Quenching Benzophenone Phosphorescence in Solution by Copolymers Containing Varying Amounts of Naphthalene Groups

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ABSTRACT: Phosphorescence decay measurements were made on samples of 4-(methoxycarbonyl)benzophenone (1) in acetone solution in the presence of a series of copolymers of methyl methacrylate and 1-naphthylmethyl methacrylate. The data were used to obtain the rate constants $k_{obs}^{(2)}$ for triplet quenching by the naphthalene [N] groups in the polymer. The data fit a model where diffusion of photoexcited 1 into the polymer coil is followed by a competition between reaction with the N groups and diffusion back into the bulk solution. The model accommodates the rate changes observed with changes in the N-group content of the copolymers.

Several years ago Schnabel et al.[1] carried out an interesting series of pulsed radiolysis experiments in which they generated •OH in aqueous solution and monitored the rate of its consumption due to the reaction with dissolved polymer molecules. When the polymer concentration was low ($c \ll c^*$) and the coils were well separated, the second-order rate constant obtained from the measurements, $k_{obs}^{(2)}$, varied in proportion to the hydrodynamic radius, R_h, of the polymer. These findings were interpreted in terms of a diffusion-controlled rate of reaction between •OH and the polymer, with the subsequent H-abstraction reaction occurring essentially instantaneously after the encounter between the polymer coil and the •OH radical.

Under these circumstances, the proper form of the Smoluchowski equation[2] to describe this reaction is

$$k_{obs}^{(2)} = k_{diff} = 4\pi N_A' D_{OH} R_h \rho \qquad (1)$$

where N_A' is Avogadro's number per millimole, D_{OH} is the diffusion constant for •OH in water, ρ is the probability of reaction per encounter, and transient effects are ignored. The key aspect of these experiments is that the reaction radius that enters into eq 1 is that of the entire polymer coil.

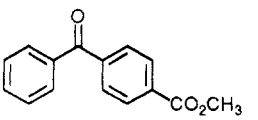
One can imagine a different kind of reaction between a small molecule in solution and well-separated polymer coils. If the small molecule can react with each monomer unit in the chain, but the reaction is much slower than diffusion-controlled, the dependence of $k_{obs}^{(2)}$ on R_h disappears and

$$k_{obs}^{(2)} \sim [\text{monomer units}] \qquad (2)$$

Under these circumstances the small molecule reactant is unable to distinguish between one long chain in solution and many shorter chains, provided that end-of-chain effects are unimportant and the monomer unit concentration is kept constant. An example of this situation is found in the reaction of benzophenone in its triplet excited state with polymethylene chains (a hydrogen abstraction reaction).[3]

Between these two limiting cases one can imagine a series of diffusion-influenced reactions where a reactive small molecule might encounter a polymer molecule in solution but where exit from the coil would be competitive with the chemical reaction. One such situation might be a fluorescence or phosphorescence quenching reaction in which the dye molecule was free in solution and some of the units of the polymer chain contained pendant quencher groups. Here it is easy to imagine a situation where the excited dye could encounter the polymer and depart before it had a chance to interact with the quencher.

We were curious to see what kind of behavior would be exhibited by this kind of system. We had in hand a series of methyl methacrylate–1-naphthylmethyl methacrylate copolymers [poly(MMA-*co*-NMMA)] of varying composition and similar molecular weight. In these polymers, the naphthalene [N] units could serve as quenchers. As the low molecular weight reactant we chose 4-(methoxycarbonyl)benzophenone (1). Its triplet state in



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solution is long lived and is easily detected by its phosphorescence emission. In acetone at 25 °C the triplet lifetime of 1 is ca. 25 μs and its diffusion coefficient D_B can be estimated to be ca. 2×10^{-5} cm^2 s^{-1}.[4] From these values we can calculate that the rms diffusion distance of 1*[3] during one lifetime ($\bar{l}^2 = D\tau$) is on the order of 50 nm. This is substantially larger than the coil radius (8 nm) of polymers examined here.

Experimental Section

The polymers were prepared by free radical polymerization in benzene using varying amounts of methyl methacrylate [MMA] and 1-naphthylmethyl methacrylate [NMMA] with AIBN as an initiator. The details of the synthesis, characterization, reactivity ratios, etc. have been published.[5] Molecular weights were determined by gel permeation chromatography (GPC) in ethyl acetate using PMMA standards to callibrate the columns. For samples rich in NMMA, these values become nominal molecular weights.

Acetone, spectrograde, was fractionally distilled after refluxing over $KMnO_4$; 4-(methoxycarbonyl)benzophenone was recrystallized three times from CCl_4 and then sublimed. All samples for flash photolysis contained 1.0×10^{-3} M 1. In one set of samples the polymer concentration was chosen to keep [N] =

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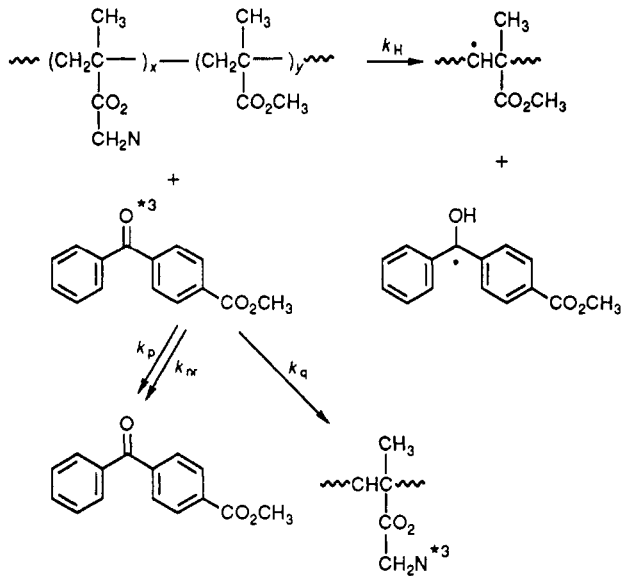
Scheme I



2.00×10^{-5} M; in a second set of samples, the polymer concentration [P] itself was kept constant at [P] = 1.0×10^{-5} M. Samples were degassed by five successive freeze–pump–thaw cycles and sealed in Pyrex tubes under a vacuum of better than 1×10^{-5} Torr.

Triplet lifetimes were determined by measuring the rate of phosphorescence decay. The apparatus was similar to that previously described,[6,7] except that a Nd:YAG laser [Quanta Ray DCR-2] was used to excite the samples at 355 nm. The excitation beam was strongly attenuated to avoid triplet–triplet annihilation contributions to the phosphorescence decay. All decay profiles measured here were exponential and were followed routinely over 1–2 decades of intensity decay.

Results and Discussion

Upon irradiation, benzophenone derivatives undergo rapid intersystem crossing to yield the triplet state with unit quantum efficiency. These triplets can undergo various kinds of reactions. They can transfer energy to naphthalene groups, a reaction known to be diffusion-controlled. They can abstract hydrogens from suitable donors containing labile CH bonds. These reactions are 10^4–10^5 times less efficient than energy transfer and are not affected by diffusive processes in low viscosity solvents. For the reaction of 1^{*3} with [MMA-*co*-NMMA] copolymers, both processes compete.

These reactions are summarized in Scheme I.

In this scheme, the triplet energy transfer rate is described by k_q and the hydrogen abstraction rate by k_H. Competing with these second-order processes are the radiative (k_p) and nonradiative (k_{nr}) decay of the triplet state. In the absence of polymer, the triplet lifetime is determined only by k_p and k_{nr}; i.e., $\tau_0 = (k_p + k_{nr})^{-1}$. In the presence of polymer, the lifetime of 1^{*3} is shortened by the two competing reaction processes. We can express these rates in either of two ways:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_H[m] + k_q^P[P] \tag{3}$$

where [m] is the molar concentration of monomer groups in the system and [P] is the molar concentration of polymer molecules, or

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_H[m] + k_q^N[N] \tag{4}$$

where [N] is the bulk molar concentration of N groups. The objective of these experiments is to try to understand which of these descriptions of the rate is the more meaningful.

A value for k_H can be obtained by examining the rate at which PMMA itself quenches 1^{*3}. We find $k_H = 1.03 \times 10^5$ $(M_{monomer})^{-1}$ s^{-1}. In the copolymers the N–CH_2O group should be somewhat more reactive than the CH_3O group to H-abstraction. We ignore this difference in analyzing our data since proximity of 1^* and N–CH_2O should favor energy transfer over hydrogen abstraction by a factor of at least 10^4. For each sample we calculate k_q^P and k_q^N by using the expressions

$$k_q^P = \frac{1}{[P]}\left[\frac{1}{\tau} - \frac{1}{\tau_0} - k_H[m]\right] \tag{5a}$$

$$k_q^N = \frac{1}{[N]}\left[\frac{1}{\tau} - \frac{1}{\tau_0} - k_H[m]\right] \tag{5b}$$

The copolymer samples we examined all had molecular weights in the range of 50 000 (M_n) with M_w/M_n values ranging from 1.7 to 2.5. While we prepared samples covering the full range of N content, those polymers containing more than 50 mol % N groups were poorly soluble in acetone and were not examined. The samples we did study and some of their properties are collected in Table I.

All of the phosphorescence decays examined here were exponential. When the measured lifetimes were analyzed in terms of eq 5a and 5b and plotted against the mole fraction of N groups in the polymer, the data in Figure 1 were obtained. If diffusion effects were unimportant, the data should fit eq 4, and k_q^N values should be independent of the polymer composition. This is clearly not the case. The magnitude of k_q^N is a decreasing function of the mole fraction of N groups in the polymer. Packaging the same number of N groups into a smaller number of chains decreases the effectiveness of each individual N group to quenching.

On the other hand k_q^P values increase with increasing N content in the chain. Increasing the number of N groups per chain increases the quenching efficiency of each polymer coil. The k_q^P values in Figure 1 appear to go through a maximum at 15 mol % N groups. This behavior is a consequence of molecular weight influencing coil dimensions, rather than some more fundamental feature of the reaction. Reference to Table I indicates that the two samples of highest content of N groups also have molecular weights substantially smaller than those of the preceding six samples.

In Scheme II we present a simple model of the quenching process. Most of 1^{*3} is generated outside the polymer coils, which are represented by the large circles in the scheme. Diffusion of 1^{*3} into the coil is described by the rate coefficient $k_{in} = k_{diff}$. Diffusion out of the coil (k_{out}) competes with quenching, described by k_x. We expect from eq 1 that k_{in} depends upon the coil dimension, R_{coil}, and the diffusion coefficient D_B of 1^{*3} in the bulk solvent. The quenching term k_x will depend upon the local concentration of N groups within the coil (assumed here to be uniform), the diffusion coefficient D_B' of 1^{*3} inside the coil, and the reaction distance R_0 characterizing triplet energy transfer from 1^{*3} to N. The rate of escape from the coil will depend upon R_{coil} and D_B', and we equate k_{out} with the reciprocal escape time from the coil τ_{esc}^{-1}, with $\tau_{esc} = R_{coil}^2/D_B'$. We can therefore write the following expressions:

$$k_{in} = 4\pi N_A' R_{coil} D_B \rho \tag{6}$$

Table I
Molecular Weights and Composition of the Copolymers Examined and Their Rate Constants for Quenching 1*[3]

	samples							
	15A	27A	78A	28A	79A	23A	83A	29A
$10^4 M_n$	5.47	4.81	6.00	5.18	5.39	6.55	4.10	3.77
M_w/M_n	1.98	1.71	1.75	1.84	1.79	2.46	2.26	2.51
[N], mol %	1.10	2.44	4.65	6.19	9.74	11.6	23.4	43.3
DP[a]	540	467	566	481	480	572	317	244
n_N[b]	5.9	11.4	26.3	29.7	46.8	66.2	74.0	105
$10^{-9}k_q^P$	12.1	18.0	30.0	27.4	41.1	46.9	36.3	28.1
$10^{-9}k_q^N$	2.06	1.59	1.14	0.92	0.88	0.68	0.50	0.27

[a] Number-averaged degree of polymerization. [b] Number-averaged naphthalenes per chain.

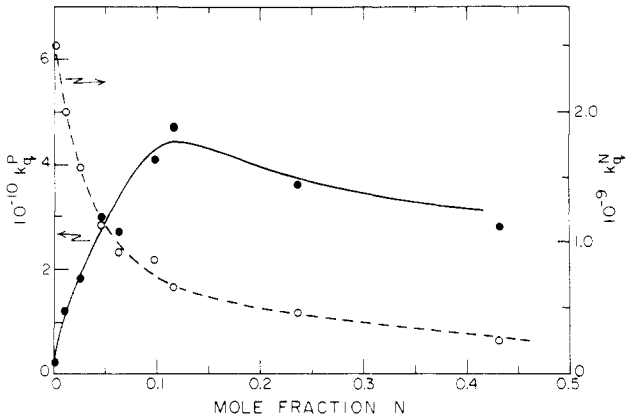


Figure 1. Plots of k_q^P (closed circles) and k_q^N (open circles) as a function of the mole fraction of N groups in the poly(MMA-*co*-NMMA) samples.

$$k_{out} = 6D_B'/R_{coil}^2 \quad (7)$$

We can also use Scheme II to derive the expression

$$k_q^P = \frac{k_{in}k_x}{k_{out} + k_x} \quad (8)$$

since k_q^P describes only the contribution of energy transfer to the quenching process. By inverting this equation

$$\frac{1}{k_q^P} = \frac{k_{out}}{k_{in}k_x} + \frac{1}{k_{in}} \quad (9)$$

we see that when k_x becomes very large or k_{out} is small, the reactant 1* is essentially swallowed by the coil and $k_q^P \rightarrow k_{in}$. This might happen, for example, if every monomer unit contained a N group.

Equation (9) forms a useful basis for testing the mechanism given in Scheme II. To employ this equation we must obtain values of R_{coil} to accommodate the fact that for the various polymer samples (Table I) molecular weight differences will lead to differences in k_{in}. In addition we have to come to grips with the factor ρ in eq 1 and 6. This factor takes into account the possibility that the effective radius in the diffusion-controlled capture of 1* by the polymer coil may be different from R_{coil}, which here is determined from intrinsic viscosity considerations. It is also helpful to recognize that the ratio k_{out}/k_x can be expressed in terms of more fundamental properties of the system:

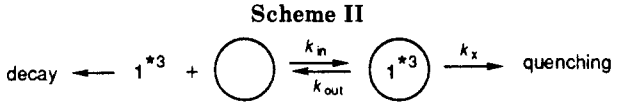
$$k_x = 4\pi N_A' D_B' R_0 [N]_{local} \quad (10)$$

$$[N]_{local} = 3n_N/4\pi N_A' R_{coil}^3 \quad (11)$$

$$\frac{k_{out}}{k_x} = \frac{2R_{coil}}{n_N R_0} \quad (12)$$

Since quenching of 1* by N is diffusion-controlled, we can express the first-order rate constant k_x as the product of a diffusion-controlled second-order rate constant and the local concentration $[N]_{local}$ of N groups (eq 10). This expression takes account of the fact that within the coil, the diffusion coefficient D_B' is different from (smaller than) that of 1 outside the coil and that R_0 is the radius characteristic of the molecular separation at which energy transfer occurs. The local concentration of N groups in the coil depends upon the number of N groups per chain (n_N) and the coil volume (eq 11).

Scheme II



Mark-Houwink parameters are known for PMMA in acetone.[8] We can use these values and the theory of Flory and Fox[9] to calculate the mean-squared end-to-end lengths R_F^2 for these polymers and then equate $6R_{coil}^2 = R_F^2$. In this way we obtain R_{coil} = 8.2 nm for sample 27A with $\bar{M}_w$ = 82 000. For the data analysis that follows, we need number-averaged R_{coil} values. These are not available, and the samples listed in Table I do show some variation in polydispersity. Another potential difficulty is the effect of the N groups on polymer dimensions. In order to proceed, we calculated the number-averaged degree of polymerization $\overline{DP}$ for each sample, using $\bar{M}_n$ and composition data. Using sample 27A as a reference, we estimated R_{coil} for each of the other samples by scaling a factor of $(\overline{DP}/\overline{DP}_{ref})^{0.70}$ where 0.70 is the Mark-Houwink exponent for PMMA in acetone.[8]

A measured D_B value for 1 in acetone is not available. Values are available for the diffusion of pyrene and similar sized molecules in a variety of simple alkane solvents.[4] After correcting for viscosity differences, we choose $D_B = 1.9 \times 10^{-5}$ cm^2 s^{-1}. Several years ago we determined the value of k_q for quenching of 1 phosphorescence by naphthalene in carbon tetrachloride [$k_q = 5.0 \times 10^9$ M^{-1} s^{-1}]. This value is also consistent with the idea that naphthalene, pyrene, and 1 have similar values of D, which, for simple nonviscous solvents, vary inversely with solvent viscosity. Equation 9 can be rewritten as

$$\frac{k_{in}}{\rho k_q^P} = \frac{k_{out}}{\rho k_x} + \frac{1}{\rho} \quad (13)$$

$$= \frac{2R_{coil}}{R_0 \rho n_N} + \frac{1}{\rho} \quad (14)$$

With (k_{in}/ρ) values available from eq 6, we can plot $(k_{in}/\rho k_q^P)$ vs (R_{coil}/n_N). This graph is shown in Figure 2. The plot is linear. One obtains a slope of 5.68 nm^{-1} and an intercept of 2.25. We find that ρ = 0.44 and R_0 = 0.8 nm.

In terms of Scheme II, the result that the effective radius which contributes to capture of 1* is only 44% of that

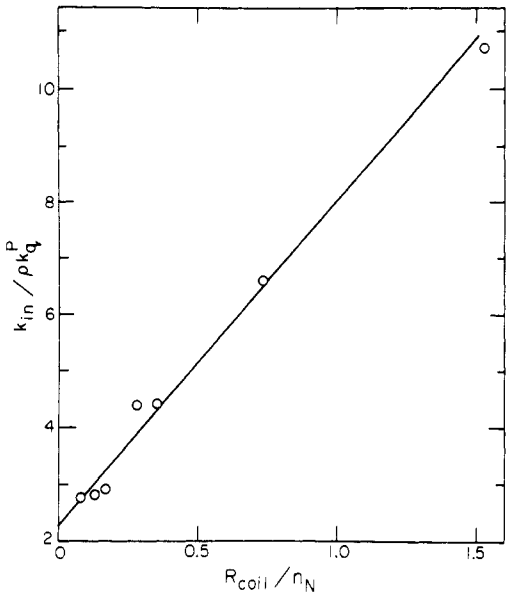


Figure 2. Plot of $k_{in}/\rho k_q^P$ vs R_{coil}/n_N. See text and eq 14.

which contributes to the intrinsic viscosity seems quite reasonable. The value R_0 = 0.8 nm also seems very reasonable, although it is a little bit larger than the value calculated (R_0 = 0.5 nm) for quenching 1* by naphthalene in carbon tetrachloride. This difference can be explained in terms of slower diffusion of 1* inside the coil, but considering the various assumptions made in fitting data to eq 14, such a detailed analysis would seem to be unwarranted.

The fit of the data to eq 14 is consistent with the concept contained in Scheme II. Another way of looking at the data is to compare k_q^P values with those that would be obtained if all the polymer samples had identical coil dimensions. According to eq 8, k_q^P would equal k_{in} times the probability that once inside the coil 1* would react rather than escape. For this analysis, we choose k_{in} = 5.3×10^{10} M^{-1} s^{-1} and obtain the curved line in Figure 3. The experimental values of k_q^P follow this line with the exception of the two samples of highest N content.

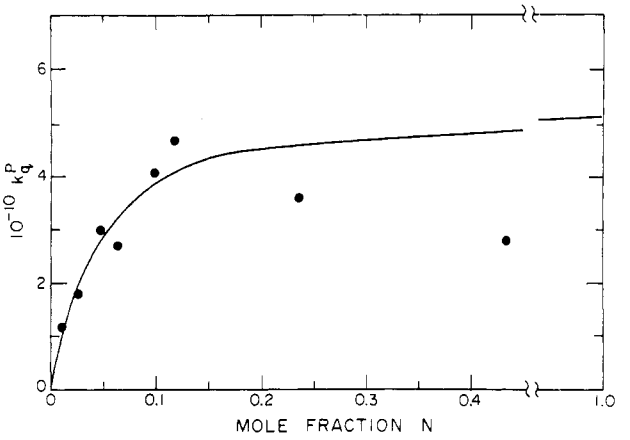


Figure 3. Plot of k_q^P data vs the mole fraction of N groups in the polymers. The curved line is obtained from eq 8 by using $k_{in} = 5.3 \times 10^{10}$ M^{-1} s^{-1}.

These two samples have molecular weights significantly smaller than the other samples. As a consequence, R_{coil} and k_{in} are smaller and this leads to the lower experimental values of k_q^P.

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Registry No. 1, 110971-37-4; MMA-*co*-NMMA, 6158-54-9.