

Photochemistry and Photopolymerization Activity of Perester Derivatives of Benzophenone

N. S. ALLEN,^{1*} S. J. HARDY,¹ A. F. JACOBINE,² D. M. GLASER,² B. YANG,²
D. WOLF,² F. CATALINA,³ S. NAVARATNAM⁴ and B. J. PARSONS⁴

¹Department of Chemistry, Faculty of Science and Engineering, Manchester Polytechnic, Manchester M1 5GD, United Kingdom, ²Loctite Company, 705 North Mountain Road, Newington, Connecticut, ³Instituto de Ciencia y Tecnologia de Polimeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain, ⁴School of Natural Sciences, The North East Wales Institute of Higher Education, Kelsterton College, Deeside, Clwydd CH5 4BR, N. Wales, United Kingdom

SYNOPSIS

The spectroscopic properties and photopolymerization activities of a mono- and tetraperester derivative of benzophenone are examined and compared with those of benzophenone. Their photopolymerization activity in methyl methacrylate (MMA) and an ethoxylated bis-phenol-A diacrylate have been studied using a combination of gel permeation chromatography (GPC), and real time Fourier transform infrared spectroscopy (RTFTIR) as well as the commercial pendulum hardness test. Using GPC analysis on the poly(methyl methacrylate) samples the *tetra-t*-butyl perester derivative of benzophenone is found to give a higher weight average (M_w) and number average (M_n) molecular weight polymer than that produced using the mono perester. For the two peresters of benzophenone photopolymerization efficiency using real time FTIR increases with increasing initiator concentration, and no self-termination is observed up to 0.75% w/w concentration with the mono perester derivative being the more efficient initiator. Similar results were obtained using the commercial pendulum hardness tester with a triacrylate/epoxyurethane acrylate resin with benzophenone exhibiting the lowest activity. Photopolymerization activities of the initiators correlate well with their spectroscopic properties. The phosphorescence quantum yield is higher for the monopерester than the tetrapерester derivative and is consistent with a shorter lifetime and lower photolysis quantum yields in 2-propanol. Compared with benzophenone, phosphorescence analysis indicates that the perester groups impart a degree of charge-transfer content to the molecule which is consistent with the degree of substitution. Ketyl radical formation on microsecond flash photolysis follows the order benzophenone > mono- > tetrapерester derivative and is consistent with the phosphorescence quantum yields. On nanosecond laser flash photolysis in nitrogen-saturated acetonitrile, triplet-triplet absorption is extremely weak for both the perester derivatives, being stronger for the monopерester.

INTRODUCTION

We recently examined the photochemistry and photopolymerization activity of *t*-butylperester derivatives of fluorenone.^{1,2} These compounds were found to initiate photopolymerization through homolytic scission at the peroxy link to give aryloxy and *t*-butyloxy radicals. Analysis of the polymer by spec-

troscopic methods showed that the former species was responsible for initiating free radical polymerization. Detailed studies on the photopolymerization activity of compounds of this type have shown that their efficiency depends on the absorption characteristics of the associated chromophore,³⁻⁵ and this was confirmed in our previous study.¹ Using second-order derivative UV absorption spectroscopy, poly(methyl methacrylate) samples prepared using the *t*-butyl perester derivatives of fluorenone were found to contain residual photoinitiator fragments. Further studies using laser flash photolysis showed

* To whom correspondence should be addressed.

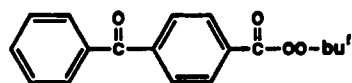
a correlation between the bulk photopolymerization activities of the fluorenone initiators and their triplet absorptions and lifetimes.²

In this paper we have extended our previous work on fluorenones to a detailed spectroscopic and photopolymerization study of the mono- and tetra-ester derivatives of benzophenone in relation to that of benzophenone itself. Here absorption spectra, phosphorescence properties, free radical behavior arising from microsecond flash photolysis, and triplet formation arising from nanosecond flash photolysis of these molecules are related to their photopolymerization activity using real time Fourier transform infrared spectroscopy and pendulum hardness testing. Earlier work¹ on the photopolymerization of methyl methacrylate has also been extended here to include a GPC study on the polymer samples which will provide valuable information on polydispersities and molecular weight distributions. A comparison of these polymerization methodologies is important from a theoretical and commercial point of view as well as for providing an understanding of the relationship among initiator structure, concentration, and photopolymerization activity.

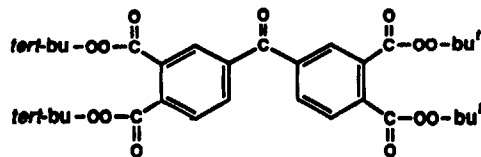
EXPERIMENTAL

Materials

The mono and tetra tertbutylperoxycarbonylbenzophenones of the Structures I and II were supplied by the Loctite Corp.:



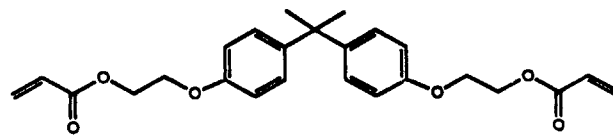
Structure I



Structure II

The latter is originally of the Nippon Fat Co. (Japan⁶). All compounds were chromatographically pure. The acetonitrile, 2-propanol, chloroform, hexane, and the methylmethacrylate monomer, all "Analar grade," were obtained from the Aldrich Chemical Co. (U.K.) and were used as supplied. The monomer, Sartomer 349 (Sartomer Co., Pennsylv-

ania) is an ethoxylated bisphenol-A diacrylate of Structure III:



Structure III

The diluent monomer, trimethylolpropane triacrylate (Photomer 4094), and epoxyurethane acrylate prepolymer (Photomer 3104) were obtained from Harcros Chemicals Ltd. (Manchester, U.K.).

Gel Permeation Chromatography

Molecular weights were obtained using a Perkin-Elmer HPLC apparatus utilizing a GPC column, Series 3B pump, and Waters 410 refractive index detector calibrated via a set of poly(methyl methacrylate) standards in tetrahydrofuran (0.2% w/w). Nelson 20900 GPC analytical software was used to evaluate the data.

Photopolymerization Methods

Polymer samples for GPC were obtained by irradiating a quartz cell apparatus containing 10 cm³ of 50 : 50 v/v ethyl acetate and methyl methacrylate and 2.5×10^{-3} M initiator for 1 hour. The light source used was a Thorn 100-W tungsten-halogen lamp set at a distance of 10 cm, and the reaction mixture was continually bubbled with white spot nitrogen gas. After irradiation the reaction mixture was poured into methanol for precipitation, and this was followed by centrifuging, filtering, and drying to constant weight in a hot air oven at 60°C for 2 h.

Real Time FTIR

Real time Fourier transform infrared analysis⁷ was carried out using a Digilab 60 FTIR system on samples of Sartomer 349 containing the initiators coated onto salt discs with a uniform thickness of 30–50 μ m. Each coated disc was placed against an aluminium lap which was set on a Harrick retromirror and focus transfer accessory for external reflection. The sample was irradiated directly with a very high intensity IR filtered UV energy source through a flexible optic wand (UVEX Model SCU 110 portable

UV spot curing system). The UV irradiance at the position of the sample was measured using an EFOS UVAR radiometer and was of the order of 200 mW/cm² between 300 and 400 nm. Spectra were scanned every 1.008 s during irradiation, and the lamp was triggered at regular intervals using a foot-operated switch. A delay time of 15 s was allowed before the lamp was triggered so that the first few spectra collected were representative of the preirradiation unsaturation, i.e., t_0 . The infrared chamber was nitrogen-purged in order to avoid oxygen inhibition of the cure. The number of double bonds remaining in the sample exposed to the UV irradiation is shown by the intensity of the peak at 1634 cm⁻¹, corresponding to the C=C stretching of the vinyl group, and 810 cm⁻¹, corresponding to the C-H deformation mode of the vinyl group. We have chosen the 810 cm⁻¹ absorption because (1) this absorption is stronger than that at 1634 cm⁻¹ and therefore will provide less experimental deviation and (2) no significant interference was observed for the presently used UV coating formulations as compared to the spectrum of the pure monomer. Because the intensity of the IR spectra is determined by the sample thickness and contact effectiveness with the salt disc, any deformation of the film, such as shrinkage, during the cure process may affect the absorption intensity; therefore, a peak at 2875 cm⁻¹ corresponding to the C-H stretch, was used as an internal standard for our degree of cure and reaction rate calculations. After a 10-min infrared run, a total of 558 scans were obtained. Spectra were then co-added for every six spectra with a 15-s interval for each set. This produced a total of 41 averaged infrared profiles over the time period. The degree of inversion was directly related to the decrease of the 810 cm⁻¹ absorption in the infrared spectra as follows:

$$\text{degree of conversion} = \frac{A_0 - A_t \times 100\%}{A_0}$$

where A_0 = area of peak from 800–820 cm⁻¹ of the first scan set

A_t = area of the same peak of the scan set at time t .

The rate of polymerization (R_p) is given by

$$R_p = [M](A_{t_1} - A_{t_2})(t_1 - t_2) \times A_0$$

where A_0 , A_{t_1} and A_{t_2} are the areas under the peaks 800–820 cm⁻¹ at times t_0 , t_1 , and t_2 .

M = original concentration of acrylic double bonds

= density/ $M_R \times 2$ (as diacrylate)

= (1127.5/424.5) $\times 2 = 5.312 M L^{-1}$

No postirradiation curing was observed under the experimental conditions used here for Sartomer 349. The infrared absorption band at 810 cm⁻¹ remained constant for periods of up to 16 h after various irradiation periods.

Pendulum Hardness

The photoinitiators were dissolved in a 50/50 v/v mixture of commercial resins, Photomer 4094 (trimethylolpropane triacrylate) and Photomer 3104 (epoxyurethane acrylate), at 0.1% w/w concentration and cured as a thin coating 12 μm thick for various periods of time under a 100-W high pressure mercury lamp on glass slides. The hardness of the coatings was measured using a pendulum hardness instrument from Sheenan Instruments Ltd., London.

Photoreduction Quantum Yields

Absolute quantum yields of photoreduction (ϕ_r) for the two perester compounds were determined in 2-propanol at $5 \times 10^{-4} M$. An irradiation wavelength of 365 nm was selected from a Philips high pressure mercury lamp (HB-CS 500 W/2) and a Kratos GM 252 monochromator. Sample cells were thermostatted at 30°C, and the solutions were deoxygenated using white spot nitrogen gas. The absorbed light intensity was measured using an International Light Model 700 radiometer previously calibrated by Aberchrome 540 actinometry.^{8,9} The photolysis of the compounds was monitored by measuring the change in their absorption maxima.

Absorption and Phosphorescence Measurements

Absorption spectra were obtained using a Perkin-Elmer Lambda 7 absorption spectrometer while phosphorescence measurements were obtained using a Perkin-Elmer Model LS-5 luminescence spectrometer at 77 K (using liquid nitrogen as the coolant). Quantum yields were obtained by comparison with benzophenone as the standard and assuming a quantum yield of 0.74 in ethanol.¹⁰

Table I Molecular Weight Averages of PMMA Samples Obtained from 60 Min Irradiation of a 50% MMA/Ethyl Acetate Solution Containing 2.5×10^{-3} M Initiator in the Absence and Presence of 2.5×10^{-3} M *N*-Methyldiethanolamine

Benzophenone	M_w	M_n	M_w/M_n	M_z
Mono	80,498	52,510	1.533	115,896
	73,483	48,363	1.519	104,944
Tetra	94,738	57,504	1.647	143,465
	82,764	51,143	1.618	122,917

Flash Photolysis

End-of-pulse transient absorption spectra were recorded using a microsecond kinetic flash photolysis apparatus equipped with two 16 kV 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 were degassed using white-spot nitrogen gas (> 5 ppm oxygen). Laser flash photolysis experiments were carried out using a frequency tripled neodymium laser (J. K. Lasers, Ltd.), which delivered 15-ns pulses of 355 nm radiation of 50–60 mJ energy. All solutions were prepared to have an absorbance of 1.0 at the laser excitation wavelength. Transient absorption changes were measured by illuminating the 1 cm path length quartz reaction cell with light from a pulsed xenon lamp. Wavelength selection was achieved with a diffraction grating high irradiance monochromator with a 5 nm bandwidth. Kinetic changes in the light signal at preselected wavelengths were detected and amplified using a photomultiplier (RCA IP28A) prior to collection by a storage oscilloscope.

Table II Real Time Fourier Transform Infrared Studies on the Benzophenone Initiators in Ethoxylated Bisphenol A Diacrylate

Compound % (w/w)	Degree of Cure at 9.25 min	Max R_p (mol/L/s)	Time of Max R_p (min)	Degree of Cure at 0.5 min (%)	
Mono	0.26	57.27	0.017	2.01	0.11
	0.50	64.31	0.043	0.51	8.83
	0.76	80.40	0.168	0.51	48.48
Tetra	0.24	39.57	0.051	0.51	14.49
	0.25	60.25	0.065	0.50	16.29
	0.74	64.14	0.031	0.51	10.10

RESULTS

GPC Analysis

Molecular weight averages of the poly(methyl methacrylate) (PMMA) samples produced in the photopolymerization of a 50% w/w MMA/ethyl acetate solution initiated by the two perester initiators are shown in Table I. The tetraperester derivative produced a polymer which had higher number and weight average molecular weight values than that produced by the monoprester. Since the weight average molecular weight is very sensitive to the presence of high molecular mass molecules, this implies that the polymer samples prepared with the tetraprester had a larger amount of such molecules than the polymer systems prepared in the case of the monoprester. The M_w/M_n values for the polymer prepared using the tetraprester were also much higher, showing a greater inhomogeneity in the polymer chains. The number and weight average molecular weight values of the PMMA samples prepared using the benzophenone derivatives were higher than those prepared using the mono and bis-*t*-butylperester fluorenones examined previously.¹¹

Real Time Fourier Transform Infrared Spectroscopy

This is a relatively new technique first proposed by Decker and Moussa.⁷ Unlike previous steady-state infrared analysis, this method allows the cure reaction to be monitored continuously and more rapidly in real time with no significant postirradiation errors. During irradiation both the unsaturation bands at 810 and 990 cm^{-1} gradually decrease with increasing exposure time. Of these two bands the former gave the most easily measurable changes for

quantification of the rate of photocuring. From this information, plots of percentage conversion versus exposure time were obtained from which rates of photopolymerization were determined. All the percentage conversion curves exhibit a plateau due to a reduction in the rate of photopolymerization caused by network formation and consequent reduction in chain mobility. This rate at which the plateau occurs is related to the cure efficiency. Table II displays the degree of cure at the end of a run, the maximum rate, and the time it occurs during a run and finally the cure achieved after 0.5 min irradiation time.

Hardness Testing

In this work 0.1% w/w of the photoinitiators were used in a 50 : 50 v/v of Photomers 4094 and 3104 supplied by Harcros Chemicals Ltd. (U.K.). The efficiency of both of the terbutylperesters was compared with the efficiency of benzophenone. The results in Figure 1 show plots of pendulum hardness versus UV curing time in minutes. From these results it is seen that the curing efficiency of the initiators follows the order monoperester > tetra-perester > benzophenone. Thus, the results on commer-

cial photocuring correlate with those obtained by other more scientific methods.

Spectroscopic Properties

The absorption maxima and molar absorptivities (ϵ) of the mono and tetra-perester derivatives of benzophenone are compared with those of benzophenone itself in Table III in three different solvent systems. All three exhibit absorption maxima about 250 nm with $\log \epsilon$ values of ca. 4.0. Long wavelength maxima are also observed at and above 300 nm with lower molar absorptivities due to the $n-\pi$ transition of the ketone group. Of the three initiators the monoperester appeared to exhibit the longest wavelength absorption, and this may account, in part, for its greater photoinitiation activity. Neither of the two perester derivatives exhibited any fluorescence emission but both gave phosphorescence with the same carbonyl symmetry as that of benzophenone. The emission maxima, quantum yields, and lifetimes are compared in Table IV with those for benzophenone. Substitution of the perester groups significantly reduces the phosphorescence quantum yield of the benzophenone, and there is a consistent increase in the emission lifetime.

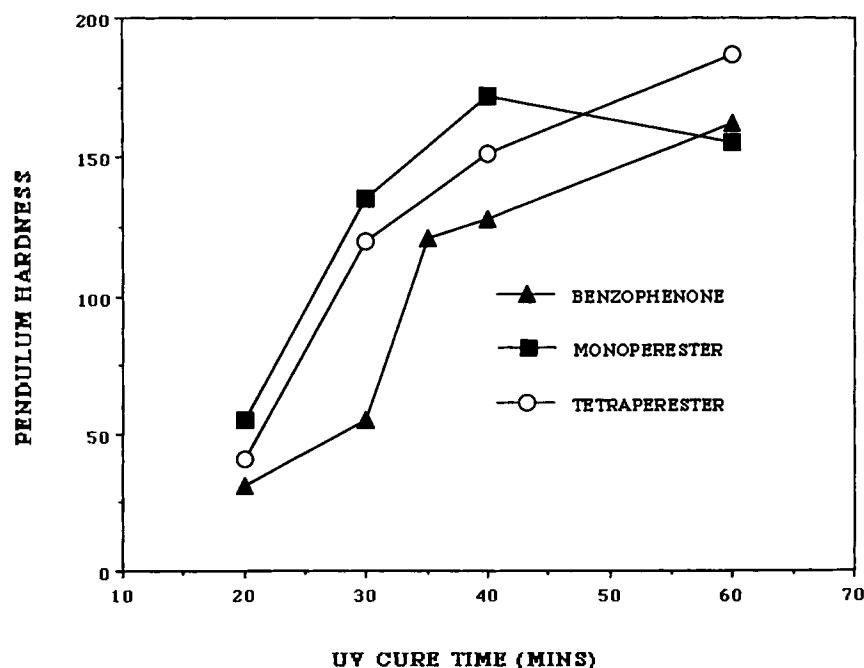


Figure 1 Pendulum hardness vs. UV curing time (min) of a 50/50 v/v mixture of Photomer 4094 and Photomer 3104 (50 μ m thick) containing 0.1% w/w of (▲) benzophenone, (■) monoperester, and (○) tetra-perester derivatives of benzophenone on irradiation with a 100-W high pressure Hg lamp.

Table III Absorption Characteristics of Benzophenone and the Perester Derivatives

Compound	Hexane		Chloroform		2-Propanol	
	λ (nm)	$\log \epsilon$	λ (nm)	$\log \epsilon$	λ (nm)	$\log \epsilon$
Benzophenone	247	4.39	253	4.28	252	4.33
	282	3.55				
	347	2.20	338	2.23	341	2.61
Monoperester	253	4.37	258	4.39	256	4.35
	349	2.20	340	2.30	352	2.26
Tetraperester	252	4.14	257	4.09	249	4.09
	299	3.40	350	2.08	300	3.11

End-of-pulse transient absorption spectra of the mono and tetra perester derivatives of benzophenone produced on conventional microsecond flash photolysis in nitrogen saturated 2-propanol are compared with that of benzophenone itself in Figure 2. Transient absorption maxima are observed at 340 and 560 nm for the benzophenone and are assigned to that of the ketyl radical formed by the photoexcited triplet state abstracting a hydrogen atom from the solvent.^{12,13} Similar absorption maxima are observed for the mono and tetra perester derivatives apart from the longer wavelength band which is redshifted to 575 and 660 nm, respectively. This is consistent with the degree of substitution in the benzophenone chromophore and hence related to the charge-transfer content of the molecules. However, some degree of radical anion formation formed through electron abstraction may also be possible.

End-of-pulse transient absorption spectra of benzophenone and the mono and tetra perester derivatives of benzophenone in nitrogen saturated acetonitrile on nanosecond laser flash photolysis are shown in Figures 3, 4, and 5, respectively, at two different time delays. All three transients exhibit absorption maxima at 310 nm whereas that for the benzophenone has an additional long wavelength absorption at 530 nm and those of the perester derivatives have a maximum at 560 nm. The transients are effectively quenched by oxygen and, in nonhy-

drogen atom donating acetonitrile are assigned to a triplet-triplet absorption.¹⁴ Finally, in oxygen-saturated acetonitrile a long-lived transient absorption is produced for both the perester derivatives on nanosecond flash photolysis with absorption maxima at 320 and a broad weaker maximum between 400 and 600 nm (Fig. 6).

DISCUSSION

It is interesting to note that the M_w/M_n values for the polymer prepared using the tetraperester derivative as photoinitiator were much higher. This suggests that because of the greater number of tetraperester groups the initiator may be involved in some way in the initiation process, giving rise to different types of linkages and hence greater polydispersity. Furthermore, the higher number and weight average molecular weights of polymer samples prepared using the benzophenone derivatives may well be associated with the lower photolysis and triplet quantum yields of these two benzophenone initiators reported below giving rise to fewer free radical sites for self-termination. From the FTIR data the rate of photocuring of the two benzophenone derivatives was found to be highly dependent upon the concentration of the initiator (Table II). From the data it is noted that the mono-*t*-butylperester derivative is

Table IV Phosphorescence Characteristics of Benzophenone and the Perester Derivatives

Compound	Emission Wavelength (nm)	Quantum Yield ϕ_p	Lifetime (ms)
Benzophenone	417, 446, 478	0.74	6.40
Monoperester	417, 446, 478	0.08	7.64
Tetraperester	417, 446, 478	0.03	8.95

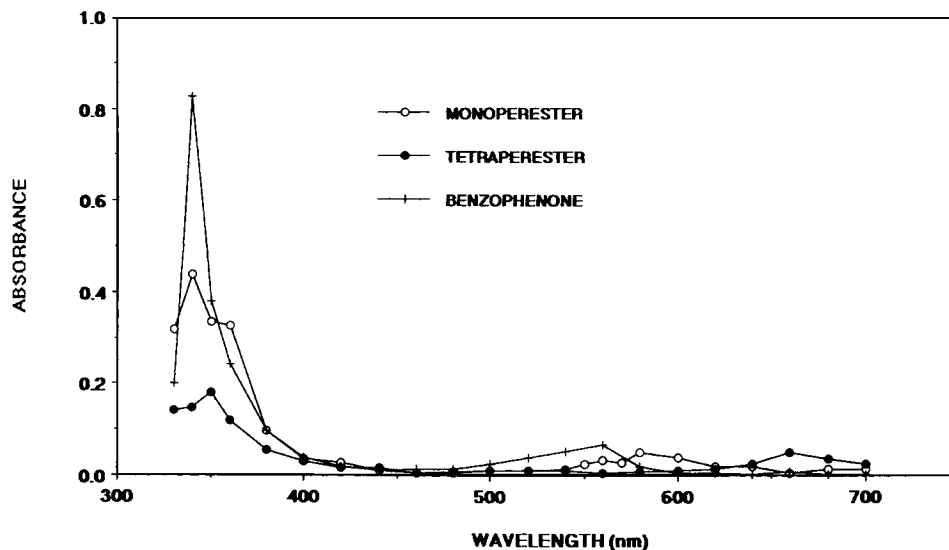


Figure 2 End-of-pulse transient absorption spectra in nitrogen-saturated 2-propanol of (+) benzophenone, (O) monoperester, and (●) tetra-perester derivatives of benzophenone ($10^{-5} M$) produced on microsecond flash photolysis.

the more effective photoinitiator, and this was also reflected in the hardness testing results. This may be associated with the fact that the *tetra-t*-butyl-perester derivative gives rise to more aryloxy radicals which may undergo self termination reactions.

The lower quantum yield and longer emission lifetime of the tetra-perester derivative is clearly reflected in its lower photoinitiation activity compared with that of the monoperester derivative and is evidently due to a greater degree of charge-transfer

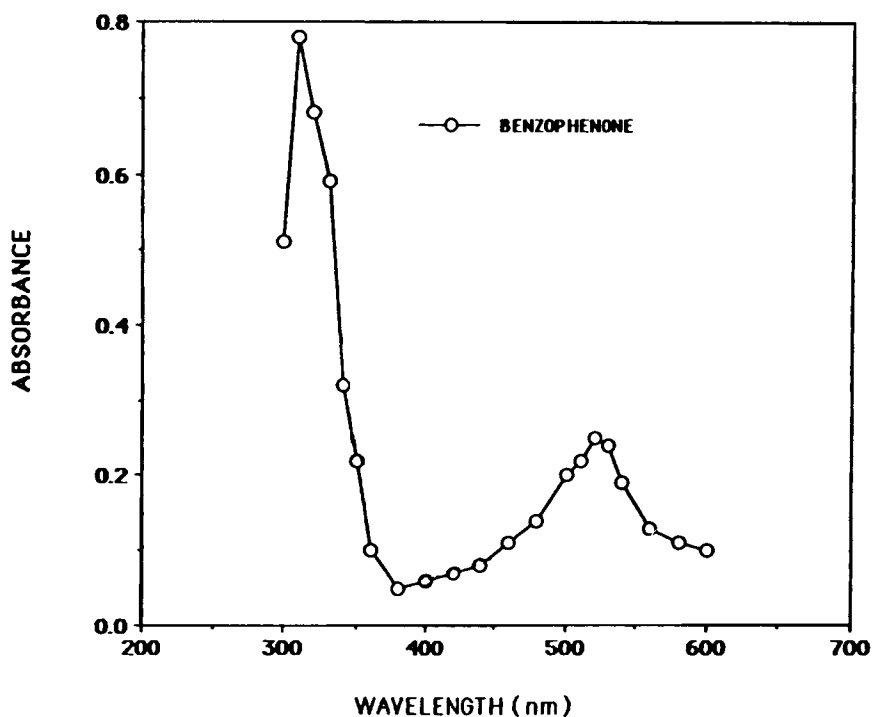


Figure 3 End-of-pulse transient absorption spectrum in nitrogen-saturated acetonitrile of benzophenone ($5 \times 10^{-3} M$) produced on nanosecond laser flash photolysis.

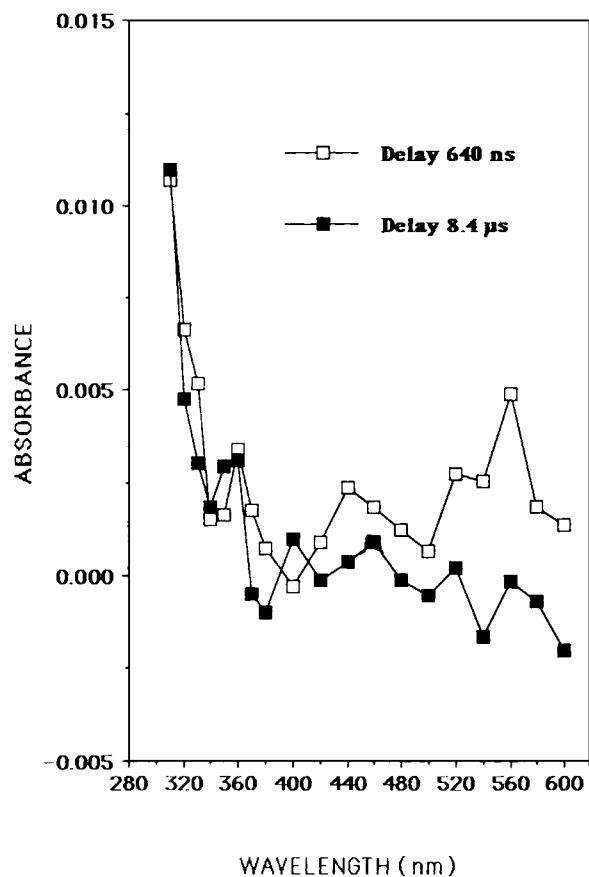


Figure 4 End-of-pulse transient absorption spectrum in nitrogen-saturated acetonitrile of the monoperester derivative of benzophenone after (□) 640 ns and (■) 8.4 μ s delay (5×10^{-3} M) produced on nanosecond laser flash photolysis.

content in its lowest excited triplet state. However, the photoinitiation activity of perester derivatives is associated with the homolysis of the *t*-butylperester group to give benzoyloxy and *t*-butyloxy groups.^{1,2} The former are then believed to initiate polymerization. Indeed differences in photoactivity are evidenced by the differences in the photolysis quantum yields of the two peresters studied here. Thus, although the monoperester was found to have a quantum yield of photolysis of 0.092 in 2-propanol, the tetraester value was found to be 0.19. Both values are much lower than the standard photoreduction quantum yield of benzophenone of 1.0. It is evident therefore that the photopolymerization activity of the *t*-butylperester derivatives is associated with homolysis of the perester groups and not hydrogen atom abstraction by the photoexcited triplet state of the aromatic ketone group, as would be expected for benzophenone. The lower activity of the tetra-

perester derivative may well be associated with the greater number of perester groups, and hence there is a greater possibility of self termination reactions taking place. On the other hand, the higher number and weight average molecular weight polymer obtained with this initiator may be due to termination reactions, resulting in the benzophenone chromophore being built-in to the polymer backbone. This was confirmed in our previous study on second-order derivative UV spectroscopic analysis.¹

It is interesting to note that the ketyl radical intensity on conventional flash photolysis is consistent with the quantum yields of phosphorescence shown in Table IV for the two perester derivatives and that photopolymerization efficiency is greater for the monoperester than the tetraester derivative. As found earlier for the fluorenone derivatives, no evidence could be found for the formation of a ben-

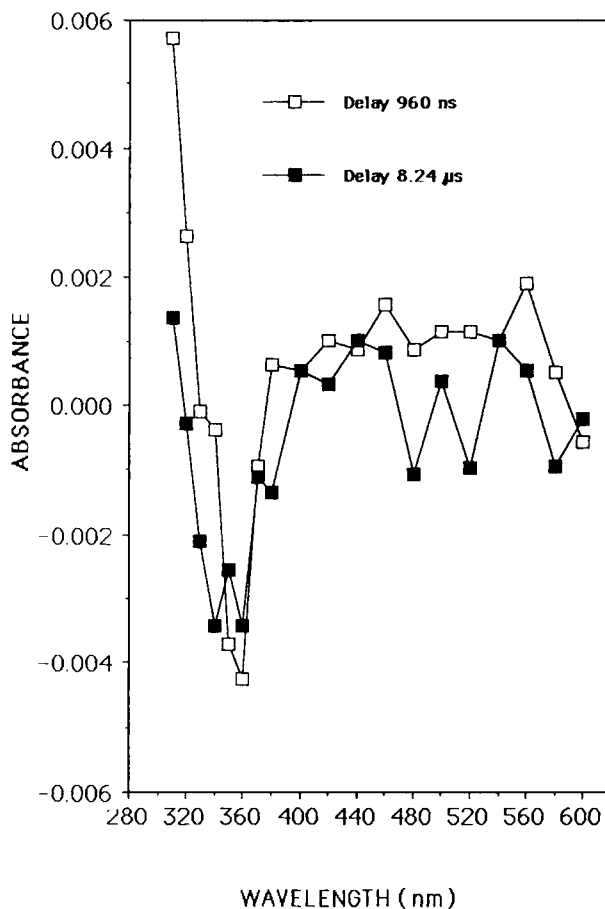
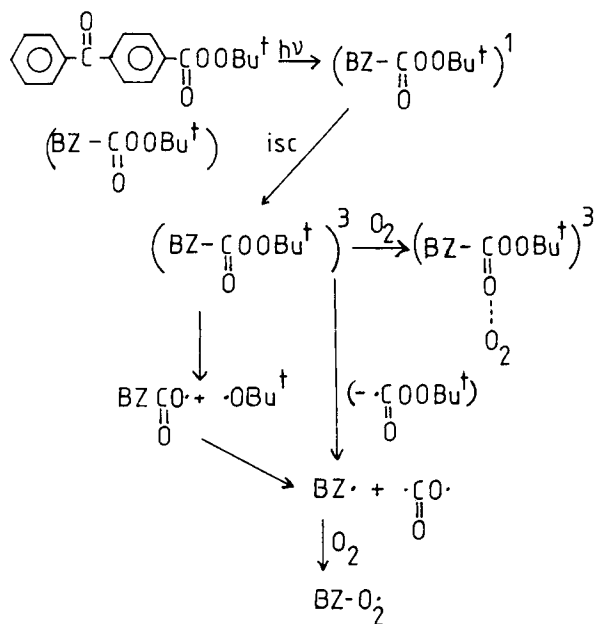


Figure 5 End-of-pulse transient absorption spectrum in nitrogen-saturated acetonitrile of the tetraester derivative of benzophenone after (□) 960 ns and (■) 8.24 μ s delay (5×10^{-3} M) produced on nanosecond laser flash photolysis.

zoxyloxy type radical produced in the homolysis of the *t*-butylperester group^{1,2} shown in Scheme 1:



Scheme 1

This is probably due to the fact that either the radical lifetime is short-lived or the transient absorbs in the UV region below the detection limits of the equipment. All three transients were also effectively quenched by oxygen, indicating the involvement of the triplet state.

Weak transient absorption in the case of both the perester derivatives on laser flash photolysis is evidently associated with the charge-transfer content of their lowest excited triplet states. The intensities of both spectra are also consistent with their longer phosphorescence lifetimes with the monoperester being shorter-lived than that of the tetra-perester derivative. Thus, the triplet activities of both the perester derivatives are related to their photopolymerization activities discussed above.

On laser flash photolysis in oxygenated solution similar long-lived transient absorption spectra were obtained in our previous work on the laser flash photolysis of perester derivatives of fluorenone and were tentatively assigned to either a triplet oxyplex or an aromatic peroxy radical formed via a decarboxylation reaction as shown in Scheme 1. Similarities between the spectra of fluorenone and that of benzophenone suggest the latter species as the more likely candidate since the triplet-triplet absorption spectra of the two chromophores are very different.

CONCLUSIONS

The photopolymerization activities of the mono- and tetra-perester derivatives of benzophenone are highly dependent upon the structure, concentration, and solubility of the compound, the type of monomer used and the methodology for photocuring. Using GPC analysis on the polymethylmethacrylate samples the *tetra-t*-butyl perester derivative of benzophenone gave higher weight (M_w) and number average molecular weight (M_n) polymers than those produced using the tetra-perester derivative. For the two peresters of benzophenone, photopolymerization efficiency using real time FTIR increases with increasing initiator concentration and no self-termination is observed up to 0.75% w/w concentration.

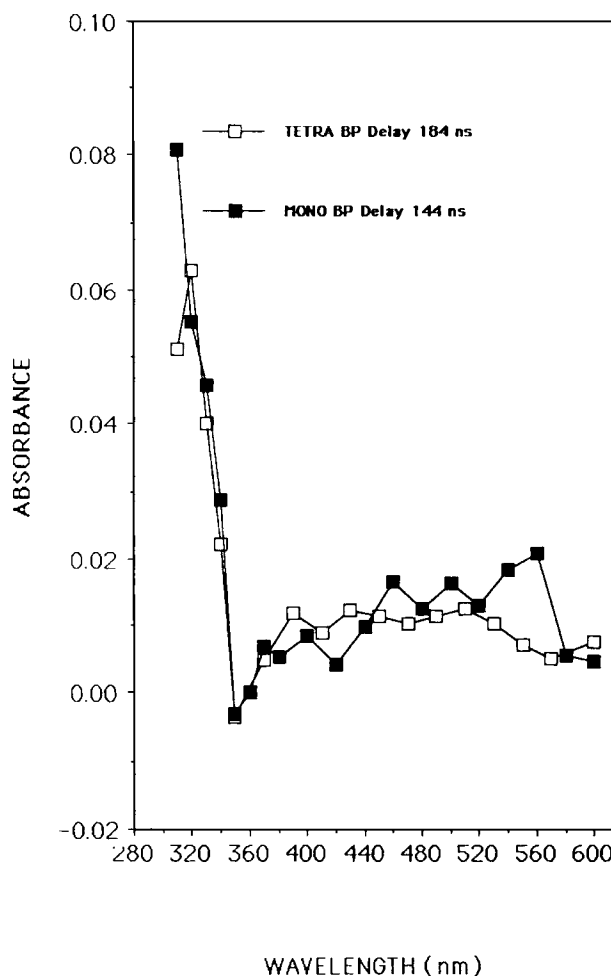


Figure 6 End-of-pulse transient absorption spectra in oxygen-saturated acetonitrile of (■) the monoperester and the (□) tetra-perester derivatives of benzophenone after 184 and 144 ns delay on nanosecond flash photolysis.

Of the two initiators the monoester derivative is the more efficient, and this is consistent with hardness testing during the photocuring of a commercial prepolymer/diluent monomer system, with benzophenone being the least efficient initiator.

The spectroscopic properties of the two perester derivatives of benzophenone are markedly different from those of benzophenone itself but are nevertheless related to their photoinitiation activity. Triplet-triplet absorptions on nanosecond laser flash photolysis are very weak compared with earlier work on benzophenone with the monoester derivative giving the strongest absorption, and these results are consistent with much lower phosphorescence quantum yields. Ketyl radical formation due to hydrogen atom abstraction by the photoexcited triplet state of the benzophenone chromophore is also much weaker for both the perester derivatives and is consistent with the nanosecond results, with the monoester giving the stronger absorption of the two. Long-lived transient formation in oxygen saturated acetonitrile is also observed for the two perester derivatives of benzophenone and is stronger for the monoester than the tetraester derivative and is assigned to that of an aromatic peroxy radical. Differences in the photoactivity of the two perester derivatives appears to be associated with the degree of substitution of the benzophenone chromophore which controls the degree of charge-transfer content, and this is reflected by the phosphorescence lifetimes and quantum yields.

The authors would like to thank the research and development staff of the Loctite Corp., Newington, CT, for

helpful discussions and advice and also a grant in support of one of us (S. J. H.).

REFERENCES

1. N. S. Allen, S. J. Hardy, A. Jacobine, D. M. Glaser, and F. Catalina, *Eur. Polym. J.*, **25**, 1219 (1989).
2. N. S. Allen, S. J. Hardy, A. Jacobine, D. M. Glaser, S. Navaratnam, and B. J. Parsons, *J. Photochem. Photobiol.*, to appear.
3. D. Neckers, U.S. Pat. 4,752,649 (1988).
4. L. Thijs, S. Gupta, and D. Neckers, *J. Org. Chem.*, **44**, 4123 (1979).
5. L. Thijs, S. Gupta, and D. Neckers, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 103, 855 (1981).
6. Nippon Oils and Fats Co. Ltd., Jpn. Pat. JP 72277 (1983).
7. C. Decker and K. Moussa, *Makromol. Chem.*, **189**, 2381 (1988).
8. H. G. Heller and J. R. Lanagan, *J. Chem. Soc. Perkin Trans. I*, 341 (1981).
9. H. G. Heller, Br. Pat., 7/1464603.
10. J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 91 (1971).
11. N. S. Allen, S. J. Hardy, A. F. Jacobine, D. M. Glaser, B. Yang, and D. Wolf, *Eur. Polym. J.*, to appear.
12. A. Beckett and G. Porter, *Trans. Farad. Soc.*, **59**, 2038 (1963).
13. G. Porter and F. Wilkinson, *Trans. Farad. Soc.*, **57**, 1686 (1961).
14. J. P. Fouassier, in *Photopolymerization and Photoimaging Science and Technology*, N. S. Allen, Ed., Elsevier Applied Science, London, 1989, Chap. 7, p. 209.

Received March 3, 1990

Accepted April 23, 1990