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2. Laser Flash Photolysis Studies on Homo- and Copolymers of Phenyl Vinyl Ketone in Solution

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ABSTRACT: The quenching of triplet excited phenyl vinyl ketone (PVK) base units either by naphthalene or by naphthalene incorporated as comonomer into poly(methyl methacrylate) (PMMA) was investigated. The quenching constant k_Q is about two times lower for homo PPVK than for a micromolecular model compound. For a copolymer of MMA and PVK k_Q was found to be about three times smaller than for homoPPVK which is explained in terms of energy migration along the chain being impossible in the case of the copolymer. Triplet excited PVK units are quenched with naphthalene incorporated in a polymer with k_Q only about two to three times smaller than for naphthalene. These results are believed to be indicative of the fact that PMMA molecules in benzene solution are capable of interpenetrating rather easily. Triplet lifetimes of excited 2,4-dibenzoylpentane and 1,3-dibenzoylpropane are about 70 ns in the absence of oxygen. Oxygen quenches triplet excited ketone groups with the following rate constants in units of M^{-1} s^{-1}: 2.4×10^9 (acetophenone), 2.0×10^9 (2,4-dibenzoylpentane), 1.5×10^9 (co-oligomer of MMA–PVK containing 9 mol % PVK), 5.4×10^8 (copolymer of MMA–PVK containing 2.8 mol % PVK). The difference between the values for low and high molecular weight compounds is explained in terms of differences of diffusion constants based on the assumption that oxygen quenching is occurring as an encounter controlled reaction.

Our laser photolysis studies on polymeric systems have been aimed at elucidating the kinetics of chemical reactions involving macromolecules in solution. Of special interest have been studies concerning (a) reactions between macromolecules possessing only a small number of reactive sites per chain, and (b) reactions of macromolecules possessing a small number of reactive sites with micromolecules (molecules of low molecular weight). Some results along these lines have been reported in part 1.[1] That work pertained to intra- and intermolecular self-quenching as well as triplet–triplet annihilation.

In this paper we wish to report (i) on triplet quenching by micromolecular naphthalene or by naphthalene incorporated as pendant group of a comonomer into PMMA, and (ii) some investigations concerning the interaction of molecular oxygen with triplet PVK units.

Besides various copolymers, micromolecular model compounds and an oligomer sample containing PVK were also investigated.

Experimental Section

A ruby laser (Korad Model K1QS2) was used as photolyzing light source (λ 347.1 nm, half-width of the flashes ca. 25 ns). Further details concerning this and also the actinometry employed have been reported earlier.[1,2]

The syntheses of polymers and copolymers as well as the preparation of samples have been described in part 1.[1] A list of samples used in this work is presented in Table I.

1,3-Dibenzoylpropane and 2,4-dibenzoylpentane were kindly provided by Drs. Hrdlovič and Lukač.

Results and Discussion

(a) Triplet Quenching by Naphthalene. Rate constants for the reaction

$$^3\text{ketone}^* + {}^1\text{Q} \xrightarrow{k_Q} {}^1\text{ketone} + {}^3\text{Q}^* \qquad (1)$$

were determined as described earlier[2] by monitoring the sensitized naphthalene triplet–triplet absorption at λ 413 nm immediately after the flash (ground state naphthalene neither absorbs light of this wavelength nor the photolyzing light at λ 347.1 nm). Straight lines were obtained in all cases when the reciprocal optical density OD^{-1} at 413 nm vs. the reciprocal naphthalene concentration $[Q]^{-1}$ was plotted. Thus, by applying the relationship

$$OD^{-1} = OD_L^{-1} + \Sigma k_1/OD_L k_Q[Q] \qquad (2)$$

the rate constant k_Q was evaluated from the slope of the straight lines. OD_L denotes the optical density obtained by extrapolating OD^{-1} to $[Q]^{-1} = 0$ and Σk_1 the first-order rate constant of triplet decay in the absence of naphthalene. Values of Σk_1 have been reported in part 1.

Results are shown in Table II. Because of the rather broad error limit the determinations were repeated several times. The k_Q values given in the table are averages from at least five or six separate runs. It turns out that k_Q for the model compound 2,4-dibenzoylpentane is about twice as high as for homoPPVK. A similar difference was found by comparing respective k_Q values obtained with butyrophenone and homoPPVK.[2] k_Q values differing by a factor of about 2 are expected for encounter controlled reactions considering the difference of diffusion constants of micro- and macromolecular compounds.[4]

In the case of CP-MMA-PVK-2.8 k_Q is markedly lower than for homoPPVK. A similar situation was encountered with CP-St-PVK-10.8 and CP-VAc-PVK-1.2. This effect may at least in part be due to the fact that energy migra-

Table I
Characterization of Copolymer and Homopolymer Samples

Series	Polymer sample	Content of 2nd monomer (mol %) PVK	VN	No. av mol wt
Methyl methacrylate/phenyl vinyl ketone (MMA/PVK)	CP-MMA-PVK-1.83	1.83		7.0×10^5
	CP-MMA-PVK-2.8	2.8		11.0×10^5
	CP-MMA-PVK-14.1	14.1		11.0×10^5
	Co-oligomer MMA-PVK-9.0	9.0		800
Vinyl acetate/phenyl vinyl ketone (VAc/PVK)	CP-VAc-PVK-0.14	0.14		3.5×10^5
	CP-VAc-PVK-1.2	1.20		10.0×10^5
	CP-VAc-PVK-1.51	1.51		10.0×10^5
Styrene/phenyl vinyl ketone (St/PVK)	CP-St-PVK-10.8	10.8		10.0×10^5
Methyl methacrylate/vinylnaphthalene (MMA/VN)	CP-MMA-VN-0.7		0.74	1.9×10^5
	CP-MMA-VN-5.7		5.7	3.6×10^5
	CP-MMA-VN-5.9		5.9	1.5×10^5
Homopoly(phenyl vinyl ketone)	PPVK-1	100		1.5×10^5
	PPVK-8	100		8×10^5

Table II
Quenching of Triplet Excited PVK Moieties with Naphthalene at Room Temperature

Polymer	Solvent	k_Q(micro), $M^{-1}\ s^{-1}$
HomoPPVK	Benzene	$(2 \pm 1) \times 10^9$
2,4-Dibenzoylpentane	Benzene	$(4 \pm 1) \times 10^9$
CP-MMA-PVK-2.8	Benzene	$(7 \pm 2) \times 10^8$
CP-St-PVK-10.8	Benzene	$(1.0 \pm 0.3) \times 10^9$
CP-VAc-PVK-1.2	Benzene	$(1.0 \pm 0.3) \times 10^9$

Table III
Quenching of Triplet Excited PVK Moieties Incorporated in CP-MMA-PVK-2.8 with Naphthalene Incorporated as Vinylnaphthalene in Poly(methyl methacrylate-*co*-vinylnaphthalene) in Benzene Solution at Room Temperature

Polymer	*b*	*c*	k_Q(macro), base $mol^{-1}\ l.\ s^{-1}$
CP-MMA-VN-0.74	14	0.3	$(2.2 \pm 0.8) \times 10^8$
CP-MMA-VN-5.9	88	0.3	$(2.2 \pm 0.5) \times 10^8$
CP-MMA-VN-5.7	204	0.3	$(2.2 \pm 0.5) \times 10^8$
CP-MMA-VN-5.7[a]	204	0.3	$(1.2 \pm 0.2) \times 10^8$

[a] Solvent: benzene/2-propanol (70/30 v/v). [b] Av No. of VN units per macromolecule. [c] Av No. of triplets per CP-MMA-PVK chain.

tion along the chain is a rather improbable process in the case of the copolymers. In the case of homoPPVK on the other hand the reaction of quencher molecules with excited PVK units could be alleviated by energy migration along the chain, which results in a better accessibility of excited PVK units.

Table III shows results obtained with solutions containing CP-MMA-PVK-2.8 and poly(methyl methacrylate-*co*-vinylnaphthalene). In this case PMMA molecules containing an average number of PVK triplets of only 0.3 interacted with PMMA molecules containing pendant naphthalene groups. Therefore intramolecular deactivation reactions need not be considered here. It is shown in Table III that k_Q(macro) is independent of the average number of VN groups per chain. On the other hand, the k_Q(macro) values are only about three times smaller than the value of k_Q(micro) of about $7 \times 10^8\ M^{-1}\ s^{-1}$ found for the quenching of PVK triplets incorporated in CP-MMA-PVK-2.8 with micromolecular naphthalene. In the case of CP-MMA-VN-5.7 it was found that k_Q(macro) decreased by a factor of about 2 if the experiments were carried out in a solvent mixture of benzene/2-propanol (70/30 v/v) instead of pure benzene.

The discussion of these results is based on the assumption that the quenching reaction is encounter controlled and that the coiled macromolecules interpenetrate in order to complete the reaction. Thus, it was estimated that k_Q(macro) should be about 10 times smaller than k_Q(micro), if the number of VN groups per chain would be 1 and if the diffusion coefficients of naphthalene and naphthalene containing PMMA would differ by a factor of 20. The fact that k_Q(micro) and k_Q(macro) differ only by a factor of 3 is certainly caused by the relatively large number of VN groups per chain. The latter explanation becomes plausible, however, only on grounds of freely interpenetrating macromolecules. From the independence of k_Q(macro) on the average number of VN groups per chain it is also inferred that PMMA molecules can interpenetrate easily. If the entanglement of coils is a relatively slow process, the quenching reaction should be hindered. This should result in relatively low values of k_Q(macro) and in a decrease of k_Q(macro) with decreasing number of VN groups per chain. Since effects of this kind were not observed the results indicate that PMMA molecules are capable of interpenetrating easily in a good solvent such as benzene. Along this line is the result that k_Q(macro) decreased if the solvent quality was reduced. This is demonstrated by the entry in the last line of Table III.

(b) Oxygen Quenching. Additional experiments for the determination of the rate constant of the reaction of O_2 with excited PVK units have been carried out. For comparison a co-oligomer and the model compound 2,4-dibenzoylpentane as well as acetophenone were investigated. In all cases triplet lifetimes were measured by monitoring triplet–triplet absorptions at about 400 nm. The respective absorption spectra of the model compounds 2,4-dibenzoylpentane and 1,3-dibenzoylpropane are shown in Figure 1. They are very similar to the triplet–triplet absorption spectrum of PPVK.[2] For 2,4-dibenzoylpentane the triplet lifetime in the absence of O_2 (ca. 70 ns) is somewhat shorter than that of PPVK (100 ns). For acetophenone the triplet lifetime is much longer (3 μs) due to the fact that a chemical deactivation via a Norrish type II process, as with the model compounds, is not possible. In order to determine k_{O_2}, the rate constant of the reaction of O_2 with triplet excited ketone

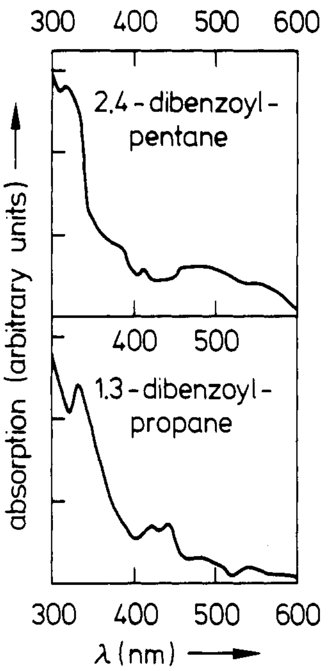

Figure 1. Absorption spectra observed immediately after the flash in benzene solution for 2,4-dibenzoylpentane and 1,3-dibenzoylpropane (1×10^{-3} M). Absorbed dose per flash 7.5×10^{-5} einstein/l.

groups, solutions were saturated with well-defined mixtures of Ar and O_2. Reciprocal lifetimes were plotted vs. the oxygen concentration. Straight lines were obtained thus proving that a relationship of the following sort holds

$$\frac{1}{\tau} = k_0 + k_{O_2}[O_2] \qquad (3)$$

(k_0 = reciprocal lifetime measured with Ar saturated solution). Results are presented in Table IV. The value of 2.4×10^9 M^{-1} s^{-1} for acetophenone agrees well with that reported by Lutz and Lindqvist[3] (2.0×10^9 M^{-1} s^{-1}). For the co-oligomer and the model compound only rather approximate values could be obtained because of the short lifetimes, which were, at the highest O_2 concentrations, comparable with the flash time. However, the results clearly show that the values observed for the macromolecular ketones are significantly lower. The extent of this effect indicates that the oxygen quenching reaction is an essentially diffusion controlled process.[1] The lower rate constants of the macromolecular ketones are due to their lower diffusion coefficients. The situation encountered here is analogous to the case of triplet quenching by naphthalene (see above and ref 2). A more quantitative experimental approach concerning the influence of chain length on the rate constant of diffusion controlled reactions has been accomplished earlier with macroradicals.[4]

Table IV
Rate Constants for Triplet Quenching by Oxygen in Benzene Solution at Room Temperature

Ketone	k_{O_2}, M^{-1} s^{-1}
CP-MMA-PVK-14.1	$(4.2 \pm 0.4) \times 10^8$
CP-MMA-PVK-2.8	$(5.4 \pm 0.5) \times 10^8$
co-Oligomer MMA-PVK-9.0	$(1.5 \pm 0.8) \times 10^9$
2,4-Dibenzoylpentane	$(2.0 \pm 1.0) \times 10^9$
Acetophenone	$(2.4 \pm 0.4) \times 10^9$

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