

Photolysis of Carbonyl Polymers in Solution*

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The photolysis of poly(vinyl phenyl ketone) (PVPK), poly(vinyl methyl ketone) (PVMK), poly(isopropenyl methyl ketone) (PIMK) and copolymers of vinyl phenyl ketone with methyl methacrylate (VPK/MMA) and with styrene (VPK/S) at 313 nm in methylene chloride solution has been studied viscometrically. The dependences of the main chain scission on time were linear which indicates random scission.

Stern – Volmer dependences of the ratio of the quantum yield of the main chain scission without and with the quencher (2,5-dimethyl-2,4-hexadiene) *vs.* quencher concentration have been linear in the studied concentration range for all polymers investigated except for PVMK. The quenching constants decrease in the following sequence: VPK/MMA, VPK/S, PVPK, PVMK, and PIMK, respectively. The lifetime of the first triplet state of the polymers decreases in the same way.

Both the photodegradation rates and the quenching constants for the copolymer VPK/MMA have been measured in various solvents of different viscosity. The photodegradation rate and the quenching constant decrease with increasing solvent viscosity (microviscosity) which indicates the diffusion-controlled transfer of triplet energy from polymer donor to low-molecular acceptor. Lower photodegradation rates and quenching constants with regard to the appropriate viscosity have been observed in the chlorinated aliphatic hydrocarbons. The quenching properties of different compounds have been followed at VPK/MMA photolysis in chlorobenzene solution.

Relationships between the structure and reactivity of the excited triplet state in the low-molecular carbonyl compounds have been thoroughly studied [1, 2]. The data characterizing reactivity of the excited carbonyl group in photolytical reaction may be obtained from quenching experiments [3, 4].

The triplet quenchers were found to retard photodestruction of carbonyl polymers. Attention was paid to the quenching of poly(vinyl phenyl ketone) photodestruction [5–7]. 1,3-Cyclooctadiene was found to retard photodestruction of copolymer ethylene/carbon monoxide [8, 9] and copolymer vinyl phenyl ketone/styrene [7]. The decrease of viscosity of irradiated benzene solution of poly(vinyl benzophenone) was retarded by

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naphthalene [10]. These findings proved to be a good basis for the study of the relationship between structure and reactivity of the excited triplet state also in polymeric systems.

In the low-molecular carbonyl compounds the reactivity of the excited carbonyl group in photoelimination (Norrish type II reaction) changes considerably with the transfer from dialkyl ketone to aryl alkyl ketone [11]. Similarly, the reactivity of the carbonyl group is strongly affected by substitution on γ -carbon with respect to carbonyl group [3, 4]. In the present paper, the reactivities of excited carbonyl states in photo-destruction of polymeric aryl alkyl ketones, dialkyl ketones with various structures on both α - and γ -carbon have been compared.

Triplet energy transfer by exchange mechanism is generally assumed to be a diffusion controlled one and dependent on solvent viscosity. *Wagner and Kochevar* [12] have thoroughly dealt with the problem of diffusion in photoelimination of the low-molecular aryl alkyl ketone. In the preceding paper [5] it was found that in poly(vinyl phenyl ketone) the quenching constant at low polymer concentration does not depend on macroviscosity. The study of the quenching of photodestruction of copolymer vinyl phenyl ketone/methyl methacrylate in solvents of various viscosities responds the question how this process is affected by the microviscosity (solvent-viscosity).

Experimental

The copolymer of vinyl phenyl ketone with styrene (VPK/S) has been prepared by bulk polymerization in nitrogen with 0.05 weight % of azobisisobutyronitrile. After 8 hours at $53 \pm 1^\circ\text{C}$ and 8 hours at $70 \pm 1^\circ\text{C}$ the conversion was 20%. The copolymer has been precipitated in the system benzene—methanol three times.

The copolymer of vinyl phenyl ketone with methyl methacrylate (VPK/MMA) has been prepared in the similar way as the copolymer VPK/S. At $53 \pm 1^\circ\text{C}$ after 4 hours the conversion was 15%.

Poly(vinyl methyl ketone) (PVMK) has been obtained by extraction with ethyl acetate from crosslinked polymer formed by spontaneous polymerization of monomer in a refrigerator. The soluble part has once been precipitated in the system ethyl acetate—*n*-heptane and twice in the system ethyl acetate—methanol.

Poly(isopropenyl methyl ketone) (PIMK) has been provided by Dr. A. R. Lyons from the University of Leicester, England. It has been prepared by polymerization initiated with triethyl aluminium at -78°C and purified by threefold precipitation in the system acetone—methanol.

Vinyl phenyl ketone (VPK) and poly(vinyl phenyl ketone) (PVPK) have been prepared in the same way as in the paper [5].

All the polymers have primarily been dried in air and then at 40 – 60°C and 0.1 Torr to constant weight. The characteristics of the polymers used are shown in Table I.

Methyl methacrylate (MMA) and styrene (S) have been purified by standard methods. Finally, they have been vacuum distilled in nitrogen from slightly polymerized material. Vinyl methyl ketone (VMK) was dried, distilled (b.p. $82^\circ\text{C}/\text{Torr}$ [13]), nonstabilized, supplied by Research Centre DUSLO, Šala, ČSSR. The product analyzed by gas chromatography contained less than 1% of impurities.

Naphthalene, biphenyl and 2,5-dimethyl-2,4-hexadiene (DMHD) have been of the same quality as in the paper [5]. 1,3-Cyclooctadiene purum (Fluka A. G., Switzerland) was used without purification. Tetrachloroethylene and trichloroethylene were purified

Table 1
 Characteristics of polymers prepared

Polymer:	VPK contents [%] (w/w)		$[\eta]^a$	$[\eta]^b$	k'^c	$\bar{M}_n \times 10^{-6}$
	monomer	copolymer	[dl g ⁻¹]	[dl g ⁻¹]		
VPK/MMA	17.9	29.6	1.81	1.76	0.44	0.350 ^d
VPK/S	5.2	12.0	1.31	1.25	0.23	0.272 ^d
PVPK			1.30	1.32	0.45	0.329 ^d
PVMK			1.12 ^g		0.26 ^g	0.240 ^g
PIMK			0.392 ^e			0.110 ^f

a) $\lim_{c \rightarrow 0} \frac{\eta_{sp}}{c}$ in benzene at 30°C graphically; b) by Berlin's one-point method [15] at 30°C; c) Huggins' constant; d) in toluene at 37°C osmometrically; e) in dioxan at 25°C; f) according to Dr. Lyons' data; g) in dioxan. \bar{M}_n corresponding to $[\eta]$ determined according to data [13].

by distillation. Ferrocene was provided for by Dr. P. Elečko from Department of Organic Chemistry, Komenský University, Bratislava.

Dioxan, dried and distilled with sodium, has been refluxed with lithium aluminium hydride for 1 hour and distilled in nitrogen. Ethyl acetate anal. grade (Lachema, Brno, ČSSR), has been purified by rectification with acetic anhydride. All the other solvents have been of usual analytical quality, distilled or used without further purification.

Content of VPK in copolymers has been determined spectrophotometrically on a single-beam non-recording VSU-1 (Zeiss, Jena) UV spectrophotometer at a wave length 326 nm, where is the maximum of PVPK ($\epsilon = 80 \text{ l mol}^{-1} \text{ cm}^{-1}$) in chloroform solution. At the wave length used, the structural units of VPK absorb only.

The viscosities of the irradiated solutions have been measured on a viscometer according to Seide—Decker for small samples [14] at $20 \pm 0.05^\circ\text{C}$. Limiting viscosity numbers have been calculated by Berlin's method [15]. Since the polymers are sensitive to the day light all operations were carried out in yellow light.

The solutions were irradiated in stoppered quartz cells (thickness 1 cm, volume 3 ml) on marry-go-round. The source consisted of medium pressure mercury arc HQE 40 (Zeiss, Jena) placed in a three-walled quartz reactor. The cooling water circulated in the inner space of the reactor. The chromane filter [16] transmitting the light composed of about 90% λ 313 nm and 10% λ 302 nm was accommodated in the outer space of the reactor. Before irradiation the solutions were bubbled by constant stream of purified nitrogen (except the cases referred to) for as long as 3 minutes.

Experimental Results

For the calculation of the main chain scissions (from viscosimetric measurements), quantum yields of main chain scissions and their ratio without and with quencher Φ_0/Φ the same relations were used as in the paper [5].

The dependence of the numbers of the main chain scissions on the irradiation time is a linear one for all of the polymers (Fig. 1) which suggests random scission. Since light intensity slightly changed from experiment to experiment, the relative quantum yields

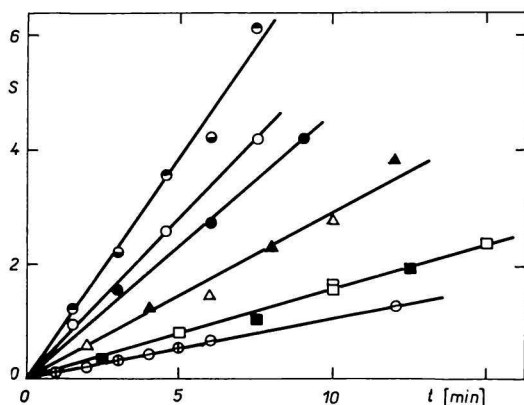


Fig. 1. Photodestruction of carbonyl polymers in CH_2Cl_2 in the air (full points) and in nitrogen (open points).

\odot PVPK 5 g/l; \blacktriangle \triangle PVMK 6 g/l; \blacksquare \square PIMK 12 g/l; \bullet \circ copolymer VPK/MMA 4 g/l; \oplus \ominus copolymer VPK/S 8.84 g/l.

of main chain scissions, with respect to PVPK, were calculated from the data obtained by simultaneous irradiation of one sample of each polymer. The data are summarized in Table 2. Since the coefficients α (from the relation $[\eta] = KM^\alpha$) for calculation of the number of the main chain scissions are not known for all polymers, the value 0.75 was used.

By simultaneous irradiation of the quencher-free solution and of more solutions with various concentrations of DMHD in methylene chloride the Φ_0/Φ has been measured. From Stern – Volmer dependences (Fig. 2) quenching constants ($k_q \tau$) shown in Table 2 have been calculated. Quenching constant for PVMK has been estimated from the linear part of the curve. The quenching constants for VPK/MMA and PIMK have been determined in the concentration range up to 0.05 M and 0.25 M, respectively. The quenching constants referred to are dependent on coefficient α . They have been calculated with average value $\alpha = 0.75$. In Table 2 there is also shown the average value by which the

Table 2

Relative quantum yields of the main chain scission of carbonyl polymers vs. PVPK and quenching constants of their photodestruction in CH_2Cl_2 solution

Polymers	k [min^{-1}]	c [g l^{-1}]	D^a	Φ	
				Φ_{PVPK}	$k_q \tau^b$ [l mol^{-1}]
VPK/MMA	0.468	4.00	0.848	0.47	1100 ± 150
VPK/S	0.185	3.98	0.270	0.44	134 ± 8
PVPK	0.870	5.00	> 2	1.00	77 ± 12
PVMK	0.251	6.00	> 2	0.48	8 ± 0.9
PIMK	0.104	12.00	> 2	0.86	2 ± 0.5

a) Optical density at thickness 1 cm; b) DMHD.

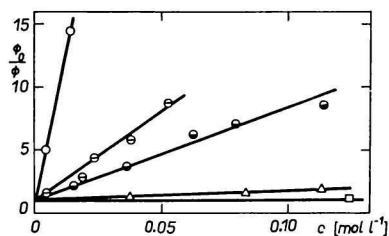


Fig. 2. Stern–Volmer dependence of photodestruction quenching of carbonyl polymers in CH_2Cl_2 with DMHD. Polymers designation and concentration as in Fig. 1.

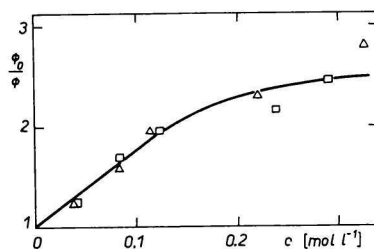


Fig. 3. Stern–Volmer dependence of quenching of PVMK photodestruction. Δ in methylene chloride 6.04 g/l; \square in ethyl acetate 10.06 g/l with DMHD calculated with $\alpha = 0.75$.

Table 3

Rate and quenching constants of the main chain scissions of the copolymer VPK/MMA in various solvents^a

Solvent	η^b [cP]	η_r^c	k [min ⁻¹]	$k_q \tau^d$ [l mol ⁻¹]
ethyl acetate	0.457	1.66	0.510 ^e	1400 ^e
benzene	0.650	2.07	0.578	1000
chlorobenzene	0.794	2.07	0.516	785
dioxan	1.29	2.05	0.293	233
diethyl oxalate	2.00	1.77	0.154 ^e	480
ethylene chlorohydrin	3.45	2.49	0.043	165
methylene chloride	0.438	2.59	0.471	1100
chloroform	0.58	2.60	0.244	510
chloroform–tetrachloromethane 1 : 1	0.68	2.43	0.300	650
1,2-dichloroethane	0.83	2.30	0.208	325

a) $c = 4$ g/l; b) solvent viscosity at 20°C; c) relative viscosity of non-irradiated solution; d) quencher DMHD; e) calculated with $\alpha = 0.64$ the rate constants in ethyl acetate is 0.68l (quenching constant 1620) and in diethyl oxalate 0.190 (quenching constant 512).

quenching constants change with the change of α by ± 0.1 . At higher quenchers concentrations Stern–Volmer dependence for PVMK (Fig. 3) is curved.

The copolymer VPK/MMA of concentration 4 g/l was irradiated in various solvents. The course of photodestructions was a linear one in all solvents. Both the rate and the quenching constants shown in Table 3 have been determined by simultaneous irradiation. For calculation, average value $\alpha = 0.75$ (except the cases marked) has been used. The constants α at 20°C for PMMA are known only for some solvents used in this study (in ethyl acetate [17] 0.64, in benzene [18] 0.73, and in chloroform [18] 0.8, respectively). As may be seen from Fig. 5, the quenching constants are more affected by the coefficient α in low viscosity solvents (benzene and ethyl acetate respectively). The coef-

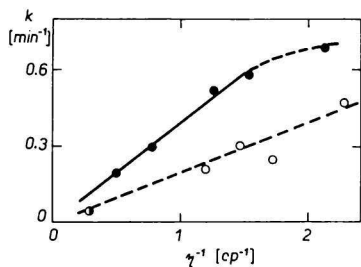


Fig. 4. Rate constants of main chain scission (k) of copolymer VPK/MMA 4 g/l in solvents of various viscosities. For both the ethyl acetate and the diethyl oxalate $\alpha = 0.64$.

○ ethylene chlorohydrin; ○ chlorinated aliphatic hydrocarbons; ● other solvents.

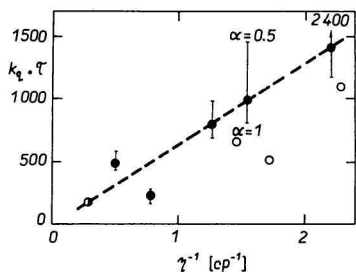


Fig. 5. Quenching constants in photodestruction of copolymer VPK/MMA with DMHD in solvents of various viscosities. Solvents designation and concentration as in Fig. 4.

efficient α for PMMA in ethyl acetate is less than 0.75. The corresponding quenching constant is most likely to be a higher one owing to which the dependence would curve upward in the region of the low viscosity as in the paper [12]. In chlorinated solvents starting with methylene chloride (Table 3, Figs. 4 and 5 respectively) both the rate and the quenching constants are lower with regard to the appropriate viscosity.

In PVPK photodestruction the influence of various quenchers was investigated in preceding paper [5]. For copolymer VPK/MMA in chlorobenzene solution the results are summarized in Table 4.

Table 4

Quenching of copolymer VPK/MMA photodestruction by various quenchers in chlorobenzene^a

Quencher	c [mol l ⁻¹]	$\frac{\Phi_0}{\Phi}$	$k_q \tau$ [l mol ⁻¹]
DMHD	0—0.01		760
ferrocene	0.0163	38.1	395 ^b
1,3-cyclooctadiene	0.0154	7.04	392
biphenyl	0.0261	10.6	367
naphthalene	0.0291	36.2	200 ^b
tetrachloroethylene	0.0150	2.73	115
trichloroethylene	0.0254	3.12	84

a) Irradiation time 3 minutes, polymer concentration 4 g/l; b) after correcting to absorption by quencher.

Discussion

The main photolytical reaction of low-molecular carbonyl compounds possessing γ -hydrogen is its intramolecular abstraction under formation of biradical six-membered ring intermediate. The biradical is decomposed under main chain scission and formation of single and double bond. The main reaction at photolysis of PVPK is the same as in low-molecular compounds. The quantum yield of photodestruction of copolymer VPK/MMA is lower than PVPK. Lower content of γ -hydrogens available for abstraction in copolymer VPK/MMA when compared with PVPK may be responsible for this decrease.

There may be assumed different mechanisms for main chain scission in copolymer VPK/MMA than in PVPK [5–7]. The β - or δ -hydrogen may participate in the photoelimination. In such a case 5- or 7-membered ring intermediate is formed which is less convenient when compared with six-membered ring intermediate [19]. Owing to the steric hindrances referred to, the reactivity of the carbonyl group decreases, and consequently the lifetime of the triplet state increases. Elongation of the lifetime of triplet state for copolymer VPK/MMA is responsible for different course of destruction in aerated solutions. It means that oxygen concentration in benzene solution is sufficient for quenching which is not observed with other studied polymers.

In copolymer VPK/S the lower reactivity *vs.* that of PVPK is most likely due to the higher energy of C–H bond on γ -carbon which makes more difficult the formation of biradical six-membered ring intermediate.

In PVMK the photoelimination is primarily responsible for the main chain scission [13]. In the transfer from aryl alkyl ketone structural units in polymer to methyl alkyl ketone structural units the decrease of the quenching constant is observed (Table 2). The same effect was observed in the low-molecular compounds. The quenching constants of the photolysis of both valerophenone in benzene and 2-hexanone in *n*-hexane with piperylene [11] are 100 and 10 l mol⁻¹. The last value is corrected on the amount of reaction from the singlet state. In PVMK the Stern–Volmer dependence starts curving at a concentration of about 0.2 mol l⁻¹ DMHD (Fig. 3). Similar curvature has been observed with 2-hexanone [1] which is caused by reaction originating from the singlet state.

In *tert*-butyl alkyl ketones photolysis, mainly α -decomposition takes place [20]. With the prolongation of the alkyl chain also the photoelimination starts to participate. In the photolysis of *tert*-butyl *n*-butyl ketone the photoelimination is responsible for one third of overall decrease of the starting ketone [20]. Ketones with longer alkyl chains bounded on tertiary α -carbon, the influence of which on photoelimination is unknown, have so far not been investigated. It is possible that in the case of PIMK the substituents on α -carbon bring about a favourable chain orientation for hydrogen abstraction in biradical formation. In cycloalkanones α -methyl substituents increase the reactivity at α -decomposition below the limit measurable by triplet quenching [21].

The photodestruction of carbonyl polymers with aryl alkyl and methyl alkyl structural units proceeds mainly through the triplet state. In the presence of triplet quencher it is reasonable to assume that the triplet state is deactivated by diffusion-controlled bimolecular quenching (rate constant $k_q = k_d$) and by formation of biradical with rate constant k_r only. In view of this fact the ratio of quantum yield of main chain scission without and with quencher may be expressed by the equation

$$\frac{\Phi_{0T}}{\Phi_T} = 1 + \frac{k_q}{k_r} [Q].$$

For diffusion-controlled quenching in one solvent the rate constant k_q is the same for a certain quencher. Therefore, in just the sequence in which the quenching constants decrease (Table 2, Fig. 2) the reactivity of triplet states increases.

The lifetime of the triplet state in inert solvents may be assumed to remain unchanged. Unlike the low-molecular compounds, the influence of solvent viscosity on the displacement of two polymer fragments is a greater one. This effect may favour the reaction of biradical to starting polymer instead to two fragments. Therefore we have observed decrease in the rate constant of photolysis with increasing solvent viscosity (Fig. 4). Chlorinated aliphatic hydrocarbons do not follow the same dependence.

In various solvents decrease of quenching constant is proportional to the increase of solvent viscosity (Fig. 5) suggesting unambiguously the processes to be a diffusion-controlled one. Chlorinated aliphatic hydrocarbons are out of this dependence.

The fact that various quenchers act with different efficiency (Table 4) suggests that in the quenching process also other effects apart from the quencher diffusion are involved.

The transfer of excitation triplet energy in polymer systems is of major importance for polymer photochemistry. It can be utilized in the sensitization and polymer stabilization [5, 22]. From this viewpoint, a detailed investigation of the energy transfer in polymer systems, complicated when compared with low-molecular compounds, seems to be necessary.

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