

# Quenching of aromatic triplet by monomeric and polymeric radicals in polymer film at 77 K

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The quenching of triphenylene phosphorescence by monomeric, dimeric or polymeric radicals in poly(methyl methacrylate) film was investigated at 77 K. The low-molecular *N*-oxyl radicals (11 types) were prepared by oxidation of parent sterically hindered amines. The phosphorescence of triphenylene in solid matrix is influenced by the type of matrix, concentration of triphenylene, and traces of the solvents which have been used for the preparations of films. The values of active spheres of quenching for monomeric *N*-oxyl radicals were in the interval (1.7 nm; 2.1 nm) while no correlation between the size of active sphere and change in radical structure could be observed outside the paramagnetic centre. In a given system, the biradical exhibited quenching efficiency which was merely slightly greater than that of monoradical. As for polymeric radical, only small fraction (about 5 mole %) of the present paramagnetic centres was effective as quencher, which corresponds to molecular dimensions.

For quenching of triphenylene by *N*-oxyl radicals in film, the parameter  $\gamma = 15$  was determined.

Исследовалось тушение фосфоресценции трифенилена мономерными радикалами, или же димерным и полимерным радикалом в пленке полиметилметакрилата при 77 К. Низкомолекулярные *N*-окисильные радикалы (11 типов) были получены окислением исходных стерически затрудненных аминов. Фосфоресценция трифенилена в твердой матрице зависит от типа матрицы, концентрации трифенилена и следов растворителей, которые использовались для приготовления пленок. Значения активных сфер тушения для мономерных *N*-окисильных радикалов находились в интервале (1,7 нм; 2,1 нм) причем не была отмечена корреляция величины активной сферы с изменениями структуры радикала вне парамагнитного центра. Бирадикал в данной системе проявлял лишь немногим большую эффективность тушения, чем монорадикал.

В случае полимерного радикала только небольшая фракция (приблизительно 5 мол. %) присутствующих парамагнитных центров была активна как тушитель, что соответствует молекулярным размерам.

Для тушения трифенилена *N*-оксильными радикалами в пленке был установлен параметр  $\gamma = 15$ .

The radiationless transfer of electronic energy was intensively studied [1—4] mainly from the view-point of physical parameters of the process in relation to the structure of donor and acceptor. But this process has not been sufficiently used for characterization of polymers as donors and acceptors of energy. The effect of polymer medium on energy transfer has also been neglected up to now. The difference between poly(methyl methacrylate) and polystyrene used as solid matrix with respect to the transfer of triplet energy from triphenylene to metallocenes was described by *Vikesland* and *Wilkinson* [5].

In this paper, we are concerned with the quenching of triphenylene triplet by sterically hindered nitroxyl radicals in poly(methyl methacrylate) film at 77 K. The nitroxyl radicals of this type are considered to be important intermediates in the cascade of stabilization reactions involving the starting amines functioning as light stabilizers [6, 7]. The quenching efficiency of the sterically hindered *N*-oxyl radicals was investigated mainly in solution [8—14] by using aromatic hydrocarbons as donors. There are two mechanisms that are proposed for quenching, *i.e.* increasing of the efficiency of intersystem crossing and electronic energy transfer. From the view-point of efficiency of these compounds as light stabilizers, it seems to us to be important to investigate in more detail both the quenching in the solid phase and the influence of molecular mass on quenching because the oligomeric light stabilizers of this type are at present introduced as new types.

### Theoretical

The radiationless transfer of electronic energy from the triplet of the donor  $^3D$  to acceptor  $^m A$  obeys the following equation



The transfer of triplet energy necessitates the resonance between energetic levels of donor and acceptor and may follow either the dipole—dipole or exchange mechanism [1—5]. The transfer of energy is quantitatively described by two limiting models put forward by Stern—Volmer and Perrin, respectively. The Stern—Volmer model is based on the assumption that a thorough mixing of donor and acceptor takes place during the life-time of the excited state. The Perrin model defines the active sphere of quenching, *i.e.* the region about the quencher where

complete quenching occurs, while no quenching takes place outside this region and the positions of donor and acceptor are fixed. The basic difference between both models consists in the assumption that the life-time of donor according to the Stern—Volmer model decreases with transfer efficiency, whereas the life-time of donor does not change according to the Perrin model.

In principle, the efficiency of transfer or quenching may be determined in two arrangements, *i.e.* under steady irradiation or in pulse regime. In the first case, the measurement gives the ratio of the quantum yields  $\eta/\eta_0$  in the presence and absence of quencher. In the second case, we obtain the decay curves which give the ratio  $\eta/\eta_0$  by numerical integration. Provided the course of decay curve is exponential, the life-time can be easily determined by logarithmic analysis. But the decay curves do not exhibit simple exponential character in the presence of quenchers. Then it holds for the mean life-time

$$\tau = \frac{\int_0^{\infty} t\Phi(t) dt}{\int_0^{\infty} \Phi(t) dt} \quad (2)$$

where  $\Phi(t)$  is the decay function in the presence of quencher. We usually do not know the analytical form of the decay function in the presence of quencher. The simplest procedure for determining the mean life-time is a numerical integration which is, however, loaded by a greater error than the direct determination of the ratio  $\eta_0/\eta$ .

If the Perrin model is valid the dependence of  $\ln(\eta_0/\eta)$  on quencher concentration is linear and it holds  $\tau_0/\tau = 1$  for all concentrations of quenchers.

A more thorough analysis of decay functions for which  $\eta/\eta_0$  and  $\tau/\tau_0$  depended on quencher concentration was carried out by *Inokuti* and *Hirayama* [2]. An analytical expression of the decay function requires to involve the mechanism of energy transfer in this function. For exchange mechanism the decay function assumes the following form

$$\Phi(t) = \exp \left[ - (t/\tau_0) - \gamma^{-3} \frac{C}{C_0} g(e^\gamma t/\tau_0) \right] \quad (3)$$

where  $\gamma = 2R_0/L$ ,  $L$  is the mean effective Bohr radius of the excited and nonexcited state of donor and acceptor, and  $R_0$  is the critical distance of transfer for which the rate of transfer is equal to the rate of other deactivation processes, for which it holds

$$k_{dd}(R_0) = \frac{1}{\tau_0} \quad (4)$$

The quantities  $R_0$  and  $C_0$  are connected by the relation

$$C_0 = \frac{3}{4\pi NR_0^3} \quad (5)$$

where  $N$  is the Avogadro number. The function  $g(e^{\gamma t}/\tau_0)$  is an integral function approximated by the following expression

$$g(z) = (\ln z)^3 + 1.731 (\ln z)^2 + 5.934 (\ln z) + 5.444 \quad (6)$$

*Inokuti* and *Hirayama* have shown that it holds

$$\eta/\eta_0 = \exp\left(-\alpha \frac{C}{C_0}\right) \quad (7)$$

and  $\alpha = 1$  for  $\gamma > 25$ . This equation is identical with the Perrin relation. This means that we may use the Perrin model for the analysis of quantitative data, if the concentrations of quencher are low and variations of  $\tau/\tau_0$  are small when compared with those of  $\eta/\eta_0$ .

## Experimental

The emission spectra of doped polymeric films were measured with an equipment described in papers [15, 16]. The exciting radiation of the wavelength 313 nm was isolated from the spectrum of a high-pressure mercury lamp HBO 200 (Narwa, BGW, Berlin, GDR) by combining a liquid filter, glass filter (width 0.5 cm, No. 9853, Corning Glass Company, Corning N. Y., USA) and interference filter UV KSIF 313 (Zeiss, Jena).

The decay curves were measured in an equipment which consisted of a photographic flash (Mikrotechna, Prague), Dewar flask with a holder of the polymer film of the dimension 2 cm  $\times$  3 cm [16], front photomultiplier (EMI 6256 B) with a source of high voltage NBZ 411 (Tesla, Liberec), and an X—Y recorder (EMG, Budapest) connected in X-t regime. The recorder was started by adapted signal of a photodiode 1PP 75 which was produced by exciting flash. The decay curves were digitized by hand. By the use of these data, the ratio  $\eta_0/\eta$ , mean life-time  $\tau$ , and ratio  $\tau_0/\tau$  were calculated by means of numerical integration.

Triphenylene (purum, Fluka A.G., Buchs, Switzerland) was used without any further purification.

Poly(methyl methacrylate) (PMMA) used as a matrix was Diakon (ICI, England).

The preparation of starting steric amines is described in paper [17]. The *N*-oxyl radicals were prepared by oxidation of the starting amines. The preparation of individual radicals will be described later.

For investigating the course of reactions and testing the purity of substances thin-layer chromatography was applied. In these investigations, plates Silufol UV 254 (Kavalier, Votice) were used.

Elemental analysis and measurements of infrared and mass spectra were performed as described earlier [18]. The e.s.r. spectra of radicals were measured with an X-band e.s.r. spectrometer (Varian E-4) in benzene or chloroform solution.

4-Oxo-2,2,6,6-tetramethylpiperidine-1-oxyl was prepared by oxidation of 4-oxo-2,2,6,6-tetramethylpiperidine with hydrogen peroxide in the presence of  $\text{Na}_2\text{WO}_4$  and EDTA (ethylenediaminetetraacetic acid) according to Rozantsev [19]. Crystallization from n-hexane yielded orange crystals with m.p. = 35 °C (79 %). According to [19], the melting point is 36 °C.

4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (*I*) was prepared according to [20]. The orange crystals with m.p. = 71–72 °C (according to [20] m.p. = 72–73 °C) were obtained in 86 % yield by crystallization from cyclohexane.

By acylation of *I* with acetyl chloride according to [20], we obtained 4-acetyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (*II*) which formed red crystals with m.p. = 47–51 °C (according to [20] m.p. = 54–55 °C).

According to paper [20], we prepared 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (*III*) in the form of red crystals of m.p. = 87–88 °C by crystallization from cyclohexane (according to [20] m.p. = 82–83 °C).

The radical polymerization of *III* initiated by AIBN for the purpose of preparation of the polymeric  $\text{NO}\bullet$  radical is not feasible because the radicals arising from initiator preferentially recombine with monomer *III* to give  $> \text{N}-\text{OR}$ . For this reason, substance *III* was firstly transformed by the effect of  $\text{H}_2\text{SO}_4$  according to [21] into 4-methacryloyloxy-1-hydroxy-2,2,6,6-tetramethylpiperidine sulfate (*IV*) which was obtained in 88 % yield in the form of white precipitate. The radical polymerization of *IV* initiated by AIBN in nitrogen atmosphere at 60 °C was used for preparing poly(4-methacryloyloxy-1-hydroxy-2,2,6,6-tetramethylpiperidine sulfate) (*V*).

Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (*VI*) was prepared according to [21] by oxidizing substance *V* with hydrogen peroxide in the presence of  $\text{Na}_2\text{WO}_4$  and EDTA. The polymer was purified by twofold precipitation of the tetrahydrofuran solution into water and single precipitation into n-heptane. Thus an orange powder with  $M_n \sim 10\,000$  was obtained.

4-Methacryloylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (*VII*) was prepared by oxidation of 4-methacryloylamino-2,2,6,6-tetramethylpiperidine according to [20]. Brick-red crystals with m.p. = 146.5–148.5 °C were obtained by crystallization from n-hexane (according to [20] m.p. = 147–148 °C).

4-Acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl (*VIII*) was prepared by oxidation of the corresponding amine alike compound *VII*. The product is represented by red crystals with m.p. = 142–146 °C (according to [22] m.p. = 144–145 °C).

15-Benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dioxo-7-oxyl (*IX*) was prepared by oxidation of the corresponding parent amine by hydrogen peroxide in the presence of acetic acid according to [23]. The crystallization from n-hexane yielded red crystals with m.p. = 73–75 °C (according to [23] m.p. = 51–52 °C).

For  $\text{C}_{21}\text{H}_{27}\text{N}_2\text{O}_3$  ( $M_r = 355.43$ )  $w_i$ (calculated): 70.99 % C, 7.61 % H, 7.89 % N;  $w_i$ (found): 71.46 % C, 7.83 % H, 7.68 % N.

Infrared spectrum ( $\text{CHCl}_3$ ):  $\bar{\nu}(\text{s}) = 1680 \text{ cm}^{-1}$  and  $\bar{\nu}(\text{m}) = 1720 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ );  $\bar{\nu}(\text{m}) = 1420 \text{ cm}^{-1}$  ( $\nu(\text{NO}\bullet)$ ) and  $\bar{\nu}(\text{m}) = 3030 \text{ cm}^{-1}$  ( $\nu(\text{C}_6\text{H}_5)$ ).

15-Benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-7-oxyl (X) was prepared by reduction of IX with  $\text{LiAlH}_4$  and subsequent oxidation by air [23]. Red crystals (n-hexane) with m.p. = 138—141 °C were obtained in 48 % yield (according to [23] m.p. = 143—144 °C).

1,8-Bis(7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dione-15-yl)-3,6-dioxaoctane (XI) was prepared by the following procedure. The amount of 10 g (0.04 mol) of 7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dione was dissolved in 150 cm<sup>3</sup> of dried methanol and 2.6 g (0.04 mol) of KOH were added. After dissolution, alcohol was evaporated *in vacuo*. Potassium salt of the starting substance was dissolved under stirring in 150 cm<sup>3</sup> of dried dimethylformamide and afterwards 3.7 g (0.02 mol) of ethylene glycol chloride were added in this mixture in nitrogen atmosphere. The mixture was heated for 3 h at 75 °C and allowed to stand for 12 h at laboratory temperature. After diluting the solution with water in volume ratio 1 : 1, the solution was extracted in 500 cm<sup>3</sup> of ether. The ethereal solution was washed with water and dried. Ether was evaporated *in vacuo* and the final product was obtained by freezing out from acetone solution. The yield was 3 g (24.3 %) of white powder with m.p. = 47—52 °C.

For  $\text{C}_{34}\text{H}_{54}\text{N}_4\text{O}_6$  ( $M_r = 614.83$ )  $w_i$ (calculated): 66.42 % C, 9.11 % H, 8.85 % N;  $w_i$ (found): 66.62 % C, 9.18 % H, 8.64 % N.

Infrared spectrum ( $\text{CHCl}_3$ ):  $\bar{\nu}(\text{w}) = 3300 \text{ cm}^{-1}$  ( $\nu(\text{NH})$ );  $\bar{\nu}(\text{s}) = 1720 \text{ cm}^{-1}$  and  $\bar{\nu}(\text{s}) = 1680 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ ).

<sup>1</sup>H-NMR ( $\text{CDCl}_3$ ): 1.63 (broad band — 42H, cyclohexyl + 2NH), 3.85 (m, 4H,  $2 \times \text{N}-\text{CH}_2-$ ), 3.56 (m, 8H,  $\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$ ).

1,8-Bis(14,16-dioxo-7,15-diazadispiro[5,1,5,3]hexadecane-7-oxy-15-yl)-3,6-dioxaoctane (XII) was prepared by oxidation of 0.5 g (0.81 mmol) of XI with hydrogen peroxide (30 % aqueous solution) under stirring in the presence of acetic acid (3.5 cm<sup>3</sup>) at laboratory temperature. In the course of reaction (3 days), red oil was formed on surface of the reaction mixture. After neutralization, this oil was extracted into benzene (50 cm<sup>3</sup>). The benzene layer was concentrated and the crude product was chromatographically purified on a column (diameter 2 cm, length 20 cm) by the use of  $\text{CHCl}_3$  as eluent. After evaporation of  $\text{CHCl}_3$  and recrystallization from n-hexane, orange crystals (0.2 g, 42 %) with m.p. = 108—112 °C were obtained.

For  $\text{C}_{34}\text{H}_{52}\text{N}_4\text{O}_8$  ( $M_r = 644.8$ )  $w_i$ (calculated): 65.20 % C, 8.12 % H, 8.68 % N;  $w_i$ (found): 64.92 % C, 7.84 % H, 8.20 % N.

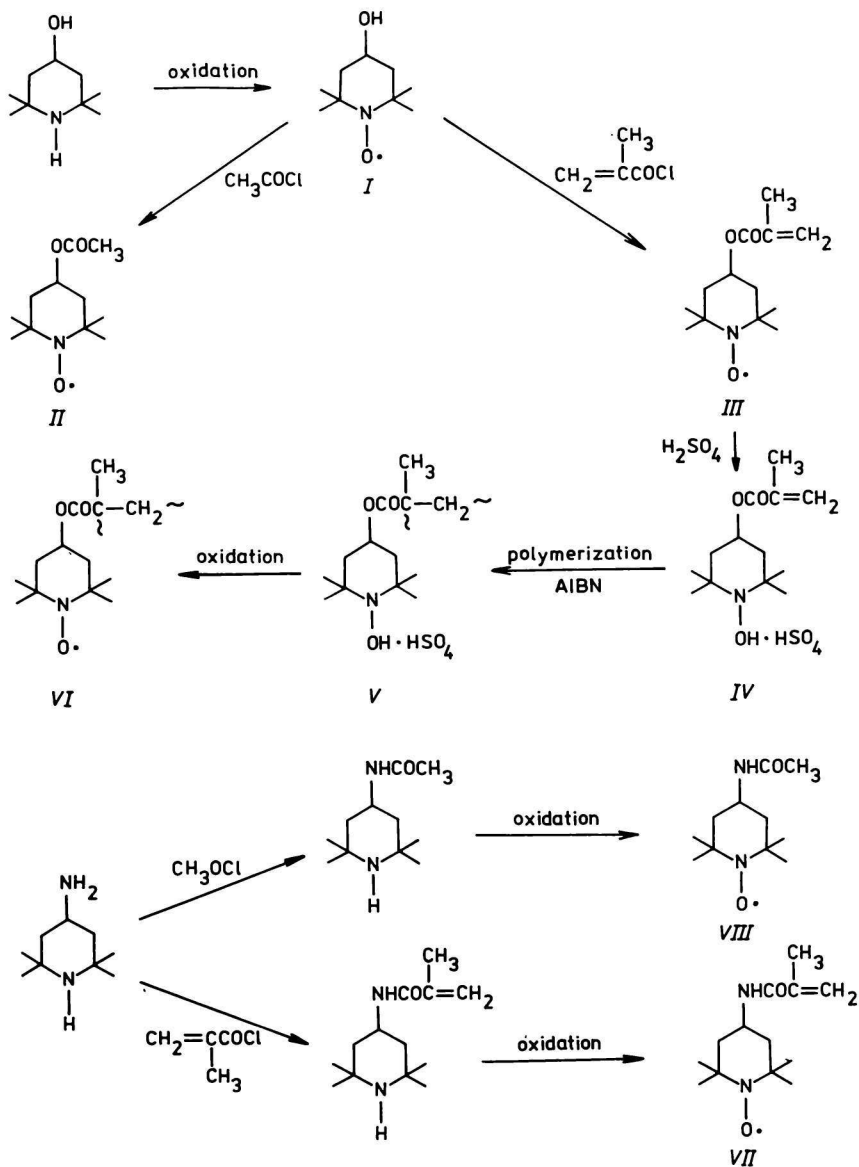
Infrared spectra ( $\text{CHCl}_3$ ):  $\bar{\nu}(\text{s}) = 1720 \text{ cm}^{-1}$  and  $1680 \text{ cm}^{-1}$  ( $\nu(\text{CO})$ );  $\bar{\nu}(\text{s}) = 1320 \text{ cm}^{-1}$  ( $\nu(\text{NO}\bullet)$ ).

## Results and discussion

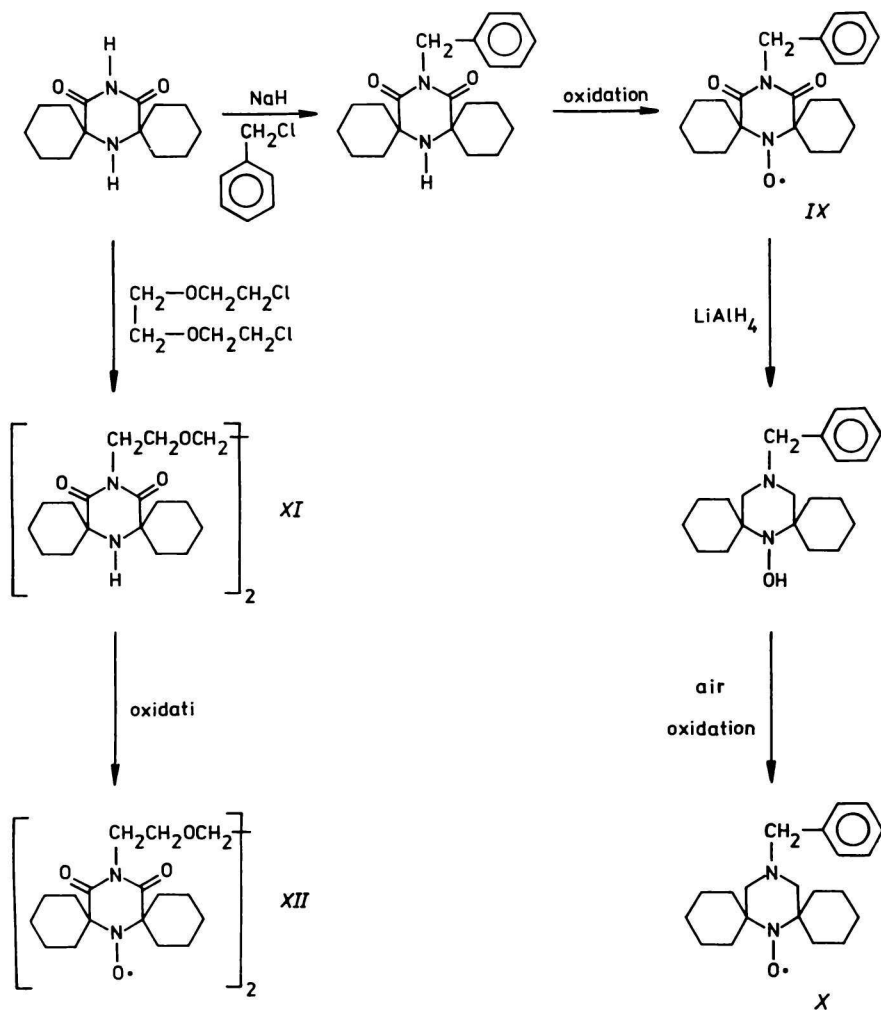
### *Synthesis and e.s.r. spectra of N-oxyl radicals*

The nitroxyl radicals are most frequently prepared by oxidation of the corresponding amines by hydrogen peroxide in the presence of the salts of wolframic acid or acetonitrile [24]. Recently, peroxy acids (*m*-chlorobenzeneperoxy carboxylic and *p*-nitrobenzeneperoxy carboxylic acid) were used for the synthesis of *N*-oxyl

radicals. The merit of these peroxy acids consists in the fact that they make possible to perform the reaction in nonaqueous solvents. The preparation of the described *N*-oxyl radicals according to Schemes 1 and 2 was based mainly on the first method, *i.e.* oxidation in the presence of hydrogen peroxide and sodium wol-



Scheme 1



Scheme 2

framate. According to [25], it seems that the peroxywolframate anion is the oxidizing agent in this case and the oxidation proceeds through the stage of hydroxylamine formation. However, the detailed mechanism is not yet known. The oxidations proceeded without difficulties with all derivatives of piperidine.

As for the derivatives of piperazine, the *N*-oxyl radicals may be prepared only if the *N*-15 nitrogen is substituted [23]. For this reason, we prepared according to Scheme 2 15-benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dione which was subjected to oxidation by hydrogen peroxide in the presence of acetic acid and thus transformed in 15-benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dioxo-



-7-oxyl. By the use of  $\text{LiAlH}_4$  the keto groups were reduced to the methylene groups and  $\text{NO}\cdot$  to hydroxylamine. The  $N$ -oxyl radical of this type was prepared by air oxidation [26] of the corresponding hydroxylamine. In the same way, the biradical 1,8-bis(14,16-dioxo-7,15-diazadispiro[5,1,5,3]hexadecane-7- $N$ -oxy-15-yl)-3,6-dioxaoctane was prepared.

The e.s.r. spectra of some stable radicals prepared are represented in Figs. 1—3. A triplet splitting due to the  $\text{N}^{14}$  atoms ( $J=1$ ) appears in these spectra and individual components have equal intensity (Figs. 1 and 2). The constants of hyperfine splitting are dependent on radical structure and solvent polarity. The

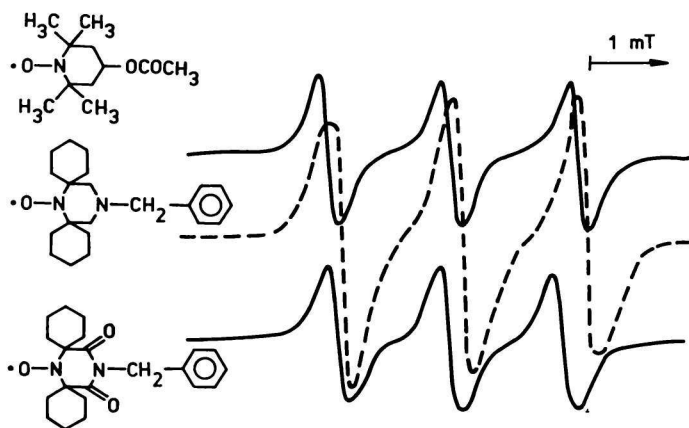


Fig. 1. Comparison of e.s.r. spectra of some monoradicals of the piperidine and piperazine type in benzene solution ( $c = 10^{-3} \text{ mol dm}^{-3}$ ).

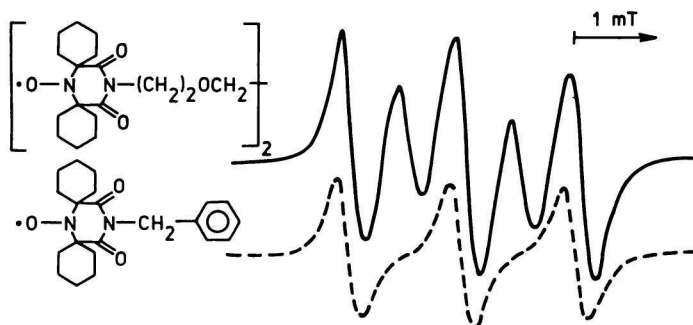


Fig. 2. Comparison of e.s.r. spectra of the monomeric and dimeric  $N$ -oxyl radical in benzene solution ( $c = 10^{-3} \text{ mol dm}^{-3}$ ).

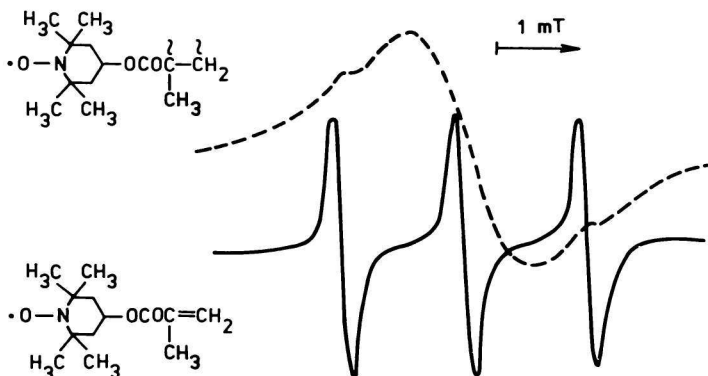


Fig. 3. Comparison of e.s.r. spectra of the monomeric and polymeric *N*-oxyl radical in benzene solution ( $c = 10^{-3} \text{ mol dm}^{-3}$ ).

interaction of each unpaired electron with two nuclei  $^{14}\text{N}$  manifests itself clearly in the e.s.r. spectrum of biradical, which brings about the change of triplet into five-line spectrum. The e.s.r. spectrum of polymeric radical considerably differs from the spectrum of monomer (Fig. 3). The spin-spin interaction of the vicinal *N*-oxyl groups is responsible for this change, e.g. the broadening of the bands.

#### *Spectral characteristic of triphenylene in polymeric matrix*

Triphenylene admixed into poly(methyl methacrylate) (PMMA) gives intensive phosphorescence with vibrational structure ( $E_T = 279 \text{ kJ mol}^{-1}$ ) at 77 K (Fig. 4). This phosphorescence was used for study of the quenching efficiency of metal-locenes [5]. However, it appears on the basis of our investigations that the decay of phosphorescence depends 1. on the type of polymeric matrix, 2. on the kind of solvent used for the preparation of films by casting, and 3. on the concentration of triphenylene.

The typical quantitative data concerning the decay of phosphorescence in different media are summarized in Table 1. At a low concentration of triphenylene (about  $0.04 \text{ mol kg}^{-1}$ ), the longest life-time is to be observed, provided benzene was used as a solvent. The replacement of benzene by chloroform results in shortening of the life-time. It is known that aromatic hydrocarbons are quenchers of the singlet state of aromatic hydrocarbons [27, 28]. However, their efficiency as triplet quenchers has not been thoroughly investigated up to the present. On the other hand, the highest intensity is to be observed for the PMMA film prepared

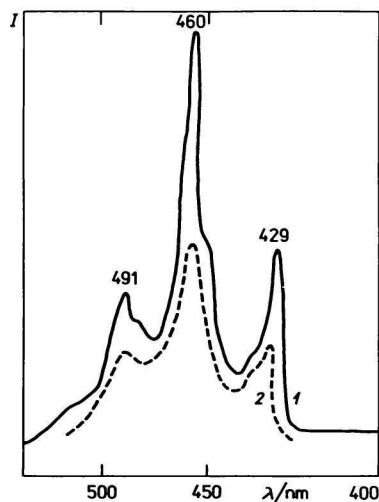


Fig. 4. Emission spectrum of triphenylene in the absence of quencher (1) and in the presence of quencher (2) (4-acetyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) in PMMA at 77 K.

Table 1

Spectral characteristics of triphenylene in films prepared from different solvents

Film	$\frac{c}{\text{mol kg}^{-1}}$	$I_r^a$	$\tau/s^b$	$\tau/s^c$
PMMA (HCCl <sub>3</sub> )	0.053	1.00	10.7	9.1
PMMA (Benzene)	0.044	0.70	13.3	12.0
PS (HCCl <sub>3</sub> )	0.044	0.43	—	9.6
PS (Benzene)	0.044	0.62	—	10.5

a) Relative intensity referred to the film with the highest intensity; b) life-time for exponential decay; c) mean life-time calculated numerically.

from chloroform. The decay of emission exhibits exponential character for both solvents in the extent exceeding two decimal orders (Fig. 5). The values of life-time calculated from the slope of the plot  $\log I$  vs.  $t$  are greater than the mean values of life-time calculated by numerical integration. That is conceivable because the numerical calculation of the integral  $\int_0^\infty t\Phi(t) dt$  imposes that the values are assessed for small  $I$  (i.e. the results recorded under 1 mm) and rapidly converge to zero, owing to which a portion of the integral is neglected.

Initially, the intensity of phosphorescence linearly increases with concentration up to the value  $0.08 \text{ mol kg}^{-1}$  and afterwards it starts to decrease (Table 2). That is caused by two effects: internal filtration effect and self-quenching. The investiga-

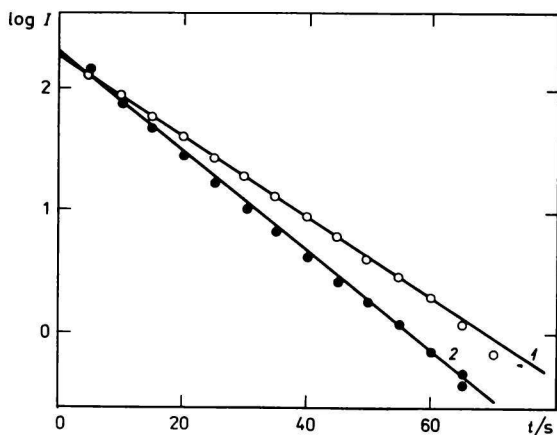


Fig. 5. Logarithmic analysis of decay curve of emission for triphenylene in film at 77 K.  
1. PMMA/benzene; 2. PMMA/CHCl<sub>3</sub>.

Table 2

Intensity of phosphorescence of triphenylene in films at 77 K as a function of composition

Film	$\frac{c}{\text{mol kg}^{-1}}$	$I_r^b$	$\tau/s$	$\tau_0/\tau$
PMMA (Benzene)	0.044	1.00	12.00	1.00
	0.088	1.02	11.93	0.99
	0.219	0.99	10.23	0.85
	0.482 <sup>a</sup>	0.38	6.21	0.52
PMMA (HClCl <sub>3</sub> )	0.053	1.00	9.01	1.00
	0.070	1.33	9.11	1.02
	0.254	0.78	7.34	0.82
PS (Benzene)	0.044	1.00	10.55	1.00
	0.088	1.00	9.51	0.90
	0.279 <sup>a</sup>	0.27	5.91	0.56
PS (HClCl <sub>3</sub> )	0.044	1.00	9.61	1.00
	0.088	0.96	8.52	0.82
	0.219	0.62	6.09	0.63

a) Films exhibited small aggregates of crystals; b) relative intensity referred to the concentration at which the maximum emission was observed.

tion of the dependence of emission on concentration is, however, hampered by low compatibility of triphenylene with PMMA. At concentrations over 0.25 mol kg<sup>-1</sup>,

a separation of crystals and agglomerates of triphenylene from the PMMA matrix is to be observed and the film gets optically inhomogeneous. Most data presented in Tables 1 and 2 were obtained with optically homogeneous films. These data show at least qualitatively that the life-time shortens with increasing concentration of triphenylene (except the PMMA matrices for which  $\text{HCCl}_3$  was used as solvent) and at the concentration of about  $0.09 \text{ mol kg}^{-1}$ , the intensity of emission starts to decrease. Besides, it can be seen that the polystyrene matrix deactivates the triplet state more efficiently than the PMMA matrix.

### *Quenching by monomeric, dimeric, and polymeric N-oxyl radical*

The analysis of the decay curves of phosphorescence of triphenylene in the PMMA matrix in the presence and absence of quencher at 77 K shows that, besides the increase in the ratio  $\eta_0/\eta$ , the ratio  $\tau_0/\tau$  also changes, but considerably slower. It means that the conditions of validity of the Perrin model are not strictly fulfilled. The dependence of  $\log(\eta_0/\eta)$  on quencher concentration was not linear in the whole concentration range. There are several possible causes of this fact.

It may be restricted solubility of quencher in the PMMA film or its partial aggregation which is not, however, optically observable.

There is a certain excess of quencher molecules for one excited donor molecule at the concentration of triphenylene  $w = 2\%$  ( $c = 0.0876 \text{ mol kg}^{-1}$ ) and concentrations of quencher over  $0.2 \text{ mol kg}^{-1}$ , owing to which a certain degree of "supersaturation" appears. Fig. 6 shows that a distinct deviation from linearity is to

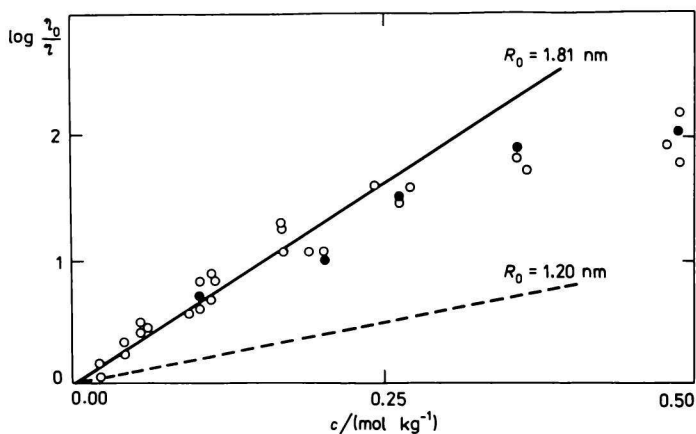


Fig. 6. Quenching of phosphorescence of triphenylene by 4-acetylamino-2,2,6,6-tetramethylpiperidine-*N*-oxyl in PMMA (chloroform).

Empty points were obtained from pulse measurements, full points were obtained from steady state measurements.

be observed at the concentrations of quencher exceeding  $0.2 \text{ mol kg}^{-1}$ . However, it is worth noticing that the scatter of experimental points is considerable but it is possible to derive plausible values of  $R_0$  from the initial linear section of the plot  $\log(\eta_0/\eta)$  vs.  $c$ . But all determined values of  $R_0$  are approximately by 1/3 higher than 1.2 nm which is a standard value for the quenching of emission of benzophenone by naphthalene [1, 2]. The obtained values of  $R_0$  for monoradicals are in the interval 1.7–2.1 nm (Table 3). In the range of this interval, no correlation between  $R_0$  and changes in radical outside the paramagnetic centre can, however, be observed. In this interval, the value of  $R_0$  found for biradical (2.27 nm) is only slightly greater than the values of  $R_0$  corresponding to monoradicals. It seems as if biradical might participate in the quenching process merely by one paramagnetic centre. An approximately twofold value is to be observed solely for  $R_0$  of the polymeric radical with  $M \sim 10\,000$  (Fig. 7). For a given monomer unit, the degree

Table 3

Radii of quenching spheres of some stable *N*-oxyl radicals for the quenching of triphenylene emission in PMMA film at 77 K

4-Oxo-2,2,6,6-tetramethylpiperidine-1-oxyl	1.72
4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl	2.00
4-Acetyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl	1.78
4-Methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl	1.91
Poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl)	3.20
4-Acetylamino-2,2,6,6-tetramethylpiperidine-1-oxyl	1.81
4-Methacryloylamino-2,2,6,6-tetramethylpiperidine-1-oxyl	2.04
15-Benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-14,16-dioxo-7-oxyl	2.02
15-Benzyl-7,15-diazadispiro[5,1,5,3]hexadecane-7-oxyl	2.10
1,8-Bis(14,16-dioxo-7,15-diazadispiro[5,1,5,3]hexadecane-7- <i>N</i> -oxy-15-yl)-3,6-dioxaoctane	2.27

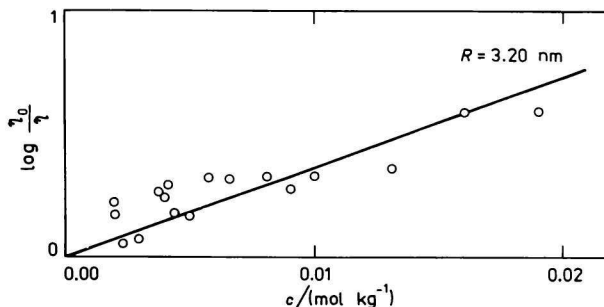


Fig. 7. Quenching of phosphorescence of triphenylene by poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl) in PMMA (chloroform) at 77 K.

of polymerization of radical is about 40. A polymer radical possesses 40 paramagnetic centres for quenching. The twofold value of  $R_0$  indicates that only about 5 mole % of a macromolecule are utilized for quenching. The value of  $R_0$  gives a certain image as regards the size of macromolecule. In the polymeric PMMA medium the dimensions of a polymeric quencher are likely undisturbed. For the time being, there are no quantitative data available concerning undisturbed dimensions of poly(4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl). The structurally related poly(cyclohexyl methacrylate) exhibits the values  $K = 8.4 \times 10^{-3}$  and  $\alpha = 0.69$  for benzene [29]. The value of limiting viscosity number calculated from the formula  $[\eta] = KM^\alpha$  is  $[\eta] = 4.83 \text{ cm}^3 \text{ g}^{-1}$ . The gyration radius  $R_g$  calculated from the equation

$$[\eta] = \Phi \frac{\langle R_g^2 \rangle^{3/2}}{M} \quad (8)$$

is 2.25 nm ( $\Phi = 4.2 \times 10^{24} \text{ mol}^{-1}$ ).

Though the value of  $R_0$  found for polymeric radical is somewhat greater than the determined gyration radius of the coil, which may be due to the not quite adequate model of polymeric radical, in principle, it is comprehensible on the basis of the

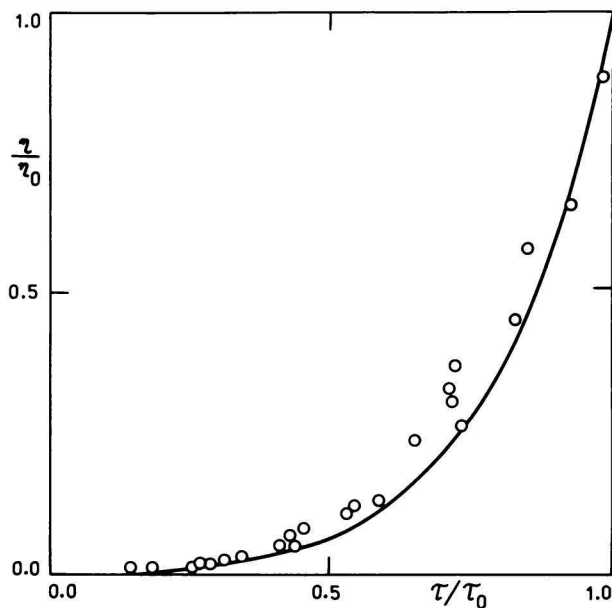


Fig. 8.  $\eta/\eta_0$  as a function of  $\tau/\tau_0$  for the quenching of phosphorescence by 4-acetyl-amino-2,2,6,6-tetramethylpiperidine-*N*-oxyl in PMMA at 77 K.

The points are experimental. The curve is theoretical for  $\gamma = 15$  [2].

data concerning molecular dimensions why only a small fraction of the paramagnetic centres bonded to macromolecule is usable for quenching.

The investigated system has some features in common with stabilization of some commercial polymers which do not have any proper absorption in the solar ultraviolet region. Though the centres of initiation are not exactly defined, it is clear that the centres of initiation occur in concentrations below  $0.01 \text{ mol kg}^{-1}$ . The concentration of triphenylene is higher, which may represent the upper limit of the centres of initiation. It results from a qualitative analysis that a polymeric stabilizer with molecular mass  $M \sim 10^4$  which has more reaction centres can affect only one initiation centre as a quencher owing to its molecular dimensions. For this reason, the efficiency of quenching by oligomeric and polymeric stabilizers is very reduced in comparison with low-molecular analogues.

The dependence of  $\eta/\eta_0$  on  $\tau/\tau_0$  gives information about the character or mechanism of the quenching process. Fig. 8 shows that the experimental points theoretically correspond to the calculated relationship for  $\gamma = 15$  [2]. Equal analysis carried out for other quenchers gave the values  $\gamma = 15\text{--}20$ . It is a lower value than found for typical organic quenchers, but it is higher than found for metallocenes [2, 5]. The value of parameter  $L$  found for  $\gamma = 15$  and  $R_0 = 2 \text{ nm}$  is  $L = 0.27 \text{ nm}$  which is the value characteristic of the  $N$ -oxyl radicals functioning as quenchers.

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