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Quenching of Triplet Macromolecules by Small Molecules. The Role of Energy Migration[1]

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Abstract: Intramolecular triplet energy migration in a macromolecule containing carbonyl chromophores has been shown to result in a decrease of the reactivity of that chromophore toward a variety of small molecules. The results contrast sharply with theoretical predictions and generally accepted ideas on polymer reactivity. The quenchers examined include conjugated dienes, 1-methylnaphthalene, stable nitroxides, and oxygen.

Energy migration processes in macromolecular systems have been the subject of considerable attention during the last few years. In the case of triplet states, energy migration occurs solely by the exchange mechanism.[4-10] Recent studies indicate that, in the case of carbonyl chromophores, triplet energy transfer between nearest neighbors in a macromolecule in solution occurs with rate constants in the 10^{10}–10^{12} s^{-1} range.[11-16] For comparison, rates of exothermic triplet energy transfer within the encounter complex in homogeneous solution are in the 10^{10} to $\geq 2 \times 10^{12}$ s^{-1} range.[17] It is generally accepted that triplet energy migration can play a role in the quenching of triplet macromolecules by small molecules. Quenching of macromolecules by small molecules is usually slower than quenching processes involving two small molecules, an effect that can be attributed to a decrease of the diffusional contribution of the energy donor.[16] When energy migration takes place in the macromolecule, the quenching process is expected to be faster than that in the case of polymers where migration does not take place, or where it is severely restricted.[9,10] This prediction is supported by theory and reflects the expected contribution of energy migration to the overall diffusion process.[9] These ideas are rather widely accepted, although in a recent publication[12] we have pointed out that the effect of energy migration on intermolecular energy transfer rates may be smaller than usually expected.[18] Kilp and Guillet,[15] in a recent study of the effect of polymer tacticity on the photochemistry of poly(acrylophenones), make ample use of these concepts, and their report illustrates well the currently accepted, though frequently unproven ideas on the role of intramolecular triplet energy migration on intermolecular reactions of carbonyl polymers.

The work leading to this report started as an attempt to quantify the reactivity enhancement resulting from energy migration. Our initial studies not only indicated the absence of the expected—and predicted—effect but in fact they suggested that energy migration can hinder intermolecular processes. As we tried to rule out different potential problems, or to find examples with more conventional behavior, we convinced ourselves that the general behavior sharply contradicts the theory. The systems examined include carbonyl chromophores with triplet states of different types, "good" and "bad" polymer solvents, diffusional and nondiffusional quenchers, and quenching processes involving a variety of mechanisms. It is our observation that triplet energy migration in a macromolecule generally reduces the probability of reaction with other molecules. While we have no doubt that exceptions to this rule can be found, our evidence conclusively shows that an such example would be the exception rather than the rule.

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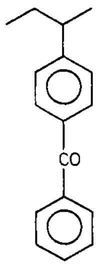
Table I. Kinetic Data for the Quenching of Various Carbonyl Triplets in Solution

label	substrate[a]	quencher	solvent	T, K	k, M^{-1} s^{-1}
A-1	*p*-methoxyacetophenone	1,3-octadiene	chloroform	300	$(5.07 \pm 0.41) \times 10^9$
A-2m	PPMA	1,3-octadiene	chloroform	300	$(8.11 \pm 0.53) \times 10^8$
A-3m	co(PMA-PVK)	1,3-octadiene	chloroform	300	$(7.58 \pm 0.24) \times 10^8$
A-4	co(PMA-Sty)	1,3-octadiene	chloroform	300	$(1.17 \pm 0.07) \times 10^9$
A-5	co(PMA-MMA)	1,3-octadiene	chloroform	300	$(1.20 \pm 0.12) \times 10^9$
B-1	*p*-methoxyacetophenone	1,3-octadiene	benzene	300	$(8.96 \pm 0.45) \times 10^9$
B-2m	PPMA	1,3-octadiene	benzene	300	$(8.49 \pm 1.83) \times 10^8$
B-3m	co(PMA-PVK)	1,3-octadiene	benzene	300	$(1.06 \pm 0.17) \times 10^9$
B-4	co(PMA-Sty)	1,3-octadiene	benzene	300	$(1.24 \pm 0.05) \times 10^9$
B-5	co(PMA-MMA)	1,3-octadiene	benzene	300	$(1.23 \pm 0.13) \times 10^9$
C-1	*p*-methoxyacetophenone	1-methylnaphthalene	chloroform	300	$(8.89 \pm 1.17) \times 10^9$
C-2m	PPMA	1-methylnaphthalene	chloroform	300	$(1.51 \pm 0.16) \times 10^9$
C-3	co(PMA-MMA)	1-methylnaphthalene	chloroform	300	$(1.66 \pm 0.06) \times 10^9$
D-1	*p*-methoxyacetophenone	oxygen	chloroform	300	$(4.15 \pm 0.24) \times 10^9$
D-2m	PPMA	oxygen	chloroform	300	$(7.23 \pm 0.33) \times 10^8$
D-3m	co(PMA-PVK)	oxygen	chloroform	300	$(7.47 \pm 0.38) \times 10^8$
D-4	co(PMA-Sty)	oxygen	chloroform	300	$(1.48 \pm 0.15) \times 10^9$
D-5	co(PMA-MMA)	oxygen	chloroform	300	$(1.06 \pm 0.05) \times 10^9$
E-1	*p*-methoxyacetophenone	oxygen	benzene	300	$(6.03 \pm 0.08) \times 10^9$
E-2m	PPMA	oxygen	benzene	300	$(1.35 \pm 0.02) \times 10^9$
E-3m	co(PMA-PVK)	oxygen	benzene	300	$(1.31 \pm 0.13) \times 10^9$
E-4	co(PMA-Sty)	oxygen	benzene	300	$(2.28 \pm 0.18) \times 10^9$
E-5	co(PMA-MMA)	oxygen	benzene	300	$(1.84 \pm 0.10) \times 10^9$
F-1	*p*-methoxyacetophenone	di-*tert*-butyl nitroxide	chloroform	300	$(1.24 \pm 0.07) \times 10^9$
F-2m	PPMA	di-*tert*-butyl nitroxide	chloroform	300	$(2.01 \pm 0.10) \times 10^8$
F-3	co(PMA-Sty)	di-*tert*-butyl nitroxide	chloroform	300	$(2.40 \pm 0.17) \times 10^8$
F-4	co(PMA-MMA)	di-*tert*-butyl nitroxide	chloroform	300	$(2.83 \pm 0.14) \times 10^8$
G-1	*p*-methoxyacetophenone	triethylamine	benzene	300	$(1.03 \pm 0.09) \times 10^8$
G-2m	PPMA	triethylamine	benzene	300	$(9.77 \pm 1.35) \times 10^6$
G-3	co(PMA-Sty)	triethylamine	benzene	300	$(1.33 \pm 0.15) \times 10^7$
H-1	acetophenone	1,3-octadiene	chloroform	230	$(2.63 \pm 0.18) \times 10^9$
H-2m	1,5-diphenylpentane-1,5-dione	1,3-octadiene	chloroform	230	$(2.06 \pm 0.27) \times 10^9$
H-3m	PPVK	1,3-octadiene	chloroform	230	$(6.75 \pm 0.35) \times 10^8$
H-4	co(PVK-MMA)	1,3-octadiene	chloroform	230	$(8.11 \pm 0.16) \times 10^8$
I-1	4-methylbenzophenone	1,3-octadiene	benzene	300	$(5.48 \pm 0.05) \times 10^9$
I-2m	PVB	1,3-octadiene	benzene	300	$(1.67 \pm 0.26) \times 10^9$
I-3	co(VB-Sty)	1,3-octadiene	benzene	300	$(2.52 \pm 0.02) \times 10^9$
J-1	4-methylbenzophenone	di-*tert*-butyl nitroxide	benzene	300	$(4.06 \pm 0.19) \times 10^9$
J-2m	PVB	di-*tert*-butyl nitroxide	benzene	300	$(1.25 \pm 0.18) \times 10^9$
J-3	co(VB-Sty)	di-*tert*-butyl nitroxide	benzene	300	$(1.46 \pm 0.06) \times 10^9$
K-1	4-methylbenzophenone	TEMPO[b]	benzene	300	$(7.51 \pm 1.30) \times 10^9$
K-2m	PVB	TEMPO[b]	benzene	300	$(1.08 \pm 0.17) \times 10^9$
K-3	co(VB-Sty)	TEMPO[b]	benzene	300	$(2.36 \pm 0.15) \times 10^9$
L-1	4-methylbenzophenone	2,5-dimethyl-2,4-hexadiene	benzene	300	$(6.19 \pm 0.09) \times 10^9$
L-2m	PVB	2,5-dimethyl-2,4-hexadiene	benzene	300	$(1.23 \pm 0.25) \times 10^9$
L-3	co(VB-Sty)	2,5-dimethyl-2,4-hexadiene	benzene	300	$(2.74 \pm 0.14) \times 10^9$

[a] See experimental for polymer abbreviations. [b] 2,2,6,6-Tetramethylpiperidinooxy free radical.

Our data have been obtained with use of laser flash photolysis techniques, monitoring directly the evolution of T–T absorptions. The donor triplets are all carbonyl compounds; however, they do cover $n\pi^*$ and $\pi\pi^*$ triplets (**1** and **2**, respectively), as well as the case of low-lying $n\pi^*$ states with a nearby $\pi\pi^*$ triplet (**3**).



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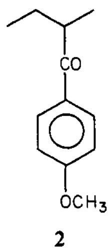

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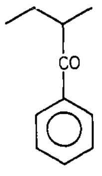

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Results

All our experiments have been carried out with use of the pulses (337.1 nm, ~8 ns, up to mJ) from a nitrogen laser for excitation. The general procedure used was the following: The samples of polymers and of a suitable model substrate were examined in the laser photolysis system and the corresponding triplet lifetimes determined from the time evolution of the signal at or near the corresponding T–T absorption maxima.[19] The laser dose was attenuated whenever necessary in order to minimize the importance of triplet–triplet annihilation processes. Plots of rates of triplet decay as a function of laser dose were used to determine a range of acceptable laser doses. Variable concentrations of

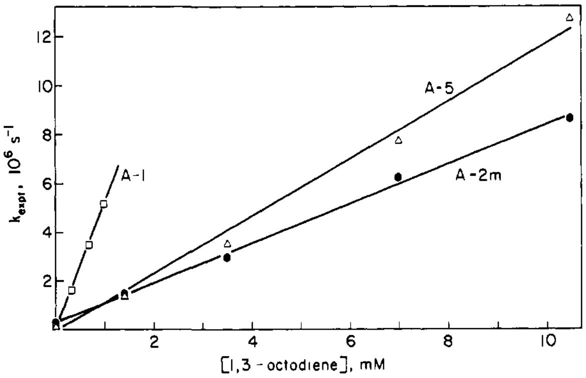

Figure 1. Kinetic data for the quenching of triplet *p*-methoxyacetophenone (□), co(PMA-MMA) (△), and PPMA (●) by 1,3-octadiene in chloroform at 300 K.

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[19] In general, triplet **1** was monitored at 525 or 540 nm, while the triplet states of **2** and **3** were followed at 390 and 370 nm, respectively. Full details are provided with the Supplementary Material.

quenchers were then added and the corresponding experimental pseudo-first-order rate constants for triplet decay (k_{expt}) were determined in each case. Representative plots of k_{expt} against the concentration of quencher are shown in Figure 1. The slope of the plot corresponds to k_q, the bimolecular rate constant for triplet quenching. Table I summarizes the results for the systems examined. Tables 2–47 are provided as supplementary material and give full kinetic details. Measurements involving poly(phenyl vinyl ketone), PPVK, cannot be carried out at room temperature because of interference by the Norrish Type II biradical.[12,20–22]

Each line in Table I has been given a label (far left) composed of a capital letter, indicating the series of measurements, a number, characterizing that particular measurement, and (if applicable) an "m" in those cases where migration is known to be an extremely fast process.[11–13,23] All the rate constants in each series (same capital letter in the label) have been obtained under "matched" conditions, usually the same day, with solvent from the same batch and the same quencher and quencher stock solution; the chromophore is the same for all the substrates in any given series. Thus, systematic errors within any series should be minimal. Random errors are included with each rate constant and quoted as twice the standard deviation. Typically 4–7 quencher concentrations were examined for each substrate, with the exception of oxygen, where only three points, corresponding to degassed, air saturated, and oxygen saturated, were measured. Thus, statistical errors in the case of oxygen are of only limited significance. Measurements in series J-2m showed substantially more dispersion than data in any of the other systems; the reasons for this peculiarity are not clearly understood.

Measurements with 1-methylnaphthalene as a quencher were carried out at 585 nm, monitoring the long wavelength weak T–T absorptions of the *p*-methoxybenzoyl chromophore.[24] This method was preferred over the (much easier) measurement of the formation of triplet 1-methylnaphthalene at 420 nm,[25] so that the approach employed would be the same for all systems.

Details of the abbreviations used are given in the Experimental Section.

Discussion

To a considerable degree, the data in the different series in Table I were acquired in an attempt to prove not the kinetic effects observed but rather the opposite ones. In fact, many experiments were designed in efforts to find out if our observations were the result of some kind of artifact, even if the possible origin of such an artifact was not clear. We feel that the following points can be established from our data:

(a) Intramolecular energy migration between carbonyl chromophores in a macromolecule results in a reduction of the rate of interaction of the macromolecule with other reagents.

(b) The effect seems to be largely independent of the nature ($\pi\pi^*$ or $n\pi^*$) of the low-lying carbonyl triplet state, as well as of the proximity of the two levels.[26]

(c) While changing from polymers where migration is efficient to others where it is not introduces changes in the macromolecular structure (because of the need to use a co-monomer), the changes in rate constants do not seem to be determined by these; series A in Table I illustrates this characteristic. The polymers in lines A-4 and A-5 show that the rates are not determined by the co-monomer properties, while A-2m and A-3m show that the rates are generally similar regardless of whether migration involves chromophores of one or more types.

(d) The effect on the rates is not limited to diffusion-controlled reactions, but instead seems to be a rather general phenomenon. In fact, the reduction in rates in the migrating cases seems larger for the slower processes: i.e., compare series A and G with C.

(e) The effect is not likely to result from changes in macromolecular conformation resulting from polymer–solvent interactions. For example, PPMA is barely soluble in benzene,[27] while it dissolves readily in chloroform; however, the same kinetic characteristics are observed in both solvents. The independence upon the nature of co-monomer units also supports the idea that our observations are not the result of solvent-related artifacts.

(f) The ability of the quencher to reach different parts of the macromolecule seems to have little or nothing to do with the kinetic changes observed. For instance, oxygen, which should not have any problems accessing different segments of the polymer, shows one of the largest effects (see series D and E in Table I). While this point seems to us well established, we cannot completely rule out the possibility that excited chromophores may be systematically better shielded from external quenchers in the case of homopolymers as compared with copolymers.

(g) The mechanism for quenching does not seem critically important; thus, energy transfer, paramagnetic quenching,[29] or charge transfer all show the same characteristics. It should be noted, however, that all these processes involve interactions of the same nature, i.e., electron exchange.

Points a–g above establish the characteristics of the rate changes observed and clearly show that, in general, we can expect triplet energy migration to reduce the reactivity of carbonyl chromophores, at least when the reactions involve electron exchange interactions. However, points a–g do not provide an explanation for the phenomena observed.

We believe that trends shown by the data in Table I are too systematic to be explained on the basis of conformational problems, limited accessibility of the excited site, local concentration effects, or minor changes in triplet energy. This last possibility deserves some comment; while several groups have pointed out that the presence of sequential chromophores does not change substantially their characteristics and reactivity,[11,30–33] minor changes in triplet energy can indeed take place. However, in processes such as quenching by dienes, trivial changes in triplet energy are not expected to have a substantial effect on the rates of triplet energy transfer. In fact, if we compare the kinetics in series I in Table I with those in series B, where the triplet energy is 3–4 kcal mol^{-1} higher, it becomes clear that the changes within a given series cannot result from a minor decrease in triplet energy when sequential chromophores are present.

We believe that the data in Table I should be interpreted in terms of a true decrease of the reaction probability during an encounter in those systems where energy migration is favored.

Balzani et al.[35,36] have recently proposed a general treatment for energy transfer processes. In terms of their model we can write the following mechanism for the case of energy transfer:

$$\mathrm{D^* + Q} \underset{k_{-\mathrm{d}}}{\overset{k_\mathrm{d}}{\rightleftharpoons}} \mathrm{D^*\cdots Q} \xrightarrow{k_{\mathrm{en}}} \mathrm{D\cdots Q^*} \xrightarrow{k_{-\mathrm{d}}} \mathrm{D + Q^*}$$

where D and Q are the donor and quencher. In Balzani's

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(20) Scaiano, J. C.; Stewart, L. C. *Polymer*, **1982**, *23*, 913–915.

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(25) Porter, G.; Windsor, M. W. *Proc. R. Soc. London, Ser. A* **1958**, *245*, 238–258.

(26) E.g., See Wagner and Nakahira (Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474–8475) for a discussion of the relative energies of $n\pi^*$ and $\pi\pi^*$ levels.

(27) PPMA disolves or simply swells in benzene depending upon the method of preparation.[13,24,28]

(28) Lukac, I.; Moravcik, M.; Hrdlovic, P. *J. Polymn. Sci., Polym. Chem. Ed.* **1974**, *12*, 1913–1924.

(29) E.g.: Scaiano, J. C. *Chem. Phys. Lett.* **1981**, *79*, 441–443 and references therein.

(30) Golemba, F. J.; Guillet, J. E. *Macromolecules* **1972**, *5*, 212–216.

(31) Salvin, R.; Meybeck, J.; Faure, J. *J. Photochem* **1976/77**, *6*, 9–16.

(32) Lukac, I.; Pilka, J.; Kulickova, M.; Hrdlovic, P., *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1645–1653. Lukac, I.; Chmela, S.; Hrdlovic, P. *J. Photochem.* **1979**, *11*, 301–311.

(33) That is to say they behave as very weakly coupled chromophores.[9]

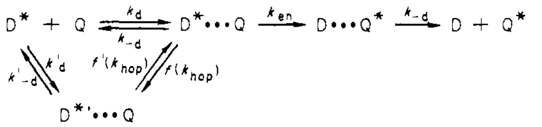
(34) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; Table 1-1.

(35) Balzani, V.; Bolletta, F.; Scandola, F. *J. Am. Chem. Soc.* **1980**, *102*, 2152–2163.

(36) Balzani, V.; Bolletta, F.; Scandola, F.; Ballardini, R. *Pure Appl. Chem.* **1979**, *51*, 299–311.

mechanism all steps are in principle reversible; however, in the systems examined here the enthalpy change is sufficiently favorable that the transfer step itself (k_{en}) can be expected to be irreversible. The kinetic differences between small molecules and macromolecules as donors are largely the result of changes in k_d (at least in cases that approach diffusion control); however, the difference between macromolecules in any given series must reflect changes in k_{en}. It should be noted that since molecular diffusion is essentially the result of contribution from the small molecule (i.e., Q),[37] the actual molecular weight of the macromolecule is not very important.

The model presented above does not differentiate between interaction of the quencher with the excited polymer generally and with the excited chromophore (or segment) in particular. A more realistic model should take this into consideration. The following scheme takes into account an overall interaction (D*′···Q) and a specific interaction with the excited segment, D*···Q. The latter may involve just one or a few chromophores.



Here k_d and k'_d have qualitatively the same meaning as before, though they refer to local and general interactions, respectively. The functions $f'(k_{hop})$ and $f(k_{hop})$ are not expected to affect the distribution of D*···Q and D*′···Q encounters if neither exciplex nor destabilizing interactions take place between D* and Q. If the quencher mobility along the polymer chain is neglected, these functions are essentially the rate constants for energy migration. The rate of migration will be substantially slower than the frequency of hopping, since the latter is a random process, which in every step transfers the energy in either direction with equal probability.[12] In general random walk models lead to a quadratic dependence between the number of chromophores traveled and the number of hops required,[18] though the function is more complex for small distances. The function $f(k_{hop})$ can be regarded as a measure of the antenna effect, i.e., the ability of the chromophore chain to bring the energy to the reactive site. A model such as the one given above cannot explain the differences observed in this work, unless one assumes that $N(\text{D*}\cdots\text{Q})f(k_{hop}) \gg N(\text{D*}'\cdots\text{Q})f'(k_{hop})$ (where N represents the probability for encounters of each type). This would require destabilizing interactions between the excited chromophore and Q (i.e., the latter "chasing" the energy away), which would be unlikely to be insensitive to quencher and quenching mechanism. Without such an assumption this mechanism could explain the absence of an effect, but not an inverse effect; in other words, the energy would be as likely to move toward the quencher as away from it. In general the data suggest that the energy migrates much faster than the interaction of the excited chromophore with the quencher. The same kinetic arguments that have been developed above for energy transfer also apply to other quenching mechanisms.

We favor a mechanism in which the decrease in polymer reactivity is induced by triplet migration as a result of changes in k_{en}, which in turn reflect a decrease in the transmission coefficient κ. The changes in κ can be explained in terms of small electronic factors due to unfavorable orbital overlap. It is well recognized that "for exchange energy transfer processes the overlap criterion is quite stringent".[35] Whenever structural rearrangements of any kind are necessary, whether we talk about them in terms of non-vertical transitions, Franck-Condon factors, or some kind of "supermolecule", we can expect as a requirement that the excitation stays in a given chromophore long enough for those changes to take place. These ideas should be regarded only as a tentative explanation, offered simply in view of the fact that currently accepted theories are inadequate to explain the experimental observations. New theoretical models are clearly necessary.

As pointed out earlier, and exemplified in recent work,[15] it is generally accepted that energy migration enhances polymer reactivity. A few reports have suggested that these effects may not be as large,[12] or as simple,[38] as usually believed; however, these remarks have not received much attention. Regardless of whether the interpretation offered is correct or not, it should be clear that the experiment leaves no doubt that the predominant effect of triplet energy migration on carbonyl reaction rates is not the one usually predicted. Finally, it should be re-emphasized that all our observations refer to triplet carbonyls, information was not obtained for other chromophores or excited states, and it is not clear whether conclusions based on triplet carbonyl behavior could be extrapolated to other systems.

Experimental Section

Materials. All polymers were prepared by radical-initiated polymerization of monomer mixtures in benzene. The procedures for preparation and purification have been discussed elsewhere.[12-14,20,24] Samples containing phenyl vinyl ketone or *p*-methoxyacrylophenone moieties were the same as those discussed in earlier publications. Molecular weights (viscosity) were typically in the 200 000 to 400 000 range, e.g., PPMA 400 000, co(PMA-MMA), 350 000, PPVK 40 000 and 200 000, and co(PVK-MMA) 300 000.

The copolymer of styrene and 4-vinylbenzophenone was prepared by partial Friedel-Crafts benzoylation[39] of a polystyrene standard (from Polysciences Inc., M_w 110 000; $M_w/M_n < 1.06$) and contained 23% benzophenone moieties.

The sample of poly(vinylbenzophenone) was a generous gift from Professor W. Schnabel and had been prepared from 4-vinylbenzophenone; its molecular weight, M_w, was 2.4×10^5 and it had been purified by reprecipitation (4 times) from the benzene solution with methanol.

Solvents and quenchers were usually from Aldrich and were distilled or recrystallized before use. Benzene was purified as indicated in earlier reports.[40]

Abbreviations. The following abbreviations were used for the monomers: PMA = *p*-methoxyacrylophenone; PVK = phenyl vinyl ketone; Sty = styrene; MMA = methyl methacrylate; VB = 4-vinylbenzophenone. In the homopolymers the monomer abbreviations is preceded by P, as in PPMA. In the copolymers, the main chromophores (not the most abundant) is always listed first.

Laser Photolysis. The samples were excited with the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a Molectron UV-24 nitrogen laser. Our apparatus allows transient absorption measurements in the 10 ns to 100 μs time scale. The system has been fully interfaced with a PDP-11/23 computer that controls the experiment and provides suitable data gathering, storage, processing, and hardcopy facilities. Further details have been given elsewhere.[41]

The concentrations of the polymer solutions were generally selected so that their optical density at 337 nm would be in the 0.3–1.0 range in the cells having 3-mm optical path.

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Registry No. PPMA, 34031-66-8; co(PMA-PVK), 77145-90-5; co(PMA-Sty), 53640-70-3; co(PMA-MMA), 53640-69-0; PVB, 25668-24-0; co(VB-Sty), 26777-91-3; TEMPO, 2564-83-2; PPVK, 26742-84-7; *p*-methoxyacetophenone, 100-06-1; acetophenone, 98-86-2; 1,5-diphenylpentane-1,5-dione, 6263-83-8; 1,3-octadiene, 1002-33-1; 1-methylnaphthalene, 90-12-0; oxygen, 7782-44-7; di-*tert*-butyl nitroxide, 2406-25-9; triethylamine, 121-44-8; 2,5-dimethyl-2,4-hexadiene, 764-13-6; 4-methylbenzophenone, 134-84-9.

Supplementary Material Available: Tables 2–47 giving detailed kinetic data (47 pages). Ordering information is given on any current masthead page.

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