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Energy Transfer and Migration Processes in the Photochemistry of Polymers and Copolymers of *p*-Methoxyacrylophenone[1]

J. C. Scaiano* and J. C. Selwyn[2]

Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6.
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ABSTRACT: The long lifetime and excellent absorption properties of the triplet state of polymers and copolymers of *p*-methoxyacrylophenone make it quite suitable for laser flash photolysis studies. The triplet lifetimes of the homopolymer (PPMA) and copolymers with phenyl vinyl ketone (PVK), styrene, and methyl methacrylate have been determined in solution at 27 °C, as well as over a temperature range for PPMA and the copolymer with PVK. Intermolecular quenching has been examined for oxygen, 1-methylnaphthalene, and conjugated dienes. Efficient energy migration plays an important role in triplet-state processes and takes place with a hopping frequency of 4.3×10^{11} s^{-1}. The possibility of energy transfer through loops in the polymer is discussed in some detail.

Introduction

Energy transfer and migration in macromolecular systems is a subject of current interest, which reflects its role in photodegradation, photostabilization, photocuring, and photooxidation.[3,4] Among the chromophores frequently present in polymer systems carbonyl groups are among the most important and abundant. In recent years laser flash techniques have made it possible to examine directly the photochemistry of some polymers containing carbonyl groups, although in many cases the observable transient phenomena are complicated by processes such as biradical formation, photoenolization, or α cleavage.[5-14] A couple of simpler examples are the cases of poly(vinylbenzophenone)[15] and copolymers of phenyl vinyl ketone with methyl methacrylate,[16] where the absence of γ hydrogens considerably simplifies the study of triplet-state processes.

We have recently[17] characterized the triplet state of poly(*p*-methoxyacrylophenone), PPMA, using laser flash photolysis techniques. We noted that the long lifetime and high extinction coefficients for the triplet state make this polymer an excellent candidate for laser flash photolysis studies. Further, the photochemistry of PPMA under steady irradiation has been examined by Hrdlovič et al.,[18,19] a fact that largely facilitates the interpretation of transient phenomena. Scheme I shows the photobehavior of PPMA. The overall efficiency for cleavage in PPMA is ca. 25% of that observed for poly(phenyl vinyl ketone).[18]

This paper reports a study of the solution photochemistry of PPMA and of copolymers of *p*-methoxyacrylophenone with styrene, methyl methacrylate, and phenyl vinyl ketone. Particular emphasis is placed on triplet energy transfer phenomena.

Results and Discussion

All the flash photolysis experiments reported in this paper have been carried out with pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser for excitation. Unless otherwise indicated, experiments were carried out under oxygen-free conditions.

T–T Absorption Spectra. Laser photolysis of PPMA in benzene at room temperature leads to an intense transient spectrum characterized by a strong maximum at 390 nm and a weaker one at ~630 nm.[20] Except for the presence of the latter the spectrum is virtually identical with those observed in the case of *p*-methoxyacetophenone and *p*-methoxy-β-chloropropiophenone, the latter being one of the precursors used in the synthesis (see Experimental Section). The transients mentioned above are assigned to the corresponding triplet states and could be quenched by typical triplet quenchers (see below). Copolymers with phenyl vinyl ketone, methyl methacrylate, and styrene all showed transient spectra similar to that in the case of PPMA, the only difference being somewhat weaker absorptions in the 630-nm region.

Table I
Lifetimes of the Triplet State of the *p*-Methoxybenzoyl Group in Different Copolymers at 27 °C

polymer[a]	% PMA[b]	solvent	τ/ns
PPMA	100	benzene	950
PPMA	100	chloroform	3100
PPMA	100	chlorobenzene	1500
co-(PMA-PVK)	80	benzene	235
co-(PMA-PVK)	80	chloroform	340
co-(PMA-Sty)	39	benzene	820
co-(PMA-Sty)	39	chloroform	2300
co-(PMA-Sty)	39	chlorobenzene	980
co-(PMA-MMA)	22	benzene	2500
co-(PMA-MMA)	22	chloroform	8800
co-(PMA-MMA)	22	chlorobenzene	3300

[a] Abbreviations: PMA ≡ *p*-methoxyacrylophenone, PVK ≡ phenyl vinyl ketone, Sty ≡ styrene, MMA ≡ methyl methacrylate. [b] The percent composition is expressed as the number of monomer units that contain the PMA moiety, not by mass.

Triplet Lifetimes at Room Temperature. Measurements were carried out at 400 nm. The polymer concentrations were chosen so that the solution would have an optical density of ~0.3 at 337.1 nm in the photolysis cell (3-mm optical path). In the case of PPMA a small fraction of the decay seems to take place by a fast process which precedes the main decay process. This will be discussed in detail below; the lifetimes given in this section and summarized in Table I correspond to the main (i.e., slow) component. No problems of this type were encountered with the copolymers at room temperature. All the values in Table I have been obtained at low excitation doses, i.e., under conditions where only one quantum per macromolecule can be absorbed.

The lifetimes measured are similar to that reported by Wagner[21] for *p*-methoxyvalerophenone ($\tau_T \sim 460$ ns) in benzene, suggesting that the *p*-methoxybenzoyl chromophore behaves similarly in polymers and in small molecules.

In the case of *co*-(PMA–PVK) the lifetime obtained suggests that the decay involves a considerable contribution from the PVK moiety.[22] The triplet state of this group is higher in energy than in the case of PMA;[23] however, when we use the approach suggested by Wagner[23] to calculate the population at each chromophore, we estimate ca. 19% population of the PVK group when its abundance is 20%. The agreement between abundance and contri-

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Scheme I

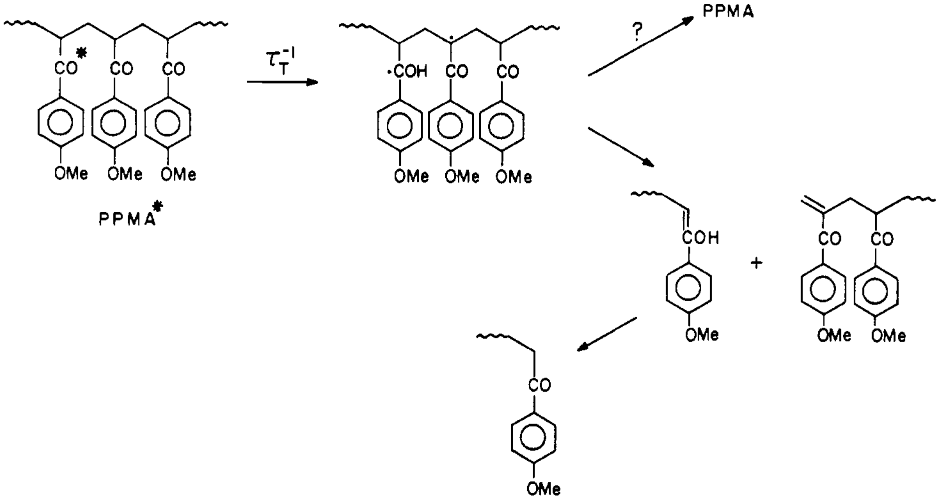


Table II
Quenching of the Triplet State of PPMA at 27 °C

quencher	solvent	k_q [a]
trans-1,3-pentadiene	benzene	1.8×10^9
2,5-dimethyl-2,4-hexadiene	benzene	1.3×10^9
1,3-octadiene [b]	benzene	0.9×10^9
1-methylnaphthalene	benzene	2.4×10^9
1-methylnaphthalene	chloroform	1.5×10^9
oxygen	benzene	1.2×10^9
oxygen	chloroform	0.66×10^9
o-hydroxybenzophenone	benzene	0.9×10^9

[a] In units of M^{-1} s^{-1}; typical errors are 15%. [b] Mixture of isomers.

bution in the decay process is somewhat surprising in view of the expected low-lying nature of the π,π^* triplet in the PMA chromophore.[23]

As shown in Scheme I the main decay path of triplet PPMA is expected to take place via the intermediacy of 1,4-biradicals, but their lifetime is expected to be short and its extinction coefficient far smaller than for the triplet state of PPMA.[24] Therefore, biradicals are not expected to interfere with the interpretation of transient phenomena. A small residual optical density is usually observed following triplet decay (see insert in Figure 1); this is attributed to the enol (Scheme I) normally produced in the Norrish type II process.

Effect of Triplet Quenchers. The rate constants for triplet quenching by conjugated dienes and by 1-methylnaphthalene were determined from plots of the rate of triplet decay as a function of quencher concentration. Figure 1 shows a representative example, and Table II summarizes the quenching data. Quenching rate constants are lower than observed for small molecules,[25] reflecting largely that the diffusional contribution by the energy donor is negligible in the case of the macromolecule. Quenching by 1-methylnaphthalene is faster than by dienes. We have made similar observations with small molecules and other macromolecules.

Quenching by Oxygen. Rate constants for oxygen quenching were determined in a manner similar to that used for the dienes and taking the solubility in benzene as 0.0096 M under a partial pressure of 1 atm.[26] The value has also been included in Table II and is in line with typical rates of triplet quenching by O_2.

Quenching by *o*-Hydroxybenzophenone. *o*-Hydroxybenzophenone (*o*-HBP) is a particularly interesting molecule because of its polymer photostabilizing properties.[27] Its high extinction coefficient at the excitation wavelength (337.1 nm) made some of the experiments quite difficult, an observation that in intself emphasizes the excellent UV-screening properties of *o*-HBP. The quenching of the PPMA triplet was measured as in the case of diene quenching (vide supra), but in this case, in addition to the rate of triplet decay becoming faster upon addition of *o*-HBP, the yield of PPMA triplets decreased. The latter effect was consistent with a simple competition for light absorption between PPMA and *o*-HBP. The rate constant for quenching has also been included in Table II.

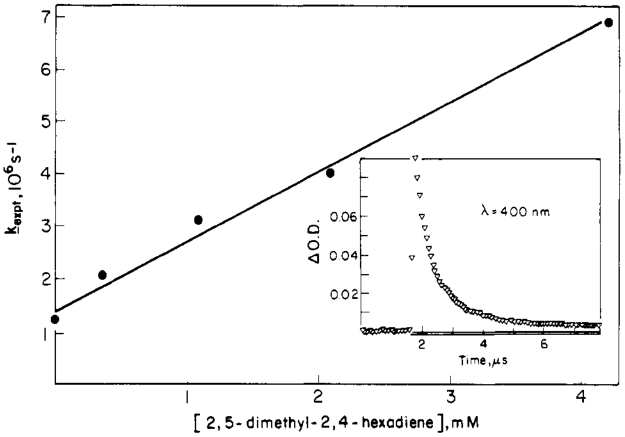
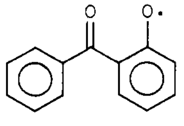


Figure 1. Quenching of triplet PPMA by 2,5-dimethyl-2,4-hexadiene in benzene at 27 °C. Insert: Trace in the absence of diene, monitored at 400 nm.

We have observed that the quenching of PPMA triplets by *o*-HBP leads to a long-lived transient showing very weak absorptions in the 400–470-nm region. Unfortunately, it was not possible to fully characterize this species, although it is clear that a small fraction of the quenching must occur via a chemical reaction. We suggest that the observed weak transient may be the corresponding phenoxyl radical, I.



I

Attempts to generate I independently by reaction of *tert*-butoxyl radicals with *o*-HBP were not very successful. Even when neat di-*tert*-butyl peroxide is used as solvent,

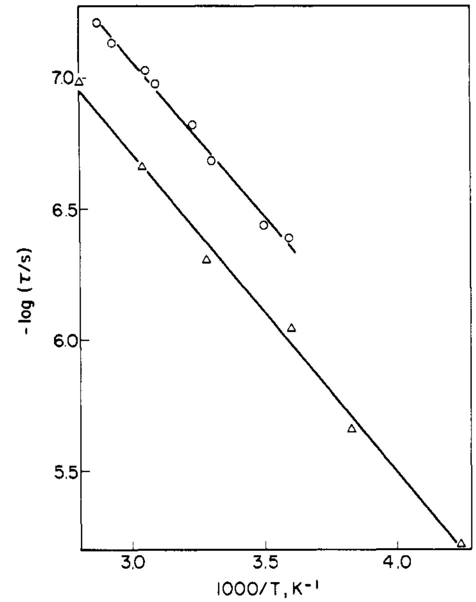


Figure 2. Arrhenius plots for the decay of PPMA in chlorobenzene (Δ) and for *co*-(PMA-PVK) in benzene (O).

Table III
Temperature Dependence of the Rate Constants for Triplet Decay

substrate	solvent	T range, K	$\log A^a$	$E_a{}^b$
PPMA	benzene	281-348	10.61	5.96
PPMA	chlorobenzene	235-357	10.37	5.61
co-(PMA-PVK)	benzene	279-349	10.62	5.46
co-(PMA-PVK)	chloroform	222-328	10.84	6.03

[a] A in s^{-1}. [b] In kcal mol^{-1}.

UV screening by *o*-HBP predominates. We did, however, observe weak absorptions in the same spectral region.

In summary, *o*-HBP prevents the photochemistry of PPMA by three different mechanisms: (i) UV screening, (ii) excited-state quenching, presumably involving triplet energy transfer, and (iii) reactive quenching of triplet PPMA, probably leading to I. It should be noted that while π,π^* triplet states are not very reactive in hydrogen abstraction from hydrocarbons and alcohols,[28] their reactivity toward phenols is known to be extremely high.[29]

Temperature Effects. The effects of temperature on the rate constant for triplet decay ($k_d = \tau_T{}^{-1}$) were examined for PPMA and *co*-(PMA-PVK). Figure 2 shows representative Arrhenius plots and Table III summarizes the data, which was fitted with a conventional Arrhenius expression. It is interesting to note that the parameters, activation energy in particular, are virtually the same for PPMA as for *co*-(PMA-PVK) even if in the latter a significant contribution to decay process seems to take place from a PVK moiety. One of the mechanisms suggested for decay in ketones with low-lying $^3\pi,\pi^*$ states is via thermal population of the reactive upper $^3n,\pi^*$ state.2[3,30] Such a mechanism would indicate that in the polymers the reactive decay will always take place from the n,π^* chromophore regardless of whether this is populated within the same chromophore (PPMA) or as a result of energy migration to neighboring PVK moieties. While our results are consistent with this model, they cannot rule out the possibility of some reactivity from the $^3\pi,\pi^*$ sate with an activation energy also in the 6 kcal/mol range.

Unfortunately, similar studies on the temperature dependence of the photochemistry of the *p*-methoxybenzoyl chromophore have not been reported in the case of small molecules, therefore limiting the possibility of comparison with model systems.

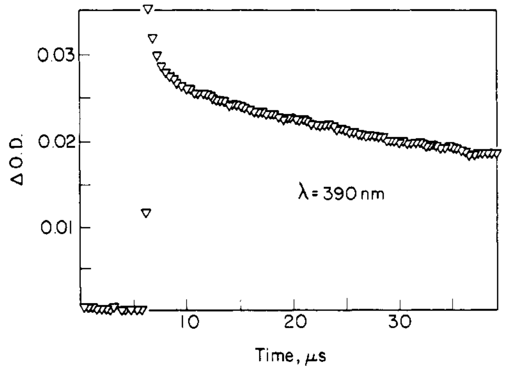


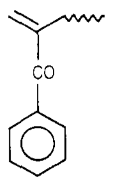
Figure 3. Decay of the PPMA triplet in chloroform at -60 °C, illustrating the fast and slow components. Data obtained at low excitation dose (12%), where T-T annihilation does not take place.

We complete this section by pointing out that in addition to the Norrish type II fragmentation (Scheme I), other processes (quenching by trace impurities, self-quenching, and radiationless decay) could be playing a limited role in the decay of PPMA triplets; this would naturally cast some doubts on the applicability of an Arrhenius expression to the treatment of the data. Even if this was the case, the Arrhenius expression still provides a convenient way of reporting the data and further elaboration at this point would be mere speculation. We note that impurity quenching is unlikely to be the main decay process, since the activation energy for such a process is expected to be considerably less than 6 kcal/mol.

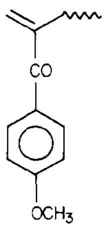
Importance of a Fast Component in the Decay of PPMA Triplets. As pointed out earlier, the decay of PPMA presents, in addition to the main component (used for the Arrhenius studies and already discussed), a fast initial component which can frequently account for ~20% of the triplet decay. The involvement of this fast process is clearly evident at low temperatures where the type II process becomes quite slow, and is detectable at all wavelengths where the triplet shows absorptions. The effect is illustrated in Figure 3. Two experimental observations are particularly important in understanding the role and origin of the fast decay: The fraction of fast decay can be increased by increasing the laser dose but cannot be completely eliminated by decreasing the dose or extrapolating to zero dose. The importance of the decay can also be increased by partially degrading the polymer (by UV irradiation) prior to the laser experiment. On the other hand, careful preparation and handling of the sample decreases the importance of the fast decay although our efforts to completely eliminate it were unsuccessful. In addition, the changes mentioned above do not have any drastic effect on the rate of the fast decay, which typically takes place with a lifetime in the 0.4-1.0-μs range in chloroform. Even changes in the temperature do not seem to have extensive effects although some slowdown at the lower temperature seems apparent.

In the case of poly(phenyl vinyl ketone), PPVK, we have shown in earlier studies[31] that the vinyl ketone and group (II) produced upon chain fragmentation acts as a quencher within the macromolecule.

The high quenching efficiency of an end group such as II is directly related to the ability of the macromolecular chain to promote energy migration, effectively behaving as an antenna. In the case of PPMA, the end group resulting from photodegradation, III, can be expected to be



II



III

as efficient as II as an internal quencher. Perhaps the main difference between PPVK and PPMA is that in the latter the triplet lifetime is long enough to allow the direct, time-resolved detection of quenching by end groups such as III. We suggest that the fast decay observed is largely the result of quenching by end groups incorporated in some of the macromolecules during the preparation, purification, and handling of the polymer samples, with some contribution, at high excitation doses, from triplet–triplet annihilation within the macromolecule. We note that most macromolecules are expected to be quencher free, with only a small fraction (responsible for the fast decay) containing quencher end groups. On the assumption that this mechanism is correct, it is possible to estimate an approximate triplet energy hopping frequency in PPMA.

The sample on which most of our measurements were carried out has a molecular weight of 8.8×10^5, which corresponds to a chain length of 5400. The fast decay in chloroform at −60 °C has a lifetime of ~700 ns. If we assume that excitation takes place at random and that the fraction of macromolecules that have a quencher at the end have a chain length of ca. 2700 units,[32] then the excitation will have to travel about 1350 units to reach the end of the chain. However, many more than 1350 hops will be required to visit this number of chromophores. According to random walk theory for one dimension,[31,33,34] the number of hops required $\langle n \rangle$, will be given by

$$\langle n \rangle = N^2/6 \tag{1}$$

where N is the number of chromophores visited. Therefore, about 3×10^5 hops will occur in 700 ns; i.e., the average time per hop is ~2.3 ps, corresponding to a hopping frequency of 4.3×10^{11} s^{-1}. The value is an excellent agreement with the frequency (1.6×10^{12} s^{-1}) estimated earlier for the case of PPVK.[31]

It should be noted that while the calculation above includes several approximations, the final value is obtained through a very simple calculation based on time-resolved measurements and on the evaluation of the chain length and can be expected to lead to an accurate "order-of-magnitude" estimation of the hopping frequency.

We were initially surprised by the observation that quenching by end groups and T–T annihilation took place in the same time domain. In fact, both processes (see Figure 4) are controlled by the same phenomena, i.e., energy migration along the chain, and can therefore be expected to occur with similar kinetics.

Possibility of Loop Transfers. The term loop transfers is used here to describe the process by which energy migration in a given segment of the polymer chain is interrupted by the transfer of the excitation to a different (formally remote) segment of the same chain, thus initiating "visits" to this new segment. These transfers can, in principle, result when the polymer conformation is such that it brings together two chromophores which are otherwise separated by many monomer units if the separation was to be probed by their distance *along* the chain.[35]

It is clear that loop transfers cannot compete with single hops; however, the question is whether they could compete with the overall migration process that frequently requires 10^4–10^6 hops.

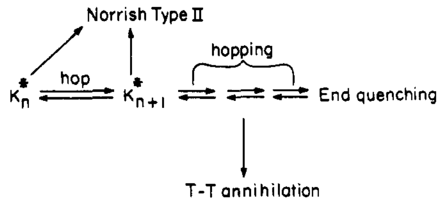


Figure 4. Mechanism of triplet decay in PPMA (K* represents an excited chromophore).

While loop transfers could lead to the energy traveling long distances in terms of chain separation, this in itself would not substantially affect the general conclusions obtained with a one-dimensional random walk model, as applied here and in earlier papers,[14,31] since those conclusions center on the examination of the number of chromophores visited. One must consider whether the number of hops required to visit a given number of chromophores is different when loop transfers occur. Qualitatively it is easy to see that the same number of hops could lead to more chromophores visited if loop transfers occur. A quantitative and general treatment of the problem is quite difficult since the answer will depend upon (i) the approach distance required for loop transfers to be possible, (ii) the probability that transfer will occur *if* the distance requirements are met (the maximum possible statistical value is 0.5),[38] (iii) the size of the loops, which will control whether the new segment where hopping occurs has chromophores in common with the donor segment of the chain, (iv) the number of chromophores visited prior to a loop transfer (see below), and (v) the kinetics with which the loops rearrange during the triplet lifetime.

Given the difficulties in modeling the system mentioned above, one wonders whether the necessary information could be obtained from a study of polymers where loop transfers would be allowed but migration would not. Studies of this type are, of course, possible and to some extent have already been carried out,[39,40] but they have at least the following limitations: (i) In order to avoid migration the chromophores need to be separated; thus their abundance is lower than in the molecules of interest. Our models usually had ≲20% carbonyl chromophores.[40] We feel that abundances larger than this value would raise the question of migration as a contributing factor. (ii) The presence of a large fraction of comonomer units makes the solution behavior (and conformation) of the model polymer different from the one it intends to model. (iii) The probability of energy transfer (given an appropriate encounter) is higher when the energy is not migrating or undergoing only limited migration. This last statement may not be what simple theory would predict, but rather, it reflects the experimentally observed phenomenon.[41]

Let us consider the case of only one loop transfer during the triplet lifetime, which is, in turn, controlled by a quencher in the chain such that on the average it requires the excitation to visit N chromophores for decay to take place. The number of hops required, $\langle n \rangle$ (see eq 1) will be given by

$$\langle n \rangle = (fN)^2/6 + [(1 - f)N]^2/6 \tag{2}$$

where f is the fraction of the required N chromophores visited before the loop transfer takes place.

$$\langle n \rangle = [2f^2 - 2f + 1]N^2/6 \tag{3}$$

The number of hops required will be a minimum for $f \equiv 0.5$ and will correspond to half of those required in the absence of loop transfers. In addition, we have assumed that the group of chromophores visited before and after transfer is entirely different; i.e., there are no common chromophores. Therefore, these conditions illustrate the maximum possible effect. In general, if loop transfers would occur at "symmetric" intervals, ω times during the triplet lifetime, the number of hops will be reduced by $(\omega + 1)^{-1}$, this being the maximum possible effect.

We will now try to combine these data with experimental results obtained in methyl methacrylate–phenyl vinyl ketone–2-vinylnaphthalene (MPN) copolymers,[39,40] where we observed that up to ~20% carbonyl units had no effect on the internal rate of energy transfer from the benzoyl to the naphthalene moieties. We concluded that energy transfer between remote carbonyl groups did not make any significant contribution to the overall process leading to the triplet state of the naphthalene acceptor groups in phenomena that took place in the 10^{-6}–10^{-7}-s time domain.

Quite clearly, the fact that loop transfers do not play a significant role in other carbonyl-containing polymers (as MPN) does not necessarily rule out their participation in the case of PPMA, and while their quantitative evaluation is difficult, we believe that it is possible to put an upper limit to the error that they could conceivably introduce. To do this, we make in each case the most unfavorable possible assumption.

We note that the data for PPMA were obtained in chloroform, which, being an excellent solvent for this polymer, makes loops less likely. We also assume that in the case of MPN copolymers mentioned above, where we did not observe evidence for energy transfer between carbonyl groups, one such transfer took place for every observable transfer to the acceptor naphthalene. In addition, we multiply by 5 to account for the increased abundance of carbonyls in PPMA. That is, we assume that 5 loop transfers take place in PPMA during the triplet lifetime. Further, and against statistics, we make the approximation that the transfers occur at "symmetric" intervals, that is, every time $N/6$ chromophores have been visited. We also assume that none of the 6 segments visited share any chromophores. This is, of course, unlikely since it requires loops of several hundred chromophores.[43] We also make the approximation that migration will not decrease the probability of transfer. If all these unlikely conditions were met simultaneously, then the error in the number of hops required (and thus in the hopping frequency) will be a factor of 6. We believe that this analysis supports our earlier statement (vide supra) that while the approximations used will introduce some error, the order of magnitude for the frequency of hopping will not change drastically.[44]

Conclusion

Poly(*p*-methoxyacrylophenone), PPMA, is an excellent model polymer for the study of time-resolved phenomena involving carbonyl chromophores in macromolecules. Efficient energy migration takes place in the triplet state with a hopping frequency estimated as 4.3×10^{11} s^{-1} in chloroform at -60 °C. Energy transfer through loops, while not completely ruled out, is shown not to occur to an extent that would vitiate the estimation of the hopping frequency. The latter is suprisingly high considering that the behavior of the chromophore and its spectroscopic properties strongly parallel those of monoketones, such as *p*-methoxyacetophenone.

The temperature dependence of triplet decay in PPMA and copolymers containing the *p*-methoxybenzoyl moiety shows activation energies in the 5–6 kcal/mol range. Interestingly, copolymers containing phenyl vinyl ketone moieties show about the same activation parameters, suggesting that the same triplet level may be populated in homo- and copolymers.

The triplet state of PPMA is quenched by conventional triplet quenchers (dienes, naphthalenes, or oxygen) with rate constants of $(1\text{–}3) \times 10^9$ M^{-1} s^{-1} in solution at room temperature.

o-Hydroxybenzophenone, a representative example of a wider range of photostabilizers, is shown to have three modes of action: (i) UV screening, (ii) triplet quenching, and (iii) reactive quenching probably involving triplet attack at the hydroxyl group.

Experimental Section

p-Methoxyacrylophenone was prepared as described in the literature.[18] The monomer was distilled under vacuum (with considerable loss). The polymers were prepared by using a 20–40% solution of monomer in benzene. The process was initiated with azobis(isobutyronitrile) (50 °C) and allowed to proceed to 15–20% conversion. The polymer, PPMA, was then precipitated with methanol and redissolved in benzene, and the procedure was repeated five or six times. The polymer sample was finally freeze-dried from benzene. The properties of PPMA agreed well with those reported,[18] except that our samples (from distilled monomer) were moderately soluble in benzene and in the laser experiments led to slightly longer triplet lifetimes. Molecular weights were determined in chlorobenzene using the reported constants.[18]

Phenyl vinyl ketone was prepared by a reported procedure[46] and distilled. Styrene and methyl methacrylate were treated with aqueous base, washed, dried, and distilled. Polymerization and purification procedures for the copolymers were the same ones described above for PPMA.

The quenchers used, dienes and 1-methylnaphthalene, were purified by distillation, and *o*-hydroxybenzophenone was purified by recrystallization from ethanol.

The samples for the laser experiments were contained in Suprasil cells and deareated by bubbling oxygen-free nitrogen. The excitation source was a Molectron UV-24 nitrogen laser and the transient absorptions were monitored by a computerized system described elsewhere.[47]

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Quasi-Elastic Light Scattering Studies of Semidilute Xanthan Solutions

J. G. Southwick,* A. M. Jamieson, and J. Blackwell

Department of Macromolecular Science, Case Western Reserve University,
Cleveland, Ohio 44106. Received May 13, 1980

ABSTRACT: Quasi-elastic light scattering has been used to investigate the properties of xanthan gum in aqueous solution over a wide range of concentrations at low ionic strength. With increasing concentration, a transition is seen at a concentration $c^* \simeq 0.02\%$ as has been reported previously, which corresponds approximately to the onset of molecular overlap. We have now observed a second transition at a higher concentration, $c_2 \simeq 0.07\%$, where, in addition to a general reduction in the relaxation times, the single (polydisperse) relaxation mode observed below c_2 is replaced by bimodal behavior above the transition. Flow birefringence experiments show an intensity transition at c_2, corresponding to a sudden increase in anisotropy, indicative of intermolecular ordering at higher concentration. A possible interpretation of the bimodal behavior is that the c_2 transition is due to the development of more permanent intermolecular associations in xanthan solutions, which ultimately result in junction zones stabilizing a three-dimensional network. Of the two relaxation modes detected above c_2, the slow mode can be assigned to motions of the junction zones. Alternatively, the bimodal behavior is qualitatively similar to that predicted by Doi and Edwards for congested solutions of totally rigid rod macromolecules. In particular, the fast mode is concentration independent, while the slow mode is inversely proportional to concentration. However, the data show significant differences from those expected for fully extended chains and may be compatible with a broken-rod conformation for xanthan in solution.

Introduction

The extracellular polysaccharide xanthan produced by the bacterium *Xanthomonas campestris* forms high-viscosity solutions when dissolved in water. This useful property has led to the commercial applications of this polysaccharide as xanthan gum. The chemical structure of xanthan[1,2] is a chain of $(1\rightarrow4)\beta$-D-glucose residues with a trisaccharide substituent on alternate glucose residues. The side chain is β-D-mannopyranosyl-$(1\rightarrow4)$-α-D-glucuropyranosyl-$(1\rightarrow2)\beta$-D-mannopyranoside 6-*O*-acetate. In addition, the terminal D-mannose residue of the side chain may have a pyruvic acid residue linked to the 4 and 6 positions. The degree of pyruvate substitution typically varies from 0.31 to 0.56[3] and has been shown to be a function of the particular bacterial strain and fermentation conditions.[4,5] This distribution of the pyruvate groups on the xanthan chain has not been determined.

The rheological properties of xanthan solutions have been studied at different concentrations over a wide range of shear rates.[6] At low concentrations of xanthan, and for very low shear rates, Newtonian viscosity behavior was observed; in contrast, solutions of higher concentrations showed an apparent yield stress. Furthermore, it has been reported[7] that aqueous xanthan solutions at low ionic strength are birefringent at concentrations above 0.25%; in the presence of salt birefringence is seen for xanthan

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*Address correspondence to J.G.S. at Shell Development Co., Houston, Texas 77001.

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