV} and τ_T taken from Table I. K_{SV} for the system homopolymers quenched by naphthalene (1, open circle), homopolymers quenched by biphenyl (2, full circles), and copolymers quenched with styrene–naphthalene (1, open squares).

if the chromophore were assumed to be stationary on the time scale of the experiment, this would only introduce a factor of 2, thus we are drawn to the conclusion that the presence of the polymer chain restricts access to the chromophore, so that a greater proportion of "collisions" between the small molecule quencher and the excited chromophore are ineffective.

A further interesting observation is that R for the homopolymer is either equal to or greater than that for the corresponding copolymer. Since triplet energy migration is more efficient in the homopolymer, this result suggests that the effect of migration is to *decrease* the efficiency of quenching, not to increase it as has been suggested by other workers; similar observations have been recently reported for various carbonyl-containing polymers.[6]

The ordering of k_q values (Tables I and III) appears to be largely independent of solvent polarity. Quenching by 4-(acetyloxy)-TEMPO (4-(acetyloxy)-2,2,6,6-tetramethylpiperidine-*N*-oxyl) is somewhat less efficient than diene quenching but shows the same kinetic trends.

Triplet quenching in a macromolecule can take place in an inter- or intramacromolecular process, depending on whether the quencher is free or covalently bound to the polymer. We have shown before that bound quenchers are more efficient than free ones. The reason for this effect is the higher local concentration that can be achieved in the former case.[2] Photolysis and quenching studies of poly(1-(4-methoxyphenyl)-2-propen-1-one) indicated the involvement of a long-lived triplet.[14,18] Copolymers of 1-(4-methoxyphenyl)-2-propen-1-one with functionalized triplet quenchers were prepared and their photolysis studied.[25,26] The results of these studies were not conclusive as far as intramacromolecular triplet energy

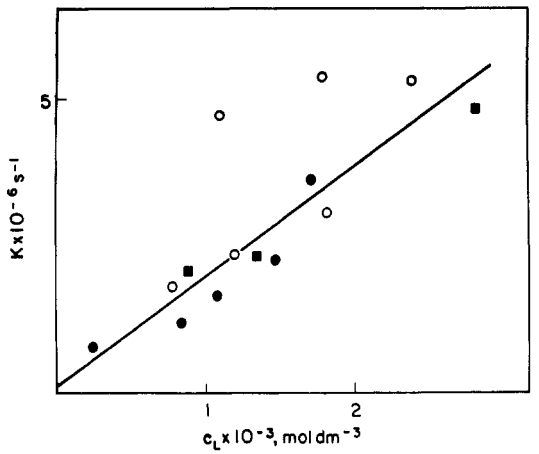


Figure 7. Dependence of the decay rate constants k on local concentration of quencher for copolymers 1-(4-methoxyphenyl)-2-propen-1-one with 2-NMA (full squares), BMA (open circles), and BPMA (full circles).

transfer was concerned, but the transient spectra were somewhat more informative. Transient spectra of these copolymers exhibit absorptions at 420 and 350 nm for 2-naphthyl methacrylate (2-NMA) and 350 nm for *p*-biphenyl methacrylate (BMA), besides the absorptions at 390 and 620 nm, which belong to 1-(4-methoxyphenyl)-2-propen-1-one. The growth of the transient absorption at 420 nm for 2-NMA was very rapid. The rate constant for this growth for BMA was $k = 2.5 \times 10^7$ s^{-1} and did not depend on the bulk quencher concentration. The quenching kinetics were determined by monitoring triplet decay at ~620 nm. The maxima at 390 and 620 nm for 1-(4-methoxyphenyl)-2-propen-1-one chromophores were used to follow the decay in the case of 2-hydroxy-4-(2-(methacroyloxy)ethoxy)benzophenone (BPMA). The local quencher concentration was calculated according to[2]

$$c_L = (1.2 \times 10^3) mw/[\eta]M$$

where w is the weight fraction of the quencher in copolymer, m is the concentration of copolymer in solution in g/L, $[\eta]$ is the limiting viscosity number in mL g^{-1}, and M is the molecular weight of the structural unit of quencher.

The triplet decay data have been summarized in Table IV. The dependence of the decay rate constants on the local concentration of quencher is linear (Figure 7). The reasons for the considerable scatter of experimental points reflect the fact that copolymers were prepared by radical copolymerization to high conversion; the distribution of the quencher in copolymers can deviate from the statistical one and the limiting viscosity number was actually determined in ethyl benzoate.[25,26] Exceptionally high quenching rate constants are observed for two copolymers quenched by BMA. We cannot account for these observations at present. Though the experimental error is rather high, the slope yields an apparent value for $k_q = 1.25 \times 10^9$ M^{-1} s^{-1}. This value agrees well with k_q for the quenching of the copolymer 1-(4-methoxyphenyl)-2-propen-1-one and methyl methacrylate with diene (Table I). Since the rate constant for the decay without quencher is low (3.4×10^4 s^{-1}) the abscissa of the plot of k vs. c_L is quite small (Figure 7). All bound quenchers show similar efficiency. Through the approximate analysis indicated above it is possible to conclude that bound quenchers are not intrinsically more efficient than free ones. The same will probably apply if a chemical reaction of the quencher is to occur instead of dissipation of energy. Consequently, we cannot expect substantially higher reactivity in a triplet reaction center of this type.

Table IV
Decay of Transient Absorptions in 1-(4-Methoxyphenyl)-2-propen-1-one Copolymers with Functionalized Triplet Quenchers in Chloroform at Room Temperature

quencher	content, % (w/w)	$[\eta]$,[a] mL g^{-1}	$c_L \times 10^3$,[b] M	λ_{max}, nm	$k \times 10^6$, s^{-1}
2-NMA[c]	4.20	125	2.85	600	4.79
	2.25	209	0.91	610	1.94
	2.40	150	1.36	650	2.27
BMA[d]	2.5	103	1.83	600	3.07
	3.3	208	1.20	600	2.27
	4.7	147	2.40	620	5.34
	1.8	169	0.80	620	1.77
	4.9	201	1.84	620	5.34
	2.95	199	1.11	620	4.68
BPMA[e]	1.05	240	0.24	600	0.72
	1.05	240	0.24	390	0.75
	3.54	229	0.85	390	1.20
	3.54	229	0.85	600	1.62
	4.57	236	1.07	390	1.56
	6.60	247	1.47	600	2.20
	8.25	265	1.72	600	3.60
	8.25	265	1.72	390	3.60

[a] Ethyl benzoate. [b] Local concentration of quencher at total concentration of copolymer 1.5 g/L. [c] Naphthyl methacrylate (2-NMA). [d] Diphenylmethacrylate (BMA). [e] 2-Hydroxy(4-(2-(methacroyloxy)ethoxy)benzophenone (BPMA).

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Registry No. 4-$FC_6H_4CO(CH_2)_2Cl$, 347-93-3; 4-$FC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-61-8; (4-$FC_6H_4CO(CH_2)_2Cl$)($C_6H_5CH{=}CH_2$) (copolymer), 101695-62-9; 4-$ClC_6H_4CO(CH_2)_2Cl$, 3946-29-0; 4-$ClC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-63-0; 4-$BrC_6H_4CO(CH_2)_2Cl$, 31736-73-9; 4-$BrC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-64-1; (4-$BrC_6H_4CO(CH_2)_2Cl$)·($C_6H_5CH{=}CH_2$) (copolymer), 101695-65-2; 4-$H_3CCOC_6H_4COCH_3$, 1009-61-6; 4-$H_3CCOC_6H_4COCH_3$ (homopolymer), 25702-15-2; (4-$H_3CCOC_6H_4COCH_3$)·($C_6H_5CH{=}CH_2$) (copolymer), 101695-66-3; (4-$H_3CCOC_6H_4COCH_3$)·($H_2C{=}C(CH_3)CO_2CH_3$) (copolymer), 101695-67-4; 4-$C_2H_5OCOC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-69-6; 4-$CH_3C_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-70-9; 4-$(C_2H_5C_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-71-0; 4-$(CH_3)_3CC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-72-1; 4-$CH_3OC_6H_4CO(CH_2)_2Cl$, 35999-20-36; 4-$CH_3OC_6H_4CO(CH_2)_2Cl$ (homopolymer), 101695-73-2; (4-$CH_3OC_6H_4CO(CH_2)_2Cl$)·($C_6H_5CH{=}CH_2$) (copolymer), 101695-74-3; (4-$CH_3OC_6H_4CO(CH_2)_2Cl$)·($H_2C{=}C(CH_3)CO_2CH_3$) (copolymer), 101695-75-4; 3,4-$(CH_3O)_2C_6H_3CO(CH_2)_2Cl$, 4693-38-3; 3,4-$(CH_3O)_2C_6H_3CO(CH_2)_2Cl$ (homopolymer), 101695-76-5; (3,4-$(CH_3O)_2C_6H_3CO(CH_2)_2Cl$)·($C_6H_5CH{=}CH_2$) (copolymer), 101695-77-6; (3,4-$(CH_3O)_2C_6H_3CO(CH_2)_2Cl$)·($H_2C{=}C(CH_3)CO_2CH_3$) (copolymer), 101695-78-7; $(CH_3)_2C{=}CHCH{=}C(CH_3)_2$, 764-13-6; (4-$CH_3OC_6H_4COCH{=}CH_2$)·(2-NMA) (copolymer), 58622-45-0; (4-$CH_3OC_6H_4COCH{=}CH_2$)·(BMA) (copolymer), 58622-44-9; (4-$CH_3OC_6H_4COCH{=}CH_2$)·(BPMA) (copolymer), 72414-40-5; 4-(acetyloxy)-2,2,6,6-tetramethylpiperidine-*N*-oxyl, 6599-87-7.

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Primary Thermal Decomposition Processes in Aliphatic Polyesters Investigated by Chemical Ionization Mass Spectrometry

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ABSTRACT: The thermal decomposition mechanisms of several polyesters, derived from aliphatic diols and bicarboxylic acids, and polylactones were studied by direct pyrolysis–mass spectrometry, using both positive chemical ionization and negative chemical ionization. In fact, it was found that the thermally formed compounds are not stable under electron impact conditions. Instead, the results obtained by positive and negative chemical ionization indicate that intramolecular exchange reactions predominate in the primary thermal fragmentation processes, causing the formation of cyclic oligomers, which are particularly stable under chemical ionization conditions. The only exception is given by poly(β-propiolactone); in this case the thermal decomposition mechanism involves β-hydrogen transfer reactions.

Introduction

The characterization of polymers by direct pyrolysis–mass spectrometry (DP–MS) yields important structural information.[1-5]

Typical applications of this method include structural identification of homopolymers, differentiation of isomeric structures, copolymer composition and sequential analysis, identification of oligomers formed in the polymerization reactions, and identification of volatile additives contained in polymer samples.[5]

In the direct pyrolysis–mass spectrometry technique,[5] polymers are introduced via the direct insertion probe and the temperature is increased gradually up to a point at which thermal degradation reactions occur; the volatile oligomers formed are then ionized and detected.

The mass spectrum of a polymer obtained under these conditions is therefore that of the mixture of oligomers formed by pyrolysis.

A general advantage of this technique is that pyrolysis is accomplished under high vacuum, and therefore the thermal oligomers formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and fast detection, reduces to a great extent the occurrence of secondary reactions, so that almost exclusively primary fragments are detected. Consequently, the information thus obtained is of particular importance in order to assess the primary thermal decomposition mechanism of a polymer.

Furthermore, since pyrolysis is achieved very close to the ion source and no problem of transport exists, fragments of high mass, which are often essential for the structural characterization of the polymer, can be detected, whereas they are often lost with other techniques.

The main problem connected with this technique is, however, the identification of the products in the spectrum of the multicomponent mixture produced by thermal degradation. In fact, in the overall end spectrum of a polymer, the molecular ions of the thermal oligomers will appear mixed with the fragment ions formed in the ionizing step.

In some instances, identification of thermal degradation products can be achieved by using soft ionization methods and exact mass measurements and by matching spectra of authentic samples with those obtained from the polymer.[5]

This article describes the use of positive and negative chemical ionization in the investigation of the primary thermal fragmentation processes of some polylactones and polyesters derived from aliphatic diols and bicarboxylic acids (Table I).

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