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Triplet Benzophenone Deactivation by α-Naphthyl Methacrylate–Methyl Methacrylate Copolymers

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ABSTRACT: The triplet benzophenone quenching by poly(α-naphthyl methacrylate) and copolymers of α-naphthyl methacrylate and methyl methacrylate has been measured as a function of the copolymer composition, molecular weight, and thermodynamic character of the solvent. It is found that the quenching rate constant is determined only by the volume of the macromolecular coil, as measured by the product $[\eta]\bar{M}$ (η = intrinsic viscosity and $\bar{M}$ = polymer or copolymer molecular weight). The volume of the equivalent quenching sphere obtained by applying a simple Smoluchowski equation agrees satisfactorily with the volume of the hydrodynamic equivalent sphere.

Introduction

In recent work we have studied the diffusion-controlled quenching of a small excited molecule by vinyl polymers in solution.[1] Similar studies have also been carried out by Pratte and Webber.[2] The main conclusion of both studies was that the quenching rate, per quencher unit, was smaller than that measured for a model compound of low molecular weight, and that it decreases when the molecular weight of the polymer increases. These results were interpreted in terms of a model developed by Behzadi et al.[3] for the diffusionally controlled reactions of hydroxyl radicals with macromolecules. This model allows the evaluation of a "quenching macromolecular volume" from the quenching rate constant. This "quenching volume" has been related to the actual volume of the macromolecular coil and to the volume of the equivalent hydrodynamic sphere.[1-3] In the present work, we extend our former study to the quenching of benzophenone triplets by poly(α-naphthyl methacrylate) of different molecular weights and consider the effect of the incorporation of an inert comonomer (methyl methacrylate) upon the quenching rate constant.

Experimental Section

Benzophenone and 1-naphthyl acetate were purchased from Aldrich Chemical Co. and purified by recrystallization. 1-Naphthyl methacrylate was synthesized by reaction between methacryloyl chloride and α-naphthol according to the technique described by Patai.[4] The monomer was purified by distillation under vacuum and crystallized from methanol/water mixtures (80:20 v/v).

Homopolymers and copolymers with methyl methacrylate were prepared by AIBN-initiated free radical polymerization at 70 °C (less than 10% conversion) under nitrogen atmosphere. The polymers were purified by reprecipitation and fractionated by dropwise addition of methanol to a solution of polymer in benzene at 20 °C.

Molecular weights of the polymer and copolymers were determined by using GPC elution curves, carried out in a Perkin-Elmer high-performance liquid chromatograph with Shodex columns calibrated by utilizing polystyrene standards of narrow molecular weight distribution. The solvent used was tetrahydrofuran.

The polymers were characterized by their intrinsic viscosities in different solvents. The composition of the copolymers was determined by measuring the optical absorption of the naphthyl units at λ 280 nm.

Table I
Polymer Characterization

polymer	fraction of naphthyl groups (X)	no. of fractions	chain length range
homopolymer	1	10	35–1400
copolymer CP_1	0.56	5	259–2400
copolymer CP_2	0.33	7	79–1700
copolymer CP_3	0.20	4	540–1500
copolymer CP_4	0.13	5	166–1380

Phosphorescence emission was measured in a Perkin-Elmer LS-5 spectrofluorimeter. The quenching rate constants were obtained from the decrease of the benzophenone phosphorescence in the presence of different amounts of polymer according to the Stern–Volmer equation:

$$(I_{Ph})^0/I_{Ph} = 1 + k_Q\tau_T[Q]$$

The triplet lifetime (τ_T) was determined directly from the phosphorescence decay. Excitation was achieved with a Nitronite nitrogen laser, and the signal was recorded in a Tektronix oscilloscope.

Results

The main characteristics of the polymers employed in the present work are shown in Table I.

The reaction scheme employed to interpret our results comprises only reactions 1–3

$$^3\text{benzophenone} \xrightarrow{k_Q} \text{benzophenone} \qquad (1)$$

$$^3\text{benzophenone} \xrightarrow{k_{Ph}} \text{benzophenone} + h\nu_{Ph} \qquad (2)$$

$$^3\text{benzophenone} + \text{naphthyl group} \xrightarrow{k_q} \text{benzophenone} + {}^3\text{naphthyl group} \qquad (3)$$

and leads to

$$(I_{Ph})^0/I_{Ph} = 1 + k_Q\tau_T[Q] \qquad (4)$$

If the quencher concentration is given in terms of the molar concentration of naphthyl groups [naph], plots of $(I_{Ph})^0/I_{Ph}$ against [naph] allow an evaluation of $(k_Q)_M$. On the other hand, if the data are plotted against the molar concentration of polymer molecules, $(k_Q)_P$ (the quenching rate constant in a polymer molecule concentration basis) is directly obtained from the slope of the Stern–Volmer plots. The values of $(k_Q)_P$ obtained increase and those of $(k_Q)_M$ decrease when the polymer (or copolymer) molecular

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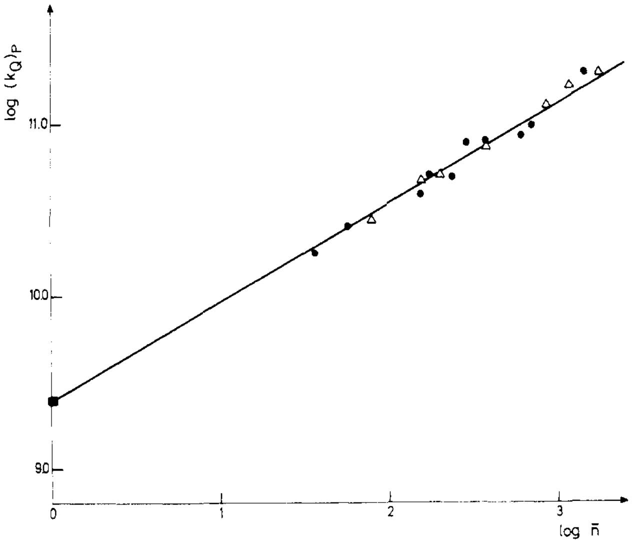

Figure 1. Dependence of the quenching rate constant $(k_Q)_P$ with polymerization degree in benzene at 20 °C: (●) homopolymer; (△) copolymer CP_2; (■) $(k_Q)_{model}/2$.

Table II
a Parameters Derived from Quenching Experiments and from Viscosimetric Determinations

polymer	solvent	a, viscosimetric	a, quenching
homopolymer	chloroform/ethyl acetate (6:4)	0.50	0.50
	benzene/acetonitrile (45:55)	0.50	0.52
	benzene	0.57	0.65
	dichloromethane	0.73	0.74
copolymer CP_2	benzene	0.63	0.63

weight increases in all the systems studied. Plots of log $(k_Q)_P$ vs. chain length were fairly linear (see Figure 1), and hence it can be considered that

$$(k_Q)_P \propto \bar{M}^{\beta} \tag{5}$$

In Figure 1 we have included the value of $(k_Q)_{model}/2$ (where $(k_Q)_{model}$ is the quenching rate obtained employing α-naphthyl acetate as quencher) as corresponding to a polymer of unitary chain length. The factor 2 was introduced to take into account the negligible diffusion coefficient of the naphthalene moiety bound to the macromolecule. The figure shows that an equation like (5) can be extrapolated fairly well to the monomeric unit.

The exponent β has been related[1-3] to the a parameter of the Mark–Houwink–Sakurada equation by

$$\beta = (a + 1)/3 \tag{6}$$

By applying this relationship, we have obtained the a values given in Table II. In this table we have also included the values of a obtained from viscosimetric measurements.

For a given polymer, the quenching rate constant is markedly dependent upon the solvent quality.[1] Typical values obtained are given in Table III. In this table we have also included values of $(k_Q)_{model}/(k_Q)_M$ and the relationship between the radius of the equivalent sphere in a given solvent and that of the Θ solvent. This ratio (r/r_Θ) was obtained from eq 7, which assumes that the processes

$$r/r_\Theta = \frac{(k_Q)_M/(k_Q)_{model}}{[(k_Q)_M/(k_Q)_{model}]_\Theta} \tag{7}$$

have rate constants expressible by Smoluchowski's equation.[1-3] In this table we have also included the expansion coefficient α_η derived from viscosimetric measurements.

Table III

polymer[a]	solvent	$10^{-8}\cdot(k_Q)_M$[b]	$(k_Q)_{model}/(k_Q)_M$	r/r_Θ	α_η
homopolymer	chloroform/ethyl acetate (6:4)	1.40	41	1.0	1.0
	benzene/acetonitrile (45:55)	1.75	40	1.0	1.0
	benzene	2.10	32	1.28	1.13
	dichloromethane	2.80	26	1.57	1.23
CP_2	benzene/acetonitrile (15:85)	5.2	16	1.0	1.0
	benzene	6.1	11	1.45	1.28
	dichloromethane	6.1	11	1.45	1.30

[a] Chain length = 370. [b] In $M^{-1}\ s^{-1}$.

Table IV
Macromolecules with 180 Naphthalene Units

polymer	X	$\bar{n}$	$10^{-10}(k_Q)_P$[a]	$r/r_{homopolymer}$
homopolymer	1	178	4.79	
CP_1	0.51	347	7.94	1.6
CP_2	0.33	537	9.55	2.0
CP_3	0.20	891	10.50	2.2
CP_4	0.13	1380	14.13	3.0

[a] Benzene as solvent. $(k_Q)_P$ is given in $M^{-1}\ s^{-1}$.

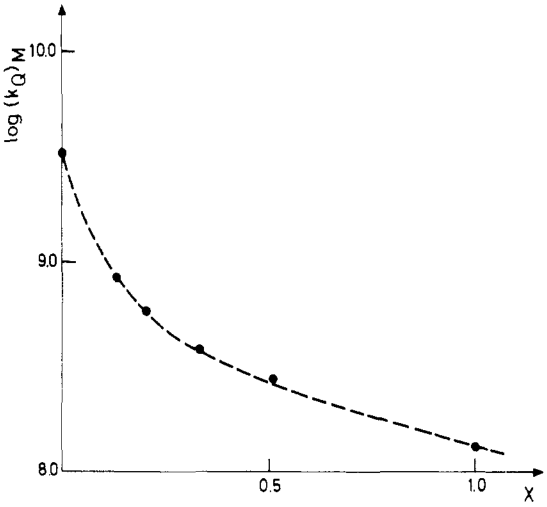

Figure 2. Dependence of the quenching rate constant with molar fraction of naphthyl groups in the polymer.

The effect of the copolymer composition upon $(k_Q)_M$ is shown in Figure 2. In this figure the values of $(k_Q)_M$ are plotted against the fraction of naphthyl groups for polymers of $\bar{n} = 10^3$. The data are extrapolated to $(k_Q)_{model}/2$ by assuming that at $X \rightarrow 0$ the value of $(k_Q)_M$ should be equal to half that of the model compound due to the reduced mobility of the naphthalene group bound to the macromolecule.[5]

The effect of the polymer chain length upon $(k_Q)_P$ for polymers having the same number of naphthalene groups per macromolecule is given in Table IV for polymers with 180 naphthalene units per macromolecule. These data were obtained by interpolation of the log $(k_Q)_P$ vs. $\bar{n}$ plots.

In Table IV are also included values of $r/r_{homopolymer}$ obtained from the quenching rate constants.

Discussion

At low polymer concentrations and for donors of long lifetimes, the diffusionally controlled quenching rate constants can be well represented by Smoluchowski's equation:

$$(k_Q)_P = 4\pi N' r D \tag{8}$$

where r is the radius of the "equivalent quenching sphere" and D is the diffusion coefficient of the excited probe.[1-3] This equation, applied to homopolymers, predicts the following:

(i) $(k_Q)_P$ must increase with the polymer molecular weight due to an increase in the size of the polymer coil. If it is assumed that the increase in quenching volume is similar to that of an equivalent hydrodynamic sphere, it can be expected that

$$(k_Q)_P \propto \bar{n}^{(a+1)/3}$$

where a is the parameter of the Mark-Houwink-Sakurada equation.

(ii) $(k_Q)_P$ must increase when the quality of the solvent increases (if possible changes in D are taken into account).

(iii) $(k_Q)_M$ must decrease when the polymer molecular weight increases. Provided that the concentration in quenching groups inside the coil is large enough to assure almost complete quenching of an excited probe reaching the volume defined by the macromolecule, points i–iii must also apply to copolymers. Furthermore, for the copolymers the following can be expected.

(iv) For a given chain length, $(k_Q)_M$ should increase when the fraction of quenching units in the copolymer (X) decreases.

(v) For macromolecules with a given number of quenching units, $(k_Q)_P$ (and hence $(k_Q)_M$) should increase when X decreases.

The data obtained in the present work both for the homopolymers and for the copolymers are in full agreement with all these points (see Tables II–IV and Figures 1 and 2). In particular, it is noteworthy that there is close agreement between the a values obtained from quenching experiments and viscosimetric determinations (see Table II) and that the linear dependence of log $(k_Q)_P$ with $\bar{n}$ seems to hold even up to the model compound. Similar results have also been observed in previous systems.[1-3]

In order to test in a more quantitative way the relationship between $(k_Q)_P$ and the macromolecular coil size, we have compared all k_Q values obtained in the present work with the coil size as measured by the polymer intrinsic viscosities. From the theory of the equivalent-sphere model,[6] it can be concluded that the radius of the hydrodynamic coil is directly proportional to $[\eta]\bar{M}^{1/3}$, irrespective of the solvent and copolymer composition. The relationship between log $(k_Q)_P$ and log $([\eta]\bar{M})$ is shown in Figure 3.

This figure shows that there exists a good correlation between k_Q and $[\eta]\bar{M}$ that includes all polymers and copolymers in solvents of widely different thermodynamic character. Furthermore, the slope obtained is 0.36, which compares favorably with the theoretical slope of 0.33. Our results, as well as those reported by Webber et al.,[2] thus indicate that the proposed model not only provides a qualitatively correct description but also gives results that can be quantitatively related to the volume of the polymer coil. This quantitative relationship can be further tested by comparing the radius obtained from $(k_Q)_P$ to other magnitudes related to the size of the polymer coil.

The radius of the equivalent quenching sphere can be directly estimated from eq 8. We have applied this equation taking for benzophenone in benzene a diffusion constant of 1.6×10^{-5} cm^2/s. This value was obtained by applying the corrected Stokes' law with a radius of 3.4 Å.[7] This radius was obtained by the method of atomic contributions.[8] With these data, the value of the equivalent quenching sphere for an homopolymer of molecular weight 151 000 in benzene at 25 °C is 82 Å.

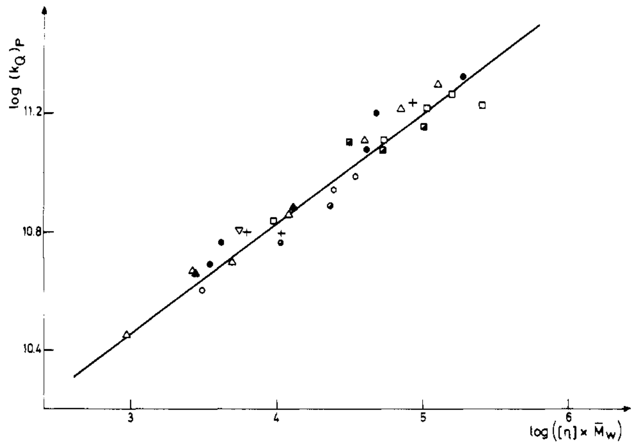

Figure 3. Dependence of the quenching rate constant with the volume of the equivalent hydrodynamic sphere (measured by the product of the intrinsic viscosity and the polymer molecular weight): (△) copolymer CP$_2$ in benzene; (□) copolymer CP$_1$ in benzene; (◪) copolymer CP$_3$ in benzene; (+) copolymer CP$_4$ in benzene; (●) homopolymer in dichloromethane; (○) homopolymer in benzene; (◑) homopolymer in chloroform/ethyl acetate (6:4); (▲) copolymer CP$_2$ in dichloromethane; (▽) copolymer CP$_2$ in benzene/acetonitrile (15:85).

The size of the macromolecular coil can be estimated from the volume of an equivalent hydrodynamic sphere,[6] given by eq 9

$$[\eta] = \frac{0.025 N V_e}{\bar{M}} \qquad (9)$$

where $[\eta]$ is the intrinsic viscosity (expressed in deciliters per gram), $\bar{M}$ is the polymer molecular weight, N is Avogadro's number, and V_e is the equivalent hydrodynamic volume of a polymer molecule.

By applying this equation to the same polymer we obtain a value of R_e = 81 Å. We can conclude then that the evaluated radius of the equivalent quenching sphere not only changes with molecular weight, copolymer composition, and solvent character in the same way as other parameters related to the macromolecular size but also provides absolute values that are compatible with the macromolecular dimensions.

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