

THE INFLUENCE OF ALKYL SUBSTITUENTS ON NORRISH TYPE II REACTIONS FOR POLY-4'-ALKYLACRYLOPHENONES

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Summary

Poly-4'-alkylacrylophenones were prepared and their emission spectra and photolysis were studied. In low temperature emission spectra of poly-4'-alkylacrylophenones a bathochromic shift with respect to low molecular weight compounds was observed. The largest bathochromic shift, which was observed for poly-4'-methylacrylophenone, is caused by hyperconjugation. The quantum yield of main chain scission of poly-4'-alkyl-substituted acrylophenones lies in the range 0.2 - 0.4. Stern-Volmer constants indicate longer lives for the lowest triplet states compared with polyacrylophenone. It seems that an electron-donating effect of alkyl substituents is decisive in this prolongation. The bulkiness of alkyl substituents in the 4' position does not influence the lifetime in solution and they do not produce any effects in emission spectra.

1. Introduction

The Norrish type II reaction has been thoroughly investigated for low [1] and high molecular weight ketones [2]. The effect of substituents on the aromatic ring and at the γ carbon on quantum yields and the rate of γ hydrogen abstraction has been studied in detail [1]. Polyacrylophenone [3 - 7] and its substituted derivatives [8 - 11] have been studied as homopolymers or copolymers with styrene and methyl methacrylate. The studies revealed that electron-withdrawing and electron-donating substituents in 4' position prolong the lifetime of the lowest triplet state. It seemed to us to be useful to study the effect of the bulkiness of a substituent in 4' position in these systems. The increasing bulkiness of an alkyl substituent does not change its electronic effect but influences skeletal vibration. This can affect radiationless deactivation of the triplet state and subsequent γ hydrogen abstraction or biradical decay. In this paper we have studied experimentally the effect of ring substitution by bulky alkyl substituents on the Norrish type II reaction.

2. Experimental

4'-Methyl-3-chloropropiophenone was prepared in the same manner as 4'-ethylacetophenone [12].

3-Chloropropionyl chloride (124.3 g, 1 mol) was added during 20 min to a suspension of anhydrous aluminium chloride (133.3 g, 1 mol) in carbon tetrachloride (500 ml) in a 1 l three neck reaction flask at 0 - 5 °C. Then toluene (74 g, 0.8 mol) was added dropwise during 1 h, the temperature being maintained below 5 °C. The reaction mixture was then stirred for 1 h at laboratory temperature. The reaction mixture was decomposed by pouring into a mixture of ice and hydrochloric acid and the product was extracted with chloroform. The chloroform layer was washed with water and dried. Chloroform was evaporated under vacuum and the crude product was crystallized from hot n-heptane. The yield was 116 g (70%), m.p. 80.5 - 81.0 °C (ref. 13 gives 79.5 - 81 °C).

4'-Methyl-3-dimethylaminopropiophenone hydrochloride [14] was prepared using 4'-methylacetophenone (45 g, 0.33 mol) synthesized according to ref. 15, dimethylamino hydrochloride (34.8 g, 0.43 mol) and para-formaldehyde (12.9 g) in a 500 ml reaction flask equipped with a cooler. After the addition of 1 ml of HCl in 60 ml of ethanol (95%) the mixture was refluxed for 2 h on a water bath. Then the hot mixture was poured into acetone (400 ml) and allowed to cool slowly. The crude product (21.4 g) was obtained and after crystallization white crystals (19.4 g, 20%), m.p. 159 °C, were obtained.

4'-tert-Butyl-3-chloropropiophenone was prepared in the same way as 4'-methyl-3-chloropropiophenone. Finally white crystals, m.p. 35 - 35.5 °C (ref. 13 gives m.p. 36 °C), were obtained by freezing them out of an ethanolic solution in 41% yield (61 g).

4'-Cyclopentyl-3-chloropropiophenone was prepared as 4'-methyl-3-chloropropiophenone by acylation of cyclopentylbenzene prepared according to ref. 16. The product was obtained by freezing it out of n-heptane solution giving a 58% yield (96 g) of slightly yellow crystals, m.p. 40 - 41.5 °C. The IR spectrum in CCl_4 showed the carbonyl valence vibration band at 1690 cm^{-1} .

The mass spectrum gave the following *m/e* peaks: 236 M^+ , 173 $\text{C}_5\text{H}_9\text{PhCO}^+$, 145 $\text{C}_6\text{H}_5\text{Ph}^+$. The nuclear magnetic resonance (NMR) spectrum (in CDCl_3) gave the following shifts δ : 1.67 (singlet(s), 9H); 3.17 - 3.47 (triplet(t), 2H); 3.68 - 3.96 (t, 2H); 7.19 - 7.20 (doublet(d), 2H); 7.75 - 7.06 (d, 2H).

In the case of 4'-methylacrylophenone preparation two different routes were followed.

(1) Solutions of 4'-methyl-3-chloropropiophenone (14.1 g, 0.077 mol) in 50 ml of ethanol and 21 g (0.15 mol) of sodium acetate in 80 ml of ethanol were mixed and heated to boiling for 2 - 3 min. After cooling to room temperature the ethanol was vacuum evaporated and the reaction mixture was extracted with chloroform. The extract was washed with water

and with NaHCO_3 solution, dried with anhydrous sodium sulphate and distilled in the presence of picric acid at 74°C , 80 Pa (ref. 17 gives 73°C at 80 Pa). The NMR (CDCl_3) spectrum gave shifts δ of: 2.35 (s, 3H); 5.68 - 5.98 (multiplet(m), 1H); 6.16 - 6.55 (m, 1H); 6.9 - 7.38 (m, 3H); 7.78 - 7.95 (d, 2H).

(2) 4'-Methyl-3-dimethylaminopropiophenone hydrochloride (12 g) was steam distilled. The mixture of products and water was extracted with ether. The extract was dried with anhydrous sodium sulphate and the ether was vacuum evaporated. Liquid monomer (6.8 g) was obtained.

4'-tert-Butylacrylophenone was prepared as method (1) for 4'-methylacrylophenone. The crude product was distilled with traces of picric acid at 82°C , 17 Pa (ref. 17 gives 110°C at 350 Pa). The yield was 72%. The IR spectrum in CCl_4 showed the carbonyl valence vibrations are at 1680 cm^{-1} . The NMR (CDCl_3) spectrum gave shifts δ of: 1.28 (s, 9H); 5.7 - 5.96 (m, 1H); 6.16 - 6.55 (m, 1H); 6.74 - 7.21 (m, 1H); 7.33 - 7.55 (m, 2H); 7.67 - 8.0 (m, 2H). The mass spectrum gave the m/e peaks: 188 M^+ ; 173 ($\text{M}-\text{CH}_3$); 161 (t-BuPh^+); 145 ($\text{C}_3\text{H}_5\text{PhCO}^+$).

4'-Cyclopentylacrylophenone was prepared by dehydrochlorination by method (2). After evaporation of ethanol at reduced pressure the reaction mixture was diluted with a tenfold excess of solvent (petroleum ether: benzene, 4:1) and separated on a short column (Kieselgel 0.05 - 0.2 mm, diameter 4 cm, length 5 cm). After evaporation of the solvent at reduced pressure 7.6 g of colourless monomer (64%) was obtained, which did not contain any polymer. The IR (CCl_4) carbonyl valence vibration was at 1670 cm^{-1} ; the NMR spectrum (CDCl_3) gave shifts δ of: 2.1 (s, 8H); 3.3 (s, 1H); 5.95 - 6.24 (m, 1H); 6.43 - 6.83 (m, 1H); 7.16 - 7.7 (m, 3H); 7.45 - 8.3 (m, 2H).

Poly-4'-methylacrylophenone (P4MeAP) was prepared by thermal polymerization of 6.8 g of the monomer prepared by route (2) for 20 min at 60°C and a reduced pressure of 1.6 Pa under nitrogen. The yield was 3.5 g.

Poly-4'-tert-butylacrylophenone (P4BuAP) was polymerized under the same conditions as P4MeAP starting with 6 g of monomer. The yield was 3.2 g.

Poly-4'-cyclopentylacrylophenone (P4CyAP) was prepared by polymerization of 7.6 g of the monomer with 0.05% azobisisobutyronitrile for 1 h at 60°C under a reduced pressure of 1.6 kPa. The yield was 3.9 g.

Polyacrylophenone (PAP) [6] and poly-4'-ethylacrylophenone (P4EtAP) [9] were prepared as described previously. Characteristics of the polymers are summarized in Table 1. All the polymers were precipitated three times in a benzene-methanol system and were dried to constant weight. All operations were carried out under red light.

Viscometric measurements were performed using an Ubbelohde viscometer modified by Seide-Decker at $30 \pm 0.1^\circ\text{C}$. Limiting viscosity numbers of photolysed solutions were calculated from single point measurements assuming that the Huggins constants did not change during degradation.

Gel permeation chromatography (GPC) measurements were made in tetrahydrofuran on an apparatus consisting of seven all steel columns

TABLE 1

Characteristics of the prepared polymers

	$[\eta] \times 10^2$ ^a (ml g)	M_v ^b $\times 10^{-5}$	M_{GPC} ^c $\times 10^{-5}$	M_n ^d $\times 10^{-5}$	M_w ^e $\times 10^{-5}$	M_w/M_n
P4MeAP	1.04	2.75	3.8	1.19	4.0	3.72
P4BuAP	1.98	5.9	6.5	3.02	8.9	2.90
P4CyAP	0.74	1.8	1.9	1.11	2.6	2.42

^a Limiting viscosity number at 30 °C in benzene.^b Average viscosity molecular weight calculated using $K = 2.82 \times 10^{-3}$ and $\alpha = 0.84$ for polyacrylophenone [4].^c GPC molecular weight.^d Average number molecular weight based on the GPC curve.^e Average weight molecular weight based on the GPC curve.

(1222 mm \times 8 mm) filled with porous glasses GPC-10 (Electro Nucleonics, Fairfield, N.Y., U.S.A.) with 7.5, 11.8, 15.6, 36.8, 72.2, 142.0 and 204.6 μ m pores. The volume of the injected sample was 3 ml. The polymer concentration was monitored by a differential UV analyser (253.8 nm) with a 20 μ l cell (Development Workshop of the Czechoslovak Academy of Sciences, Prague). The flow rate was 1 ml min⁻¹. Polystyrene standards of narrow molecular weight distribution (Pressure Chemical Co., Pittsburg, Pa., U.S.A.) between 9×10^2 and 1×10^7 daltons at a concentration of 1 mg ml⁻¹ were used for calibration.

Absorption spectra in the UV and visible ranges were taken on a Specord UV-VIS (C. Zeiss, Jena, G.D.R.) and in the IR range on a Specord IR-71 (C. Zeiss, Jena, G.D.R.). NMR spectra were measured with a 60 MHz BS 467 (Tesla, Brno, Czechoslovakia) and mass spectra with a JMFD 100 (Jeol, Japan).

The low temperature (77 K) emission spectra of polymer films were measured on an apparatus composed of available optical and electronic parts described in ref. 6 at 313 nm excitation. Polymeric films were prepared by slow evaporation of solvent. The concentration of the model compounds or polymers in polymethyl methacrylate (PMMA) was 4%.

Polymer solutions were irradiated in sealed spectroscopic cuvettes 1 cm thick in a rotating apparatus [7] giving an equal dose for eight cuvettes. The static part consisted of a 40 W medium pressure mercury arc (Narva, BGW Berlin, G.D.R.) placed in a double-walled quartz reactor. Inside the reactor cooling water circulated and outside there was a liquid filter (600 g NaBr and 2.8 g Pb(NO₃)₂ in 1 l of water). The rotating part had the form of a regular octahedral vessel which on each inner face had a hole in front of which a glass filter, Corning No. 5860 (0.5 cm thick) with 366 nm maximum of transmission, was put. On the outside of the rotary carrier spectroscopic cuvettes were placed in holders. The volume of the irradiated solutions was 3 ml. Oxygen was removed by bubbling with purified nitrogen for 3 min. The intensity of the 366 nm radiation was determined by ferrioxalate actinometer [18] to be about 1.10^{-4} einstein min⁻¹ l⁻¹.

3. Results

3.1. Spectral measurements

UV spectra of all 4'-alkyl-substituted polyacrylophenones are the same and exhibit distinct $n-\pi^*$ bands (Fig. 1). No difference was observed between the UV spectra of the homopolymers and model compounds (4'-alkyl-substituted-3-chloropropiophenones) indicating that there is no interaction between the side chain chromophores of acrylophenone-type homopolymers in the ground state.

The low temperature emission spectra of the homopolymers are bathochromically shifted with respect to the emission spectra of model compounds, as is evident from Figs. 2 - 5 and Table 2. To exclude any environmental effect, *i.e.* the effect of the polymer matrix, both the model compound and the homopolymer were doped in PMMA. The emission spectra obtained from the homopolymer films are the same as those of PMMA film doped with homopolymers (Figs. 3 and 4). This means that there is no difference between the emission spectra of the pure homopolymers and of the homopolymers dispersed in a PMMA matrix although some difference in the physical state of films is observed, namely films of the homopolymers are clear and those of PMMA doped with the homopolymers are opaque because of mutual incompatibility.

The greatest difference is between the emission spectrum of a model compound and P4MeAP (Fig. 3). The emission spectrum of P4MeAP shows

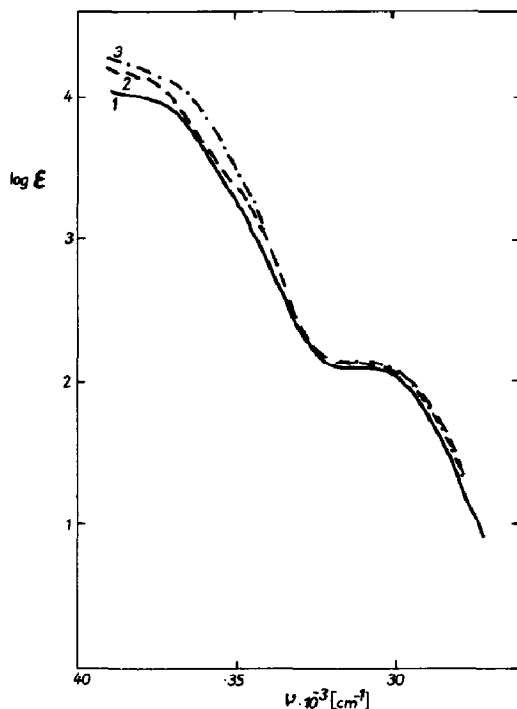


Fig. 1. UV absorption spectra in chloroform: 1, P4MeAP; 2, P4BuAP; 3, P4CyAP.

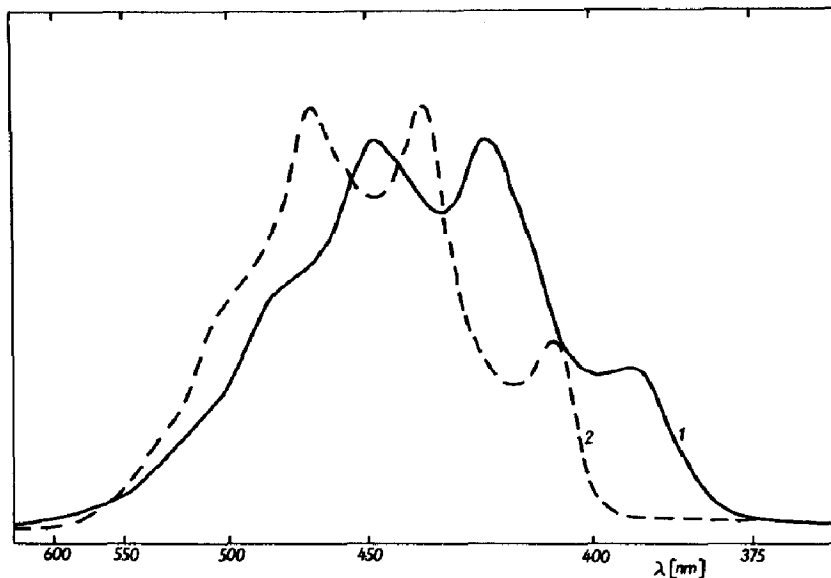


Fig. 2. Low temperature (77 K) emission spectra in PMMA: 1, 3-chloropropiophenone; 2, polyacrylophenone.

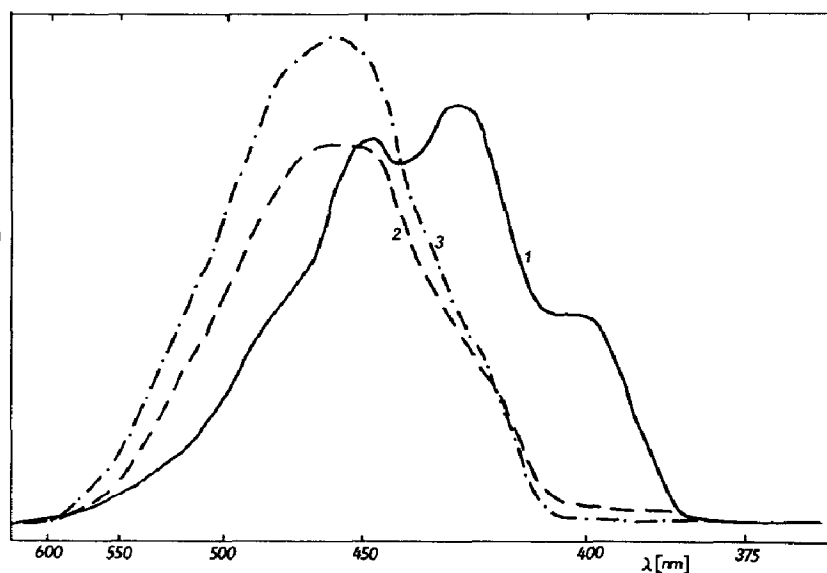


Fig. 3. Low temperature (77 K) emission spectra: 1, 4'-methyl-3-chloropropiophenone in PMMA; 2, P4MeAP in PMMA; 3, a film of P4MeAP.

the complete loss of vibrational structure as for poly-4'-methoxyacrylophenone [6]. This indicates that the methyl group has a stronger electron-donating effect than other alkyl groups probably because of hyperconjugation.

Other 4'-alkyl-substituted polyacrylophenones do not show any loss of vibrational structure and the bathochromic shift in the emission spectra of

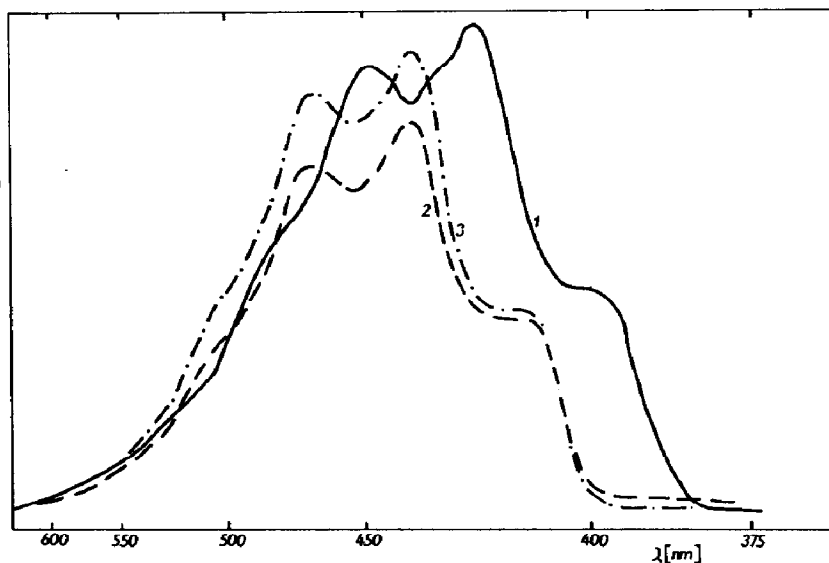


Fig. 4. Low temperature (77 K) emission spectra: 1, 4'-tert-butyl-3-chloropropiophenone in PMMA; 2, P4BuAP in PMMA; 3, a film P4BuAP.

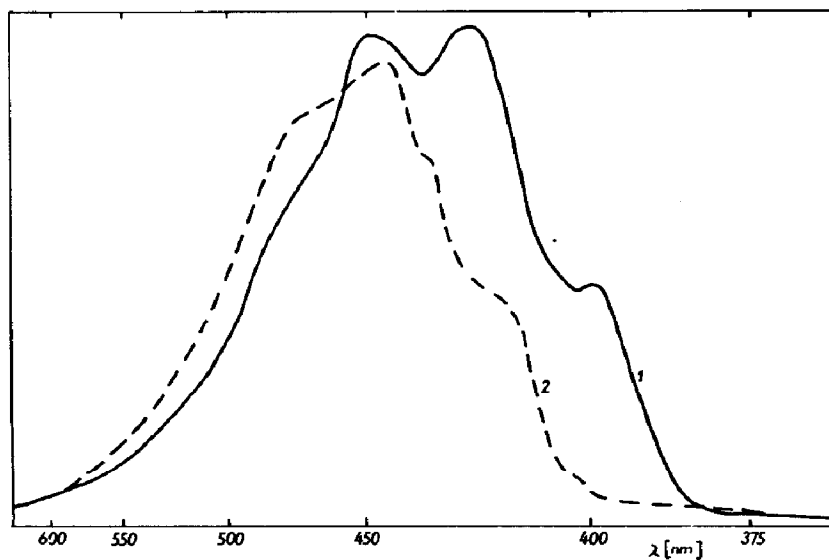


Fig. 5. Low temperature (77 K) emission spectra in PMMA: 1, 4'-cyclopentyl-3-chloropropiophenone; 2, P4CyAP.

their homopolymers is about 15 - 20 nm. The reason for this shift is not clear but it may be associated with perturbations due to dense packing of the chromophores in homopolymers which have a lower triplet energy as in low molecular weight models.

Spectral data indicate that alkyl substitution does not substantially influence the $n-\pi^*$ band and therefore we expect the quantum yield for main chain scission to be similar to that for polyacrylophenone.

TABLE 2

Emission spectra of carbonyl polymers

Polymer ^a	λ_{\max}				$E_T(0-0)$ (kJ mol ⁻¹)
3-Chloropropiophenone	394	422	499	477 ^s	304
PAP	408	436	459	498 ^s	293
4'-Methyl-3-chloropropiophenone	403	428	449		297
P4MeAP	428 ^s	459			280
P4MeAP ^b	428 ^s	461			280
4'-Ethyl-3-chloropropiophenone ^c	400	425	449	476	299
P4EtAP ^c	425	456	476		281
4'-tert-Butyl-3-chloropropiophenone	402	424	449	477 ^s	297
P4BuAP	414	439	467	484 ^s	289
P4BuAP ^b	414	439	467	484 ^s	289
4'-Cyclopentyl-3-chloropropiophenone	400	425	450	470	299
P4CpAP	421	445			284

^a PMMA film doped with 4 wt.% of low molecular weight compound or homopolymer.^b Films of homopolymers.^c The model compound and homopolymer were the same as in ref. 9.

3.2. Photolysis and its quenching

The photolysis of the polymers under study proceeds by a random mechanism, as is seen from linear plots of the number of main chain scissions against the time of irradiation (Fig. 6). The number of main chain scissions was calculated from viscometric data in the same way as previously [4, 6, 8]. From the slope of the time dependence of the number of main chain scissions the quantum yield of main chain scission was evaluated according to [4, 6]

$$\phi = \frac{c_p S}{\bar{M}_{n0} I_0 t (1 - 10^{-A})}$$

where c_p is the polymer concentration in grams per litre, s is the number of main chain scissions (which equals $([\eta]_0/[\eta])^{1/\alpha} - 1$ where $[\eta]_0$ and $[\eta]$ are the limiting viscosity numbers before and after irradiation and α is the Mark-Houwink coefficient), \bar{M}_{n0} is initial number average molecular weight, I_0 is the intensity of radiation, t is the irradiation time and A is the absorbance of the irradiated solution.

Figure 6 shows a small difference in the rate of photolysis between de-aerated and aerated solutions. The photolysis is inhibited by triplet quenchers such as naphthalene and diphenyl. A typical Stern-Volmer plot is shown in Fig. 7. The slope of this dependence is given as the product of the lifetime of the excited state and the rate constant for quenching.

The quenching rate constant for the polymeric donor PAP and the low molecular weight acceptor naphthalene in benzene is 4×10^9 l mol⁻¹ s⁻¹ [19]. The same value can be assumed for the systems studied. Naphthalene

is about 50% more effective as a quencher than diphenyl, the effect being associated with the different structure of diphenyl in the ground and excited states [11]. All pertinent data concerning photolysis and its quenching are summarized in Table 3.

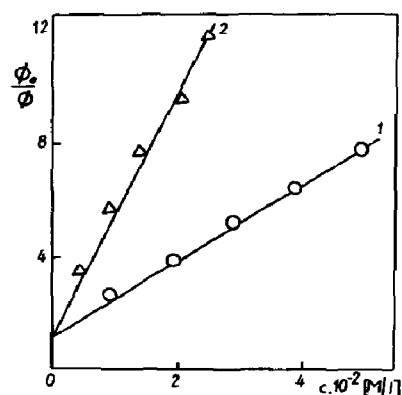
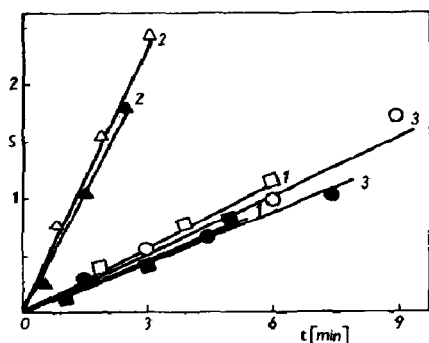


Fig. 6. A plot of the number of main chain scissions against the irradiation time for: 1, P4MeAP; 2, P4BuAP; 3, P4CyAP. Open points, deaerated solution; full points, aerated solutions.

Fig. 7. Quenching of P4MeAP photolysis by diphenyl (1) and naphthalene (2).

TABLE 3

Quantum yield of photolysis and Stern-Volmer constants of quenching for 4' alkyl-substituted polyacrylophenones in benzene

Polymer	c (g l ⁻¹)	A	$I_0 \times 10^{-4}$ (einstein min ⁻¹ l ⁻¹)	ϕ^a		K_{SV}^b	
				N ₂	Air	Naphthalene	Diphenyl
PAP [4]	10	> 2	—	0.22	0.22	68	25.5
P4MeAP	8	0.33	0.94	0.26	0.21	436	133
P4EtAP [9]	3	0.22	—	0.25	0.22	345	78
P4BuAP	5	0.19	0.98	0.37	0.32	336	96
P4CyAP	8	0.292	0.784	0.33	0.30	386	115

^aQuantum yields were calculated using values of M_n given in Table 1.

^bThe polymer solution concentration was the same as that for quantum yield determination. The solutions were bubbled with nitrogen and sealed.

4. Discussion

It is well established that the Norrish type II reaction of aryl alkyl ketones proceeds through formation of the lowest triplet biradical [1]. The triplet biradical collapses in several ways: the original ketone is formed, β scission takes place or cyclobutanol is formed. Cyclobutanol formation in polymeric systems, however, has not been observed so far. A substituent on the aromatic ring influences firstly the lowest triplet state and γ abstraction

and perhaps also the decay of the triplet biradical. Alkyl substituents on the aromatic ring with different numbers of carbon atoms exhibit electronic and vibrational effects. The most pronounced effect is observed for the methyl group as is shown in the emission spectra by bathochromic shifts and the loss of vibrational structure. The Stern–Volmer constant for P4MeAP is the largest in a series of 4'-alkyl substituents which indicates that this compound has the longest lifetime. A similar effect was observed for the 4'-methoxy substituent [6, 8]. The 4'-methyl substituent is the strongest electron donor among the alkyl groups studied, probably because of hyperconjugation. Other 4'-alkyl substituents show some bathochromic shift in the emission spectra and longer lifetimes in solution based on the Stern–Volmer constant than polyacrylophenone. No prolongation or shortening of the lifetime is observed on increasing the number of carbon atoms in the alkyl substituent. The small differences in quenching constants could also be caused by differences in the α coefficient. This means that aromatic ring substitution with alkyl substituents does not affect vibrations that are decisive in γ abstraction or triplet biradical decay. Position 4' on the aromatic ring seems to be distant from the reaction centre so that the chemical and physical deactivation routes of the lowest triplet state are not influenced.

A bulky alkyl substituent in position 4' does not manifest itself in the emission spectra either. During preparation of the polymer films by precipitation from solution there is probably enough time for the polymer segments to take up a relaxed conformation. Therefore no blue shift typical of a strained conformation is observed in the 0–0 band [20]. *tert*-Butyl and cyclopentyl substituents are probably not large enough to cause formation of less energetically favourable conformations.

The spectral and lifetime data based on Stern–Volmer constants lead to the conclusion that the methyl group exerts the most pronounced electronic effect in the series of alkyl substituents under study. Moreover, our data indicate that the bulkiness of an alkyl group in the 4' position does not affect γ abstraction or decay of the triplet state and biradical.

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