Photochemistry and photoinitiator properties of 4-substituted amidobenzophenones and imidobenzophenones

Norman S. Allen [a,*], Nik G. Salleh [a], Michele Edge [a], Teressa Corrales [a], Milla Shah [a], Iain Weddell [b], Fernando Catalina [c], A. Green [d]

[a] *Chemistry Department, Faculty of Science and Engineering, Manchester Metropolitan University, Chester Street, Manchester M1 5GD, UK*
[b] *Zeneca Specialities Ltd., Blackely, Manchester M9 3DA, UK*
[c] *Instituto de Ciencia y Tecnología de Polímeros, CSIC, 3 Juan de la Cierva, 28006 Madrid, Spain*
[d] *Great Lakes, Halebank Industrial Estate, Lower Road, Widnes, Cheshire WA8 8NS, UK*

Abstract

The photoinduced polymerization activities of ten novel 4-substituted amidobenzophenones and imidobenzophenones were determined in different monomers and prepolymers using real-time IR (RTIR) and data related to their spectroscopic activities. The relative order of the photoinitiator efficiency is found to be highly dependent on the method used, the amine co-synergist and the monomer. Absorption, phosphorescence analysis and photoreduction studies were also undertaken on the compounds and the data were interrelated to the photopolymerization activities. Fluorescence and phosphorescence analyses indicate a high rate of intersystem crossing to the triplet state. The latter is strongly mixed with a close-lying $\pi\pi^*$ state due to substitution and electron donation by the nitrogen atom. Transient absorption spectra on microsecond flash photolysis are assigned to the radical anion species formed by electron transfer. The photoinduced polymerization activities of the benzophenones, measured by RTIR, appear to be closely related to the formation of such transient species. Oxygen quenching in all cases indicates that the triplet state is the active precursor.

1. Introduction

In previous work [1–4] on the photoinduced crosslinking and initiation properties of 2-substituted anthraquinone molecules, a peculiar high degree of photoactivity was observed for compounds possessing amido groups. For example, 2-acrylamido-anthraquinone exhibited the highest activity with a spectral sensitivity above 400 nm, and induced significant levels of crosslinking in thermoplastics such as nylon 6,6. Through laser flash photolysis studies, this was associated with the importance of a long-lived, active, low-lying, excited triplet state. In the presence of tertiary amines, the photoactivity was significantly enhanced through electron transfer via the formation of a triplet exciplex.
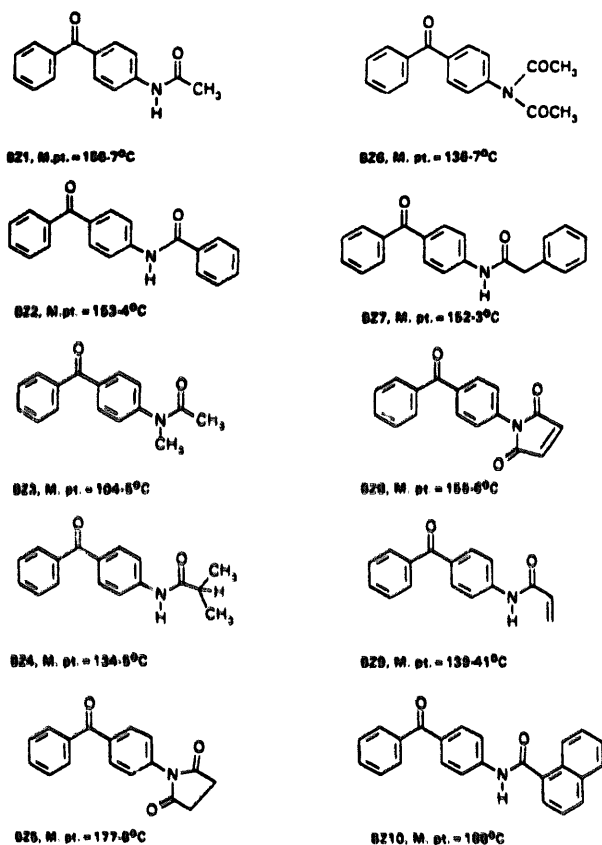
In terms of UV sensitivity, benzophenones have also been actively investigated [5–8]. In these investigations, modification of the benzophenone chromophore by 4-substitution with alkylamino and perester groups [5,6] gives rise to enhanced activity. In the former case, this effect was associ-

ated with intermolecular and intramolecular triplet exciplex formation, whereas in the latter, photofragmentation gave rise to active tert-butoxyl radicals. Water-soluble benzophenones with high activity have also been developed [7], whereas the 4-substitution of cinnamate ester groups has been found to reduce the photoinitiation activity of benzophenone [8]. In the latter case, 2 + 2 cycloaddition of the cinnamate ester groups competed with free radical formation from the triplet benzophenone.

In view of the high photoactivity induced by the substitution of amido groups in our anthraquinone work, we have extended this study to include the substitution of not only amido but also imido groups into the 4-position of benzophenone. Thus we present a range of novel 4-substituted amidobenzophenones and imidobenzophenones (Scheme 1) and examine their photoinitiated polymerization activities and spectroscopic properties. This comparative study will enable the importance of structural features to be interrelated to the photophysical properties of the initiators. Microsecond flash photolysis studies have also been conducted to determine the nature of the free radical intermediates. Photoin-

* Corresponding author. Tel: 0161 247 1432; fax: 0161 247 1438.

BENZOPHENONE AMIDES / IMIDES

B21, M.pt.=188-7°C

B26, M. pt.=138-7°C

B22, M.pt.=163-4°C

B27, M. pt.=152-3°C

B23, M. pt.=104-5°C

B28, M. pt=155-6°C

B24, M. pt.=134-5°C

B29, M. pt.=139-41°C

B25, M. pt.=177-8°C

B210, M. pt.=188°C

Scheme 1.

duced polymerization studies have been undertaken in different monomers and prepolymers using real-time IR (RTIR). Polychromic irradiation in the UV region shows that many of the derivatives exhibit a higher degree of activity than benzophenone.

2. Experimental details

2.1. Materials

All the solvents, butyl acrylate, benzophenone-2-diethylaminoethanol and triethylamine used in this work were obtained from Aldrich Chemical Co. Ltd., UK and were of Analar, spectroscopic or high performance liquid chromatography (HPLC) grade quality. The compounds 4'-benzoylacetanilide (BZ1) (m.p., 156–157 °C), 4'-benzoylbenzanilide (BZ2) (m.p., 153–154 °C), 4'-benzoyl-N-methylacetanilide (BZ3) (m.p., 104–105 °C), 4'-benzoylisobutyranilide (BZ4) (m.p., 134–135 °C), N-(4-benzoylphenyl)succinimide (BZ5) (m.p., 177–178 °C), N-acetyl-4'-benzoylacetanilide (BZ6) (m.p., 136–137 °C), 4'-benzoyl-2-phenylacetanilide (BZ7) (m.p., 152–153 °C), N-(4-benzoylphenyl)maleimide (BZ8) (m.p., 155–156 °C), 4-acrylamidobenzophenone (BZ9) (m.p., 139–141 °C) and 4-naphthylamidobenzophenone (BZ10) (m.p., 188

°C) were supplied by the Great Lakes Company, Widnes, UK.

2.2. Spectroscopic measurements

Absorption spectra were obtained using a Perkin–Elmer Lambda 7 absorption spectrometer. Fluorescence and phosphorescence excitation and emission spectra were obtained using a Perkin–Elmer LS-50B research luminescence spectrometer. Fluorescence quantum yields were obtained by the relative method using quinine sulphate in 0.05 M sulphuric acid as standard [9]. The quantum yield of quinine sulphate was assumed to be 0.55. Phosphorescence quantum yields were obtained in ethanol at 77 K using the relative method with benzophenone as standard, assuming a quantum yield of 0.74 in ethanol [9]. All spectra were corrected using a Perkin–Elmer IBM-compatible GEM package with an appropriate file for this purpose.

2.3. Photoreduction quantum yields

The absolute quantum yields of photolysis (ϕ_r) of the initiators were determined in 2-propanol at 10^{-5} M using an irradiation wavelength of 365 nm, selected from a Philips high-pressure Hg lamp (HB-CS 500 W) and a Kratos GM252 monochromator. Sample cells were thermostatically controlled at 30 °C and the solutions were oxygen and nitrogen (less than 5 ppm O_2) saturated. The absorbed light intensity was measured using an International Light model 700 radiometer previously calibrated by the Aberchrome 540 actinometer [10,11].

2.4. RTIR

The benzophenones were dissolved in a minimum quantity (2–3 cm³) of tetrahydrofuran, followed by mixing with a prepolymer (Sartomer 348, Sartomer Company, PA, USA). Traces of solvent were then removed by flushing with argon for 30 min, followed by the addition of 1% or 5% w/w of the co-initiator ethyl-p-(dimethylamino)benzoate (EDB) (Great Lakes, Widnes, UK).

The resin was placed between pieces of low-density polyethylene using a separator to give a film thickness of 50 μm. The polyethylene holder was then placed between two IR salt flats and positioned in the sample beam. Two polyethylene film samples were used as reference. The decrease in absorbance at 1638 cm⁻¹ of the vinyl absorption band was monitored in real-time mode during irradiation using a fibre-optic arrangement. The irradiation source used here was an ILC 302UV (Laser Lines Ltd., Beaumont Close, Banbury, Oxon., UK), switchable between UV and visible light with a cut-off point at 400 nm [12].

2.5. Microsecond flash photolysis

End-of-pulse transient absorption spectra on the microsecond time scale were obtained using a kinetic flash photolysis

Table 1

Absorption maxima and extinction coefficients of benzophenones in different solvents

Compound	Code	Chloroform		Ethanol		Acetonitrile		DMF	
		λ_{max} (nm)	Log ϵ	λ_{max} (nm)	Logϵ	λ_{max} (nm)	Log ϵ	λ_{max} (nm)	Log ϵ
4'-Benzoylacetanilide	BZ1	293	3.24	298	3.23	297	3.26	303	3.31
4'-Benzoylbenzanilide	BZ2	302	3.40	305	3.35	302	3.38	308	3.42
4'-Benzoyl-N-methylacetanilide	BZ3	260 (272s)	3.20	257	3.10	255 (274s)	3.10	280	3.04
4'-Benzoylisobutyranilide	BZ4	294	3.35	301	3.25	297	3.33	303	3.29
N-(4-Benzoylphenyl)succinimide	BZ5	292	3.32	301	3.23	297	3.30	303	3.29
N-Acetyl-4'-benzoylacetanilide	BZ6	291	3.17	297	3.07	295	3.17	302	3.20
4'-Benzoyl-2-phenylacetanilide	BZ7	294	3.35	300	3.25	296	3.33	303	3.35
N-(4-Benzoylphenyl)maleimide	BZ8	261 (317s)	3.27	304	3.18	260 (326s)	3.19	269 (332s)	3.17
4-Acrylamidobenzophenone	BZ9	300	3.36	306	3.34	304	3.23	309	3.32
4-Naphthylamidobenzophenone	BZ10	303	3.44	304	3.41	303	3.44	308	3.43

DMF, dimethylformamide; s, shoulder.

apparatus equipped with two xenon-filled flash lamps (operated at 10 kV) and a 150 W tungsten–halogen monitoring source. Transient decay profiles were stored using a Gould model 1425 storage oscilloscope. Solutions (5×10^{-5} M) were degassed using white spot nitrogen gas (less than 5 ppm O_2). Flash photolysis measurements were also carried out in the presence of triethylamine at 10^{-3} M concentration.

3. Results and discussion

3.1. Spectroscopic properties

The longest wavelength absorption maxima of the benzophenone compounds are shown in Table 1, together with their corresponding extinction coefficients. With increasing solvent polarity from chloroform to dimethylformamide, the absorption maxima undergo a small red shift of between 5 and 10 nm. The corresponding (logarithm) extinction coefficients range from 3.1 to 3.5 and remain relatively unchanged with respect to the solvent polarity. This main absorption band is typically associated with the benzenoid $\pi\pi^*$ transition and may well have some partial $n\pi^*$ character. The latter,

normally observed for benzophenone [13] at high solute concentrations, was masked for these compounds, except for the 4-N-maleimide derivative (BZ8). The 4-naphthylamidobenzophenone exhibited the highest extinction coefficient of 3.4, which is evidently due to enhanced conjugation and electron donation via the naphthyl ring.

None of the benzophenone compounds examined in this study exhibited significant fluorescence emission ($\phi_f < 10^{-4}$). As expected for most benzophenone derivatives, this is indicative of rapid deactivation of the lowest excited singlet $n\pi^*$ state by efficient intersystem crossing to the lowest lying excited triplet state [14]. The phosphorescence emission spectra of the benzophenones are all highly structured, exhibiting typical aromatic carbonyl symmetry as observed for benzophenone itself (Table 2). However, the bands are markedly red shifted for the substituted compounds BZ1–BZ10. This is associated with substitution in the 4-position, with the amide groups exhibiting electron-donating characteristics. Thus the $n\pi^*$ triplet state is strongly mixed with the lower lying triplet $\pi\pi^*$ state, as shown by the much longer triplet lifetimes and lower emission quantum yields compared with those observed for benzophenone. One interesting anomaly is N-methylacetanilide, whose emission spec-

Table 2

Phosphorescence emission maxima, quantum yields and lifetimes of benzophenones in absolute ethanol

Compound	Code	Emission λ_{max} (nm)	ϕ_p	τ_p (ms)
Benzophenone	BZ0	413, 445, 477, 518(s)	0.74	5.17
4'-Benzoylacetanilide	BZ1	423, 454, 474(s), 489, 580(s)	0.4	21.5
4'-Benzoylbenzanilide	BZ2	430, 461, 488(s), 495, 583(s)	0.35	31.7
4'-Benzoyl-N-methylacetanilide	BZ3	419, 449, 481, 523(s), 584(s)	0.52	7.2
4'-Benzoylisobutyranilide	BZ4	426, 455, 488, 529(s), 582(s)	0.47	48.8
N-(4-Benzoylphenyl)succinimide	BZ5	426, 457, 490	0.51	21.7
N-Acetyl-4'-benzoylacetanilide	BZ6	424, 454, 487, 581(s)	0.31	26.7
4'-Benzoyl-2-phenylacetanilide	BZ7	425, 456, 490(s), 582(s)	0.35	28.5
N-(4-Benzoylphenyl)maleimide	BZ8	424, 457, 489(s), 582(s)	0.24	43.2
4-Acrylamidobenzophenone	BZ9	425, 458, 490(s), 582(s)	0.18	22.83
4-Naphthylamidobenzophenone	BZ10	437(b), 481, 519, 559(s), 583(s)	0.05	75.6

s, shoulder; b, broad.

Table 3
Photoreduction quantum yields of benzophenones in 2-propanol on irradiation at 365 nm

Compound[a]	Code	ϕ_r	ϕ_r + TEA[b]
4'-Benzoylacetanilide	BZ1	0.11	0.22
4'-Benzoylbenzanilide	BZ2	0.04	0.05
4'-Benzoyl-N-methylacetanilide	BZ3	0.01	0.01
4'-Benzoylisobutyranilide	BZ4	0.09	0.12
N-(4-Benzoylphenyl)succinimide	BZ5	0.09	0.2
N-Acetyl-4'-benzoylacetanilide	BZ6	0.39	0.5
4'-Benzoyl-2-phenylacetanilide	BZ7	0.15	0.21
N-(4-Benzoylphenyl)maleimide	BZ8	0.02	0.04
4-Acrylamidobenzophenone	BZ9	0.01	0.06
4-Naphthylamidobenzophenone	BZ10	0.009	0.06

[a]10^{-5} M. [b]TEA, 10^{-3} M triethylamine.

trum is not significantly shifted from that of benzophenone and whose emission lifetime is only about 2 ms longer. Furthermore, this compound exhibits the highest emission quantum yield of the ten compounds studied and its absorption maximum (Table 1) is significantly blue shifted in all solvents relative to the maxima of the other compounds. In this case, electron donation into the ring system is restricted in some way. The only possible explanation is that the methyl group twists the lone pair electrons on the nitrogen atom out of plane with the benzene ring, thus minimizing such an interaction. The excited states of benzophenone are normally insensitive to solvent polarity changes, and recent evidence has indicated that the photoreduction abilities of excited triplet states are due to the ability of the excited triplet state of the ketone to form an associated complex with the solvent [15].

3.2. Photoreduction

The photoreduction quantum yields of the benzophenones are interesting (Table 3), particularly when compared with that of benzophenone. Benzophenone exhibits a quantum yield in 2-propanol of unity [14]. All the substituted compounds studied here exhibit significantly lower values. Hence their ability to undergo direct hydrogen atom abstraction is

markedly reduced. This is no doubt associated with the strong $\pi\pi^*$ character of the lowest excited triplet state. The addition of triethylamine enhances the rate of photoreduction, although not significantly. This may be due to the competitive nature of the interaction or the association of the excited triplet states of the benzophenones with propanol. In this case, the role of electron transfer may be implicated possibly through a simple mechanism of intermolecular interaction.

3.3. Rates of photopolymerization

The rates of photoinduced polymerization by the different benzophenones are compared in Table 4 using the technique of RTIR spectroscopy. RTIR analysis was undertaken at two amine concentrations of 1% and 5% w/w EDB. At 1% w/w amine concentration, all the compounds, except BZ4, BZ7, BZ9 and BZ10, exhibit a higher activity than that of benzophenone. Again compound BZ10 exhibits the lowest overall photoactivity. At 5% w/w concentration, all the compounds, except BZ10, exhibit a higher photoinitiation activity than that of benzophenone. In both cases, compound BZ2 exhibits the highest overall activity. These data are pictorially represented in Fig. 1 and Fig. 2 for ease of comparison. The trends show that benzophenone BZ10 exhibits the lowest activity in all cases, followed by compound BZ9. Benzophenone BZ7 shows a proportional increase in R_p to the amount of amine

Table 4
Rates of polymerization by benzophenones from RTIR (mol $dm^{-3} s^{-1}$)

Compound	Code	RTFTIR (R_p)[b]	RTFTIR (R_p)[c]
Benzophenone	BZ0	1.61	2.19
4'-Benzoylacetanilide	BZ1	3.03	5.53
4'-Benzoylbenzanilide	BZ2	3.95	6.52
4'-Benzoyl-N-methylacetanilide	BZ3	2.01	4.75
4'-Benzoylisobutyranilide	BZ4	1.07	5.04
N-(4-Benzoylphenyl)succinimide	BZ5	2.67	4.1
N-Acetyl-4'-benzoylacetanilide	BZ6	2.28	4.77
4'-Benzoyl-2-phenylacetanilide	BZ7	0.86	5.08
N-(4-Benzoylphenyl)maleimide	BZ8	2.41	6.21
4-Acrylamidobenzophenone	BZ9	1.37	3.4
4-Naphthylamidobenzophenone	BZ10	0.71	1.89

[a]Diethylethanolamine (10^{-3} M) in butyl acrylate. [b]1% w/w EDB in Sartomer 348. [c]5% w/w EDB in Sartomer 348.
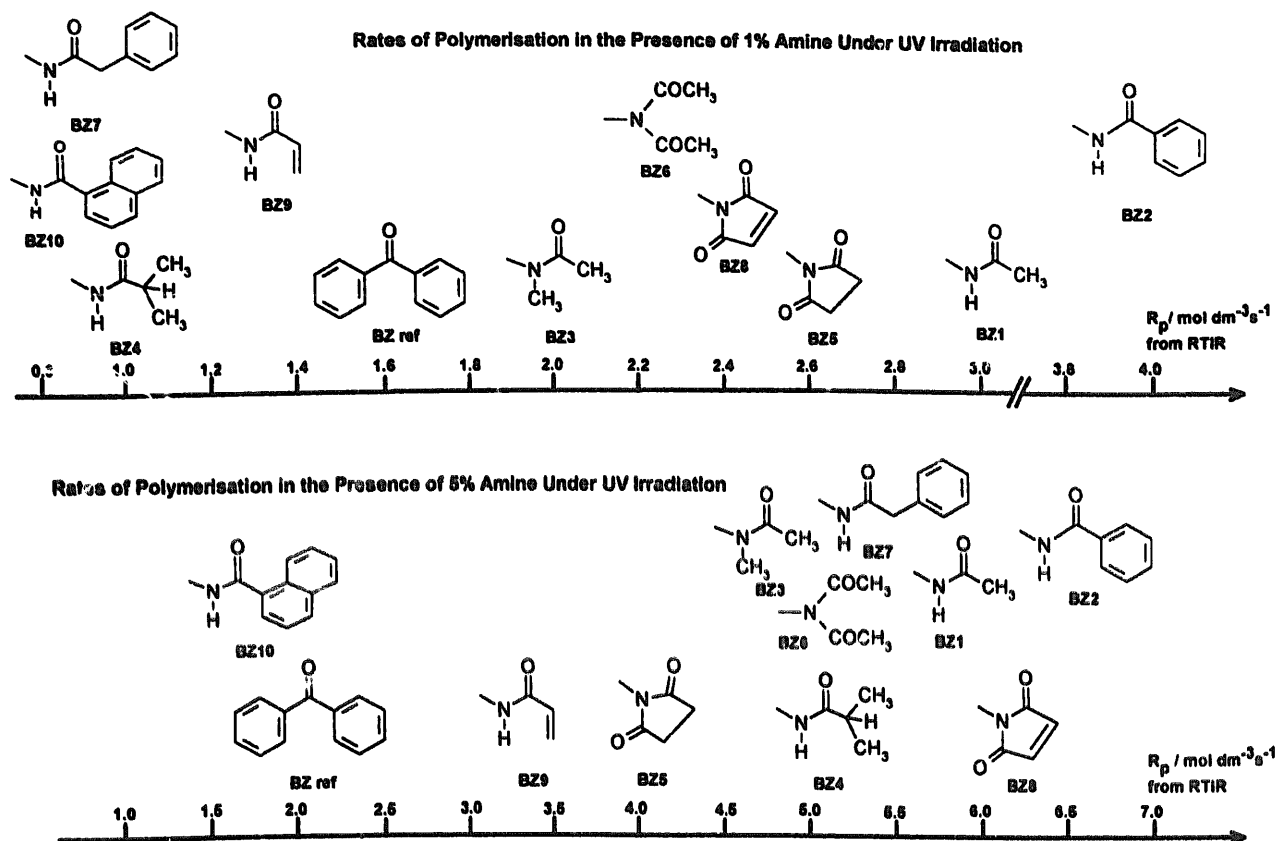
Fig. 1. Comparison of the photoinitiation activities of benzophenones using RTIR at 1% and 5% w/w amine concentration.

co-synergist added to the system, i.e. R_p increases by a factor of five when 5% amine is added.

3.4. Microsecond flash photolysis

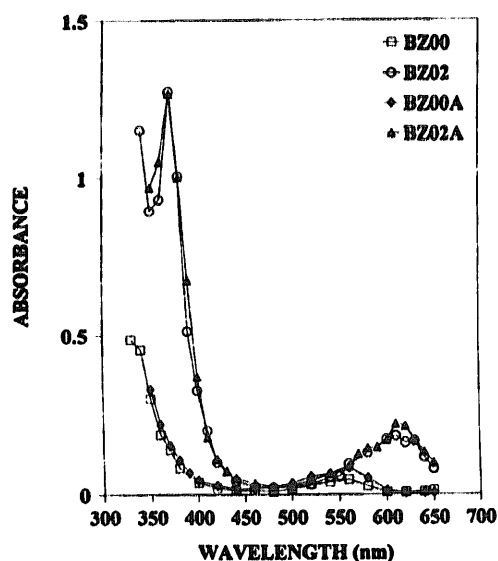The end-of-pulse transient absorption maxima of the benzophenones in anaerobic 2-propanol are compared in Table 5,

Fig. 2. End-of-pulse transient absorption maxima in anaerobic 2-propanol (5×10^{-5} M) of benzophenone and benzophenone compound BZ2 in the absence ($\square$, $\bigcirc$) and presence ($\blacklozenge$, $\blacktriangle$) of triethylamine (10^{-3} M).

together with their respective absorbances. All the spectra have two distinct absorption maxima at 300–350 nm and 560–620 nm. The spectrum for benzophenone is normally assigned to the ketyl radical, formed by hydrogen atom abstraction by the excited triplet state from 2-propanol. In the presence of triethylamine, the long-wavelength band is only slightly red shifted by 5 nm. This shift may be assigned to the radical anion species, formed by electron transfer, which is known to exhibit an absorption spectrum close to that of the ketyl radical [5,14]. However, the most significant feature of these data is the marked increase in absorbance for both maxima for all the substituted benzophenones BZ1–BZ10 compared with the values observed for benzophenone. Furthermore, there is a notable marked red shift in the absorption wavelength maxima of both bands. An example of this effect is illustrated by the absorption spectra in Fig. 2 for benzophenone and compound BZ2. It is interesting to note that the presence of triethylamine has no significant effect on either of the absorption maxima. Oxygen has a marked quenching effect on the transient absorbance, implicating the triplet state as the active precursor.

Thus the higher photoactivity of the benzophenones is reflected in their greater radical formation as shown by flash photolysis. In this case, ketyl radical formation appears to be unlikely, particularly in view of the low photoreduction quantum yields observed (Table 3). The red spectral shift and enhanced absorbance must therefore be assigned to the formation of the radical anion species formed by electron trans-

Table 5
End-of-pulse transient absorption maxima of benzophenones in anaerobic 2-propanol (5×10^{-5} M)

Compound	Code	No amine λ_{max} (nm)	ABS	Amine λ_{max} (nm)	ABS
Benzophenone	BZ0	330; 560	0.48; 0.05	330; 565	0.48; 0.08
4'-Benzoylacetanilide	BZ1	350; 590	1.4; 0.18	350; 590	1.43; 0.18
4'-Benzoylbenzanilide	BZ2	375; 620	1.35; 0.18	375; 620	1.35; 0.20
4'-Benzoyl-N-methylacetanilide	BZ3	340; 565	0.95; 0.08	340; 565	0.95; 0.08
4'-Benzoylisobutyranilide	BZ4	350; 590	1.4; 0.10	350; 590	1.3; 0.10
N-(4-Benzoylphenyl)succinimide	BZ5	350; 580	1.1; 0.08	350; 580	0.95; 0.08
N-Acetyl-4'-benzoylacetanilide	BZ6	350; 580	1.3; 0.13	350; 580	1.25; 0.13
4'-Benzoyl-2-phenylacetanilide	BZ7	360; 595	1.4; 0.15	350; 580	1.6; 0.13
N-(4-Benzoylphenyl)maleimide	BZ8	340; 580	1.6; 0.15	340; 580	0.75; 0.07
4-Acrylamidobenzophenone	BZ9	330; 580	0.6; 0.06	330; 580	0.6; 0.06
4-Naphthylamidobenzophenone	BZ10	330; 600	0.75; 0.06	330; 580	0.85; 0.06

Amine, 10^{-3} M triethylamine.

fer. The addition of triethylamine has no significant effect on the transient absorption maxima. It is interesting to note that, of the ten benzophenone compounds, the least photoactive are compounds BZ9 and BZ10 and this is reflected in their significantly lower transient absorbances.

4. Conclusions

The spectroscopic and photoinduced polymerization activities of ten novel 4-substituted amido and imido derivatives of benzophenone have been examined. Their lowest excited triplet states appear to exhibit strongly mixed $n\pi/\pi\pi^*$ characteristics. From photoreduction and flash photolysis data, it can be concluded that they undergo photoreaction via an electron transfer process to produce the active radical anion species. The relative photopolymerization activities appear to be reflected in the formation of the latter species.

Acknowledgements

References

[1] N.S. Allen, G. Pullen, M. Shah, M. Edge, D. Holdsworth, I. Weddell, R. Swart, C. Peinado and F. Catalina, Polymer, 36 (1995) 4665.

[2] N.S. Allen, J.P. Hurley, D. Bannister and G.W. Follows, Eur. Polym. J., 28 (1992) 1309.

[3] N.S. Allen, J.P. Hurley, D. Bannister, G.W. Follows, S. Navaratnam and B.J. Parsons, J. Photochem. Photobiol. A: Chem., 68 (1992) 213.

[4] N.S. Allen, J.P. Hurley, A. Rahman, G.W. Follows and I. Weddell, Eur. Polym. J., 29 (1993) 1155.

[5] N.S. Allen, E. Lam, J.L. Kotecha, W.A. Green, A. Timms, S. Navaratnma and B.J. Parsons, J. Photochem. Photobiol. A: Chem., 54 (1990) 367.

[6] N.S. Allen, S.J. Hardy, A.F. Jacobine, D.M. Glaser, B. Yang, D. Wolf, F. Catalina, S. Navaratnam and B.J. Parsons, J. Appl. Polym. Sci., 42 (1991) 1169.

[7] N.S. Allen, F. Catalina, R. Sastre, J.L. Mateo, P.N. Green and W.A. Green, J. Photochem. Photobiol. A: Chem., 44 (1988) 171.

[8] N.S. Allen, D. Mallon, A. Timms, A.W. Green and F. Catalina, Eur. Polym. J., 29 (1993) 533.

[9] J.N. Demas and G.A. Crosby, J. Phys. Chem., 75 (1971) 991.

[10] H.G. Heller and J.R. Lanagan, J. Chem. Soc., Perkin Trans. I, (1981) 341.

[11] H.G. Heller, British Patent 7/1464603.

[12] N.S. Allen, F. Catalina, C. Peinado, R. Sastre, J.L. Mateo and P.N. Green, Eur. Polym. J., 23 (1987) 985.

[13] R.S. Becker, Mol. Spectrosc., 3 (1959) 1.

[14] A.M. Braun, M.T. Maurette and E. Oliveros, Photochemical Technology, Wiley, New York, 1991.

[15] J.P. Fouassier and J.F. Rabek, Radiation Curing in Polymer Science and Technology, Vol. 1, Elsevier, 1993, Chapter 1.