Effect of Triplet Quenchers on the Photolysis of Poly(Vinyl Phenyl Ketone) in Film*

P. HRDLOVIČ, I. LUKÁČ, and Z. MAŇÁSEK

*Institute of Polymers, Slovak Academy of Sciences,
Bratislava 9*

The photolysis of poly(vinyl phenyl ketone) in film has been utilized to evaluate quenching efficiency of some aromatic hydrocarbons and different types of light stabilizers. The quenching efficiency was expressed as a slope of Stern—Volmer dependence.

The quenching constants of aromatic hydrocarbons with first triplet level lower by 6 kcal mole^{-1} than first triplet level of poly(vinyl phenyl ketone) were about 220 l mole^{-1}. No difference of quenching efficiency has been observed between naphthalene added to poly(vinyl phenyl ketone) and bonded in copolymer vinyl phenyl ketone 2-vinylnaphthalene. It has been concluded that the energy transfer along the polymer chain does not arise in poly(vinyl phenyl ketone) at room temperature. The quenching efficiency of u.v. absorbers was substantially higher than that of nickel chelates. Ferrocene has been found to be the only efficient quencher among metal chelates studied by this technique.

From the physicochemical viewpoint, light stabilizers are mainly evaluated according to absorption spectra characterizing their efficiency as light filters. Less attention has been paid to the study of light stabilizers as quenchers of excited states. In application tests, it is practically impossible because of the difficulty involved in the separation of both the screening and the quenching effects of light stabilizers for polychromatic light. In addition, neither the chromophores responsible for photooxidative degradation, nor their excited states have so far been known.

The quenching studies of polymer photodegradation as well as the quenching effects of light stabilizers has been reviewed by *Klöpffer* [1] and partly by *Heller* [2] and *Cicchetti* [3]. *Heskins* and *Guillet* [4, 5] have studied the inhibition of photolysis of copolymer ethylene/carbon monoxide by 1,3-cyclooctadiene in both the solution and the film. Recently, *Eastman et al.* [6] have found that excimer and monomer fluorescence of alkyl naphthalenes is quenched by some light and heat stabilizers. To evaluate the quenching efficiency of light stabilizers, the quenching of both the emission and the photolysis of polymer may well be utilized [1—6]. The photolysis of polymer, however, has to proceed through precisely defined excited states which is the case with poly(vinyl phenyl ketone). Recently, its photolysis and emission spectra have been studied in detail [7—9]. First

---

triplet state involved in poly(vinyl phenyl ketone) photolysis is formed in aryl alkyl ketones with unit efficiency [10]. The photolysis proceeds in the same way in both the solution and the film [7] not being affected by air [11]. To minimize the screening effect of the investigated compounds, the photolysis is to be carried out in film.

In this paper, we would like to report the results of the study of inhibition effect of some aromatic hydrocarbons known as triplet quenchers, as well as of some commercial u.v. absorbers and metal chelates in poly(vinyl phenyl ketone) photolysis. We extend our previous study [9] of the photolysis of copolymer vinyl phenyl ketone with 2-vinyl-naphthalene in solution to include the film.

Experimental

Poly(vinyl phenyl ketone) (PVPK) was prepared in the same way as in paper [9]. The same copolymers of vinyl phenyl ketone with 2-vinylnaphthalene (VPK/2VN) were used as in paper [9].

Aromatic hydrocarbons, such as diphenyl, fluorene, naphthalene, acenaphthalene, pyrene, phenantrene, anthracene, were zonally refined (Lachema, Brno, ČSSR). Acenaphthylene was the product of EGA-Chemie KG (Keppler and Reif, Steinheim/Albruch, G.F.R.).

The u.v. absorbers and metal chelates: 2-hydroxy-4-methoxy benzophenone (Cyasorb UV-9), 2-(2′-hydroxy-5′-methyl phenyl)benztriazole (Tinuvin P), p-tert-butyl phenyl salicylate (Eastman OPS), 2-naphthyl salicylate, nickel chelate of 2,2′-thiobis-4-(1,1,3,3-
-tetramethylbutyl) phenol (Ferro AM 101), nickel chelate with ligands 2,2′-thiobis-4-
-(1,1,3,3-tetramethylbutyl) phenol and n-butylamine (Cyasorb 1084) and nickel salt of monoethyl ester of 3,5-ditert-butyl-4-hydroxybenzyl phosphoric acid (Irgastab 2002) [2] were either commercial products or synthesized in the Research Centre of J. Dimitrov Chemical Works, Bratislava. Ferrocene was provided by Dr. Elečko from the Chemistry Department, Faculty of Natural Sciences of Komenský University, Bratislava.

The polymer films have been prepared on Petri dishes of diameter 4 cm by pouring 2 ml 5% w/v copolymer solution and 4% w/v of PVPK solution in chloroform which has slowly been evaporated. The films contained about 10% w/v of solvent. The reproducibility
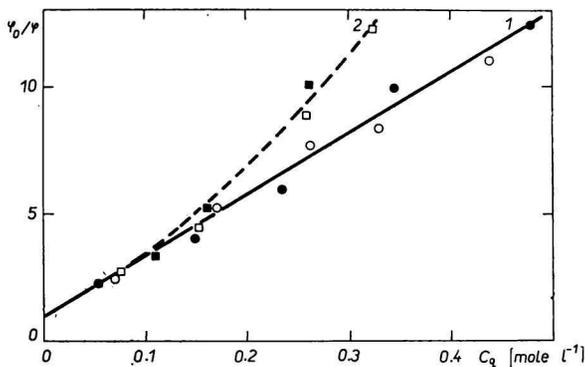

Fig. 1. Dependence of φ_0/φ on quencher concentration for acenaphthalene ($\bigcirc$ and $\bullet$) and acenaphthylenes ($\square$ and $\blacksquare$).

of the independent experiments was good (Fig. 1). There may then be concluded that the dispersion of the quencher in polymer film is both reproducible and homogeneous. In reducing the solvent content by drying the films under vacuum and increased temperature, the reproducibility changed for the worse. All quenchers were compatible over the concentration range 0.05—0.40 mole l^{-1} except anthracene. At the concentration exceeding 0.25 mole l^{-1}, the formation of anthracene crystals in polymer film and consequently quite a great scatter of experimental results have been observed.

The polymer films were irradiated on a marry-go-round apparatus of special design. The light source consisted of a 40 W medium pressure mercury arc (HQE 40, Zeiss, Jena) placed in a pyrex cooler with circulating water. The cooler was surrounded by a concentric glass cylinder, providing annular space of 1 cm. The filtering solution composed of 600 g NaBr · H_2O and 3 g $Pb(NO_3)_2$ per litre transmitting [9] light in the region above 340 nm was placed in this space. The polymers PVPK and VPK/2VN absorb light in the region below 375 nm. We may assume the light of the wave length 366 nm to be photochemically efficient. The screening effect of the compounds under study is calculated for this wave length.

Table 1

Stern—Volmer constant of different quenchers

Quencher	$\varepsilon_q(366)$ l mole^{-1} cm^{-1}	K l mole^{-1}	K_f l mole^{-1}	K_q l mole^{-1}	E_T^c kcal mole^{-1}
structural unit of PVPK	10				70.5[d]
fluorene	0	1.0	0.0	1.0	67.6
diphenyl	0	1.3	0.0	1.3	65.6
naphthalene	0	21.0	0.0	21.0	60.6[d]
copolymer VPK/2VN	0	21.0	0.0	21.0	59.7[d]
acenaphthene	0	23.5	0.0	23.5	
phenantrene	30	22.0[a]	0.2	21.8	62.2
acenaphthylene	305	23.5[a]	1.5	22.0	
pyrene	187	26.0	0.9	25.1	48.7
anthracene	2130	59.5	12.5	47.0	42.0
Eastman OPS	0	0.0	0.0	0.0	
2-naphthyl salicylate	10	22.0	0.1	21.9	
Cyasorb UV-9	1350	34.0[b]	6.0	28.0	62.0[e]
Tinuvin P	8300	152.0	51.0	111.0	56.0[f]
ni-*p-tert*-butyl phenyl salicylate	560	4.1	2.4	1.7	
Ferro AM 101	240	9.8	1.0	8.8	
Cyasorb 1084	240	1.6	1.0	0.6	
Irgastab 2002	3	3.1	0.1	3.0	
ferrocene	45	34.0[b]	0.2	33.8	50.0[g]

a) The Stern—Volmer dependence is slightly curved upward.

b) The Stern—Volmer dependence is strongly curved upward.

c) Ref. [25].

d) Calculated from phosphorescence spectra.

e) Ref. [26].

f) Ref. [27].

g) Ref. [28].

Ultraviolet absorption spectra were measured on a recording spectrophotometer SP 700 A Unicam (Cambridge, England) and on a single-beam nonrecording spectrophotometer VSU-1 (Zeiss, Jena).

Poly(vinyl phenyl ketone) (density 1.31 g cm^{-3}) was determined by the method of electromagnetic float.

The molecular weight decrease of irradiated films was followed viscometrically on Ubbelohde viscometer in benzene solution at 30°C. The limiting viscosity number was calculated using single-point measurements according to *Berlin* [12].

All the operations were carried out in yellow light because of the light sensitivity of the polymer.

The emission spectra of PVPK and copolymer VPK/2VN was measured by Dr. Geuskens and co-workers from Université Libre de Bruxelles, Belgium on a spectrofluorimeter of their own design [13]. The excitation was made at the wave length 366 nm.

Results

The ratio of the quantum yield of the main chain scission without and with quencher was calculated in the same way as in the previous paper [9] and plotted *vs.* the quencher concentration according to Stern—Volmer relation

$$\varphi_0/\varphi = 1 + K c_q,$$

where c_q is the quencher concentration in mole l^{-1}.

Most compounds studied in this paper absorb at 366 nm. The correction for the screening effect can be calculated for monochromatic radiation provided that the Lambert—Beer law is valid for polymer film. Presuming the screening effect of quencher only, the ratio $(\varphi_0/\varphi)_t$ can be calculated according to relation [14]

$$(\varphi_0/\varphi)_t = [(1 - 10^{-D_p})/D_p] [D/(1 - 10^{-D})],$$

where D_p and D are optical densities of the polymer film without and with quencher. The optical density of the polymer is given by $D_p = \varepsilon_p c_p l$, where ε_p is the molar extinction
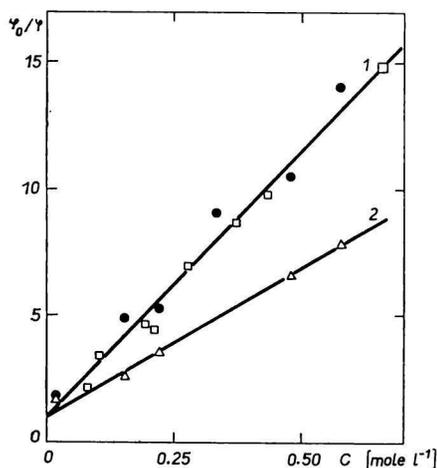

Fig. 2. Dependence of φ_0/φ on quencher concentration for added naphthalene (□) and copolymers VPK/2VN (●) in polymer film (line *1*) and (△) in solution at concentration 12 g/l (line *2*).

coefficient equal to 10 l mole^{-1} cm^{-1} for 366 nm; c_p is the molar concentration of phenyl ketone structural units in bulk PVPK equal to 10 mole l^{-1} and l is the thickness of polymer film equal to 45 μ. Optical density $D = D_p + D_q$, where $D_q = \varepsilon_q c_q l$; ε_q is molar extinction coefficient of quencher at 366 nm (Table 1) and c_q is molar concentration of quencher in film. Calculated values $(\varphi_0/\varphi)_f$ were plotted *vs.* the concentration of the quencher according to the relation

$$(\varphi_0/\varphi)_f = 1 + K_f c_q.$$

K_f values characterizing screening efficiency of the quenchers are summarized in Table 1. The K values of quenchers exhibiting absorption at 366 nm are corrected by substracting K_f (Table 1).

The reproducibility of our experiments is satisfactory. In Fig. 1, two independent experiments for quenchers of both acenaphthene and acenaphthylene are shown. The estimated error for the determination of the quenching constant is about ± 20%.

In Fig. 2 the plot of the dependence φ_0/φ on the quencher concentration for both PVPK and copolymer VPK/2VN is shown. The different initial molecular weight of copolymers was corrected in the same manner as in paper [14]. The values of $\alpha = 0.84$ and $K' = 2.82 \times 10^{-5}$ for PVPK [9] were used for molecular weight calculation of copolymers VPK/2VN. This calculation is valid only in the case of copolymers with a low content of the second component. The scatter of the φ_0/φ values in the case of copolymer exceeds that in the case of PVPK with freely added naphthalene. It is evident, however, that a common line may be drawn through the experimental points (line *1*). The slope is 21 l mole^{-1}. The straight line *2* in Fig. 2 was obtained by plotting the values φ_0/φ from paper [9] for VPK/2VN copolymer photolysis in benzene solution of a concentration 12 g/l *vs.* quencher concentration in polymer film. In this case the slope is 11.6 l mole^{-1}.
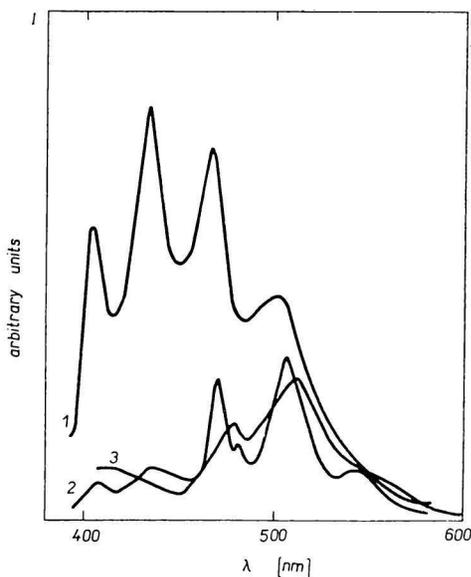

Fig. 3. Emission spectra of PVPK (*1*), added 1.8% w/w naphthalene in PVPK (*2*) and copolymer VPK/2VN with 1.8% w/w of naphthalene (*3*).

The emission spectra without and with naphthalene and copolymer VPK/2VN are shown in Fig. 3. The emission of polymer films at liquid nitrogen temperature is composed of short lived phosphorescence of PVPK and of long lived phosphorescence of naphthalene. The emission spectrum of PVPK (curve *1*) appears to be the most intensive one having four maxima at λ_{max} 406, 437, 470, 503 nm, respectively. The 0—0 transition from the first triplet state corresponds to an energy of 70.5 kcal mole^{-1} [8]. In the emission spectrum of PVPK with 1.8% w/w of naphthalene the emission bands corresponding to PVPK are suppressed. New emission bands corresponding to naphthalene at 472, 483, and 507 nm are observed (curve *2*). In VPK/2VN copolymer with 1.8% w/w of naphthalene structural units an equally intensive spectrum as in PVPK with naphthalene addition is observed with the maxima being shifted towards higher wave lengths (curve *3*).

Discussion

The Stern—Volmer constant for quenching low molecular donor by low molecular quencher is interpreted according to relation [6]

$$K_q = pk_d\tau,$$

where p is the quantum yield for the net irreversible loss of energy at the site of quencher's molecule [6]; k_d is the rate constant for the diffusion-controlled bimolecular reaction and τ is the lifetime of the excited state of the donor in the absence of quencher. The rate constant of the diffusion-controlled bimolecular reaction is given by the approximate relation

$$k_d = 4\pi\varrho DN_A/1000,$$

where ϱ is the sum of the diameters of the molecules of both the quencher and the donor; D is the sum of diffusion coefficients of the quencher and donor and N_A is Avogadro number.

The Stern—Volmer constant for quenching high molecular donor by low molecular quencher has been interpreted in the same way [4, 5]. Different analysis has been made for the quenching of low molecular donor by high molecular quencher [15].

The quenching constants K_q corrected for screening effect are about 220 l mole^{-1} for most aromatic hydrocarbons. K_q values for both fluorene and diphenyl are substantially lower. The difference of triplet levels between donor and acceptor in solution is to be $\Delta E_T = 6$ kcal mole^{-1} for an efficient transfer of triplet energy [16]. The differences of lowest triplet energies between PVPK and both diphenyl and fluorene are 4.9 kcal mole^{-1} and 3.9 kcal mole^{-1}, respectively. These values are below the limit 6 kcal mole^{-1}. There can be expected even lower quenching efficiency of both compounds in film than in solution.

The quenching constant in the system PVPK—naphthalene (*I*) in benzene solution is 68 l mole^{-1} [9] and in film 21 l mole^{-1} (Table 1). The quenching constant in the system PVPK—diphenyl (*II*) in benzene solution is 25.5 l mole^{-1} [9] and in the film 1.3 l mole^{-1} (Table 1). In view of the simple interpretation of K_q we might expect the changes of the lifetime, p-factor and diffusion coefficient in transfer from solution to film for both naphthalene and diphenyl to be equal and the ratio K_q(solution)/K_q(film) constant. This ratio, however, is —3 for the system *I* and —20 for the system *II*. This indicates that p-factor in diphenyl quenching is strongly influenced in polymer films. The changes in lifetime and diffusion coefficient are nearly the same for both systems. It has been suggested by *Wagner* [17, 18] that twisted conformation of diphenyl is involved in triplet energy transfer. The twisted conformation can be more easily reached in solution than

438

in film. This is then reflected in greater change of p-factor for diphenyl than for naphthalene.

A higher value of K_q has been observed for pyrene and a substantially higher one for anthracene. For a series of aromatic hydrocarbons with increasing molecular weight the diffusion coefficient should decrease and, consequently, K_q as well. The K_q increase for pyrene and anthracene reflects most likely the p-factor increase which we cannot so far account for.

Two independent experimental results obtained in the study of both degradation (Fig. 2) and emission spectra (Fig. 3) of PVPK—naphthalene and copolymer VPK/2VN suggest unambiguously equal efficiency of the freely added and bonded triplet quencher. The value of the quenching constant 21 l mole^{-1} is in agreement with those K_q of other aromatic hydrocarbons. In viewpoint of these results the triplet energy transfer in both systems suggests to occur with equal efficiency. By building in, the quencher's ability to participate in the energy transfer by exchange mechanism does not decrease due to steric hindrances. Simultaneously, its efficiency does not increase by trapping energy transferred between the phenyl carbonyl chromophores along the polymer chain.

In the polymer film the dispersion of bonded and freely added quencher is nearly the same. The freely added quencher in solution dissolves statistically all over its volume. The bonded quencher in solution is invariably in the proximity of the excited chromophore on the macromolecule. That is why the bonded quencher is more effective than freely added one at the same molar concentration in solution. On the other hand, the ratio φ_0/φ for the copolymer of the given composition should be the same for the diluted solution and the film. The values φ_0/φ for copolymers VPK/2VN at the concentration 12 g/l plotted *vs.* quencher concentration in film result in a slope 11.6 l mole^{-1}. To explain the decrease of the quenching constant the suppression of the intermolecular energy transfer by dilution is suggested. In highly diluted solutions, only the quenchers built in the macromolecules prove to be effective because the intermolecular quenching is suppressed due to low diffusion coefficient of the whole macromolecule.

The situation is completely different in the case of high concentration of a quencher added to the solution. The diffusion coefficient of the low molecular quencher, mobility of polymer segments and solvent viscosity are responsible for its efficiency [18, 19].

Our results suggest that in PVPK or in its copolymers the energy transfer along the polymer chain does not take place *i.e.* there is no delocalization of the excited energy between phenyl carbonyl chromophores. In other polymers with aromatic hydrocarbons in the side chain such a process has already been proved experimentally [20, 21].

Quenching effects of the typical representatives of three commercial u.v. absorbers are quite different with p-*tert*-butyl phenyl salicylate not quenching at all. It means that its triplet level is equal or higher when compared with PVPK. The quenching constant for 2-hydroxy-4-methoxy benzophenone and 2-(2'-hydroxy-5'-methyl phenyl) benztriazole are of 28 and 111 l mole^{-1}, respectively. In both cases the Stern—Volmer dependence is strongly curved upward.

Nickel chelates investigated in this paper are considered in [2, 3] as quenchers of excited states. It has been shown that some nickel complexes quench effectively anthracene triplet [22]. It has therefore been concluded that they also quench the lowest triplet state of carbonyl group in polypropylene [22, 23]. The most effective compound among nickel chelates studied in this paper was nickel chelate of 2,2'-thiobis-4-(1,1,3,3-tetramethylbutyl) phenol. The quenching efficiency of this compound in photooxidation initiated by diethyl ketone has been investigated by *Chien* and *Connor* [24]. On the basis

of their results, the energy transfer by dipole-dipole interaction according to Förster was suggested. Our results show that this compound may quench by exchange mechanism as well. The quenching efficiency of all other nickel chelates is poor.

On the other hand, ferrocene turned out to be an efficient quencher. This is in agreement with the well-known fact that ferrocene derivatives are excellent light stabilizers in the space [1], their screening efficiency being poor.

Our results show unambiguously that except ferrocene, other nickel chelates are less efficient quenchers of triplet states when compared with commercial u.v. absorbers. In outdoor tests, however, their overall efficiency is comparable with that of u.v. absorbers. This suggests that it will be necessary to correct existing views of the efficiency mechanism of these compounds as light stabilizers. The results obtained by the study of triplet quenching may be transferred only to a limited extent to photooxidative degradation of polymers.

References

1. Klöpffer W., *Kunststoffe* **60**, 385 (1970).
2. Heller H. J., *Eur. Polym. J.*, *Suppl.* **1969**, 105.
3. Cicchetti O., *Advan. Polym. Sci.* **7**, 70 (1970).
4. Heskins M., Guillet J. E., *Macromolecules* **1**, 97 (1968).
5. Heskins M., Guillet J. E., *Macromolecules* **3**, 224 (1970).
6. Eastman J. W., Smutný E. J., Coppinger G. M., *J. Chem. Phys.* **53**, 4346 (1970).
7. David C., Demarteau W., Geuskens G., *Polymer* **8**, 497 (1967).
8. David C., Demarteau W., Geuskens G., *Eur. Polym. J.* **6**, 1405 (1970).
9. Lukáč I., Hrdlovič P., Maňásek Z., Belluš D., *J. Polym. Sci. A-1*, **9**, 69 (1971).
10. Wagner P. J., Hammond G. S., *Advan. Photochem.* **5**, 21 (1968).
11. Hrdlovič P., unpublished results.
12. Berlin A. A., *Vysokomol. Soedin.* **8**, 1336 (1966).
13. David C., Demarteau W., Geuskens G., *Eur. Polym. J.* **6**, 537 (1970).
14. Lukáč I., Hrdlovič P., Maňásek Z., Belluš D., *Eur. Polym. J.*, *Suppl.* **1969**, 523.
15. Duportail G., Froelich D., Weil G., *Eur. Polym. J.* **7**, 977 (1971).
16. Nordin S., Strong R. L., *Chem. Phys. Lett.* **2**, 429 (1968).
17. Wagner P. J., *J. Amer. Chem. Soc.* **89**, 2820 (1967).
18. Wagner P. J., *Mol. Photochem.* **1**, 71 (1969).
19. Lukáč I., Hrdlovič P., Zvara I., Maňásek Z., *Chem. Zvesti*, in press.
20. Geuskens G., David C., *Preprint 371, XXIII IUPAC Conference*, Boston, 1971.
21. Schneider F., Springer J., *Makromol. Chem.* **146**, 181 (1971).
22. Briggs P. J., McKellar J. F., *Chem. Ind.* (London) **1967**, 622.
23. Briggs P. J., McKellar J. F., *J. Appl. Polym. Sci.* **12**, 1825 (1968).
24. Chien J. C. W., Connor W. P., *J. Amer. Chem. Soc.* **90**, 1001 (1968).
25. Lamola A. A., *Energy Transfer and Organic Photochemistry* in *Technique of Organic Chemistry*, Vol. XIV, p. 92. (P. A. Leermakers and A. Weisberger, Editors.) Interscience, a division of J. Wiley, New York, 1969.
26. Kyseľ O., Záhradník R., Pakula B., *Collect. Czech. Chem. Commun.* **35**, 3020 (1970).
27. Mohyla F., unpublished results.
28. Scott D. R., Becker R. S., *J. Chem. Phys.* **35**, 516 (1961).