Photopolymerization of 1,6-hexanediol diacrylate with deoxybenzoin as photoinitiator

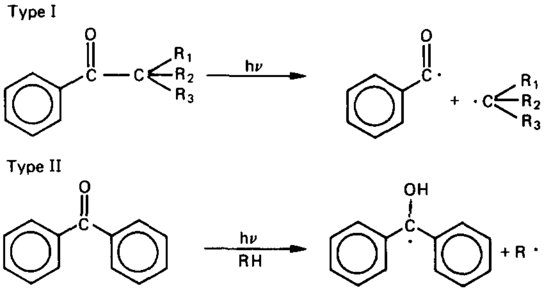
Charles E. Hoyle, Melissa Cranford, Martin Trapp, Young Gil No and Kyu-Jun Kim
Department of Polymer Science, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, MS 39406–0076, USA
(Received 23 February 1988; accepted 18 April 1988)

Rates of the photopolymerization of 1,6-hexanediol diacrylate (HDODA) using deoxybenzoin (DOB)/amine photoinitiator systems have been measured. Triethylamine (TEA), *N,N*-dimethylethanol amine (DMEA), *N,N*-dimethylaminoethyl methacrylate, and *N,N*-diethylaminoethyl methacrylate (DMEMA) are postulated to form excited state complexes (exciplexes) with DOB from whence photoreduction of DOB occurs to give the ketyl radical (identified by laser flash photolysis) and an initiating radical species. Rate enhancements on the order of 5 to 7 are reported both in nitrogen and air-saturated HDODA. Thus, deoxybenzoin which acts as a rather poor cleavage type photoinitiator in the absence of a hydrogen-donating species, becomes an effective co-photoinitiator when used in conjunction with tertiary amines.

(Keywords: photopolymerization; deoxybenzoin; photoinitiator; 1,6-hexanediol diacrylate)

INTRODUCTION

There are two basic types of initiators commonly employed in the photopolymerization of vinyl monomers[1–4], a cleavage type (type I) and a hydrogen abstraction type (type II) as shown in *Scheme 1*.

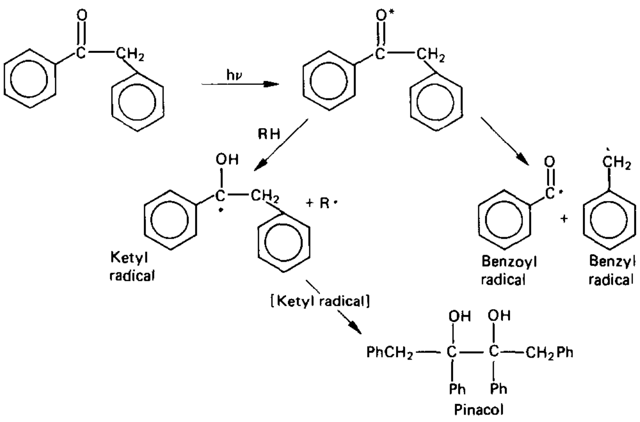


Scheme 1

For type I photoinitiators R_1, R_2 and R_3 are either hydrogen atoms or alkyl, aryl or alkoxy chromophores. Type II photoinitiators are usually based on a benzophenone derivative plus a co-initiator which is a hydrogen donor such as an aliphatic or aromatic amine. In each instance (type I and type II) upon excitation, a radical species capable of initiating polymerization is generated. In the case of the type II photoinitiator the R· radical is commonly believed to be the initiator while for Type I photoinitiators either radical or subsequently derived species (depending on the nature of the substituents R_1, R_2 and R_3) may be the initiating radical.

Interestingly enough, it has recently been shown that tertiary aliphatic and aromatic amines can be used to accelerate the photopolymerization of air-saturated acrylates initiated with cleavage (type I) photoinitiators[5–9]. The acceleration process is due to a radical-chain oxygen scavenging mechanism which is dominant at low amine concentrations. Caution must be exercised when using amines as oxygen scavengers since in some instances they also act as chain transfer agents which may retard the polymerization of acrylates when employed in high concentrations or the absence of oxygen.

In this paper, we present results for the photopolymerization of a difunctional acrylate 1,6-hexanediol diacrylate (HDODA) with deoxybenzoin (DOB) as the photoinitiator. DOB is a particularly interesting compound since it has been reported to photolytically decompose by both an α-cleavage and a hydrogen abstraction process, depending on the nature of the solvent medium. As shown in *Scheme 2*, although DOB in neutral (non-hydrogen-donating) solvents undergoes an α-cleavage process to give a benzyl radical, it has been reported[10,11] that in the presence of alcohols



Scheme 2

0032-3861/88/112033-08$03.00

such as isopropanol, the ketyl radical is generated by a hydrogen abstraction reaction. Fouassier and co-workers have taken advantage of the hydrogen abstraction reaction of excited DOB to develop a DOB/THF (tetrahydrofuran) system capable of efficiently initiating the polymerization of methyl methacrylate in benzene[12]. The present paper describes the use of various DOB/aliphatic amine systems to initiate the photopolymerization of neat 1,6-hexanediol diacrylate. Since aliphatic amines have been demonstrated to be highly effective (compared with alcohols and ethers) hydrogen donors for excited state benzophenone[13-15], it is anticipated that such compounds will be effective in producing free radical initiators, even in the presence of neat HDODA. Moreover, aliphatic amines should serve a dual purpose in air-saturated systems due to their unique oxygen-scavenging properties.

EXPERIMENTAL

HDODA was used as received (Aldrich). DOB from Aldrich was recrystallized three times from ethanol. *N*,*N*-dimethylethanol amine (Aldrich), triethylamine (Aldrich), *N*,*N*-dimethylaminoethyl methacrylate (Polysciences) and *N*,*N*-diethylaminoethyl methacrylate (Polysciences) were each distilled before use. Exotherm measurements for the photopolymerization of air-saturated HDODA were accomplished on a thin-foil exotherm unit[13]. The lamp source, a high pressure pulsed xenon lamp from Chadwick-Helmuth (Model 271-B), was placed at a distance of 36 cm from the sample. All the thin-foil exotherm samples were run at 100 Hz. The lamp repetition rate was controlled with a Wavetek Model 142 HF VCG waveform generator. The lamp source power was measured with an International Light 700A Research Radiometer. The power at 100 Hz was 3.09×10^{-4} W cm^{-2}. The voltage from the thin-foil exotherm unit was recorded on a Keithley Model 1155 microvolt meter connected to a strip chart recorder. The HDODA samples were placed between two thin glass cover slips separated by a glass fibre scrim to give a constant thickness of about 100 μm.

The exotherm measurements for HDODA in the absence of oxygen were accomplished using a modified Perkin–Elmer 1B model differential scanning calorimeter (d.s.c.) with a pyrex top[5,6]. The lamp source was the same one used for the thin-foil measurements. HDODA (6 μl) was injected into the aluminium sample pan. An empty pan was used as reference. The sample chamber was continuously flushed with nitrogen before and during the polymerization.

The laser-flash photolysis system consisted of a Lumonics HyperEx-440 excimer laser source and an Applied Photophysics Ltd pulsed 150 W xenon lamp analysis system. The output of the monitoring photomultiplier tube was recorded on a Tektronix 7912-AD transient digitizer. Sample solutions were prepared and housed in a quartz cell with a 1 cm optical path length.

RESULTS AND DISCUSSION

Figure 1 shows previously described[5] exotherm curves for the photoinitiated polymerization (benzoin isopropyl ether photoinitiator, 0.035 wt%) of HDODA obtained on the thin-foil (air-saturated) and d.s.c. (nitrogen-

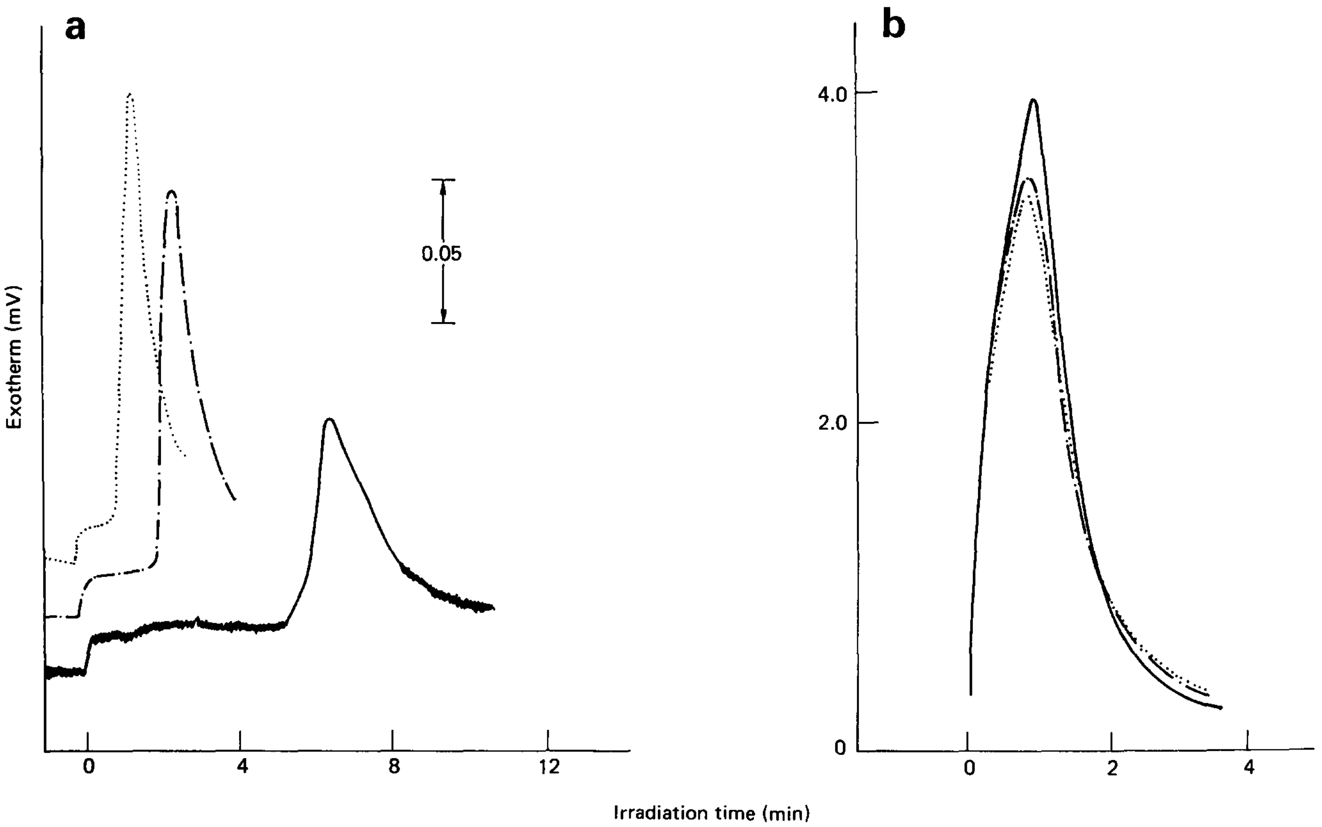


Figure 1 Exotherm curves for the BIPE (0.035 wt% to monomer) polymerization of HDODA with various concentrations of DMEA. (a) Thin foil unit: —— (0 wt%), —·—· (0.25 wt%), ······ (2 wt%). (b) D.s.c.: —— (0 wt%), —·—· (1 wt%), ······ (3 wt%)

blanketed) exotherm units with increasing concentration of *N,N*-dimethylethanol amine (DMEA). The exotherm maximum (H_{max}) obtained on the thin-foil unit increases with increasing concentration of amine (*Figure 1a*) due to a combination chain-transfer/oxygen-scavenging process which is highly efficient in removing oxygen from the HDODA thereby allowing polymerization to proceed. The increase in H_{max} is accompanied by a decrease in the time (T_{max}) required to reach H_{max}. On the other hand, H_{max} for the exotherms recorded on the d.s.c. (*Figure 1b*, nitrogen-saturated HDODA) decreases with increasing amine concentration. Presumably DMEA acts as a retarder in the absence of oxygen. *Scheme 3* has been postulated to account for the photopolymerization of HDODA with a type II (cleavage) photoinitiator such as benzoin isopropyl ether in the presence of tertiary amines[5,6]

$$\mathrm{I} \xrightarrow{h\nu} \mathrm{I}^* \qquad \text{Step 1}$$

$$\mathrm{I}^* \xrightarrow{k_d} \mathrm{R}\cdot \qquad \text{Step 2}$$

$$\mathrm{R}\cdot + \mathrm{M} \xrightarrow{k_i} \mathrm{RM}\cdot \qquad \text{Step 3}$$

$$\mathrm{P}_n^{\cdot} + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}^{\cdot} \qquad \text{Step 4}$$

$$\mathrm{P}_n^{\cdot} + \mathrm{P}_m^{\cdot} \xrightarrow{k_t} \mathrm{P}_{n+m} \qquad \text{Step 5}$$

$$\mathrm{P}_n^{\cdot} + \mathrm{P}_m^{\cdot} \xrightarrow{k_{td}} \mathrm{P}_n + \mathrm{P}_m \qquad \text{Step 6}$$

$$\mathrm{P}_n^{\cdot} + \mathrm{AH} \xrightarrow{k_{tr}} \mathrm{P}_n\mathrm{H} + \mathrm{A}\cdot \qquad \text{Step 7}$$

$$\mathrm{A}\cdot + \mathrm{M} \xrightarrow{k_a} \mathrm{AM}\cdot \qquad \text{Step 8}$$

$$\mathrm{A}\cdot + \mathrm{O}_2 \xrightarrow{k_{\mathrm{O}_2}} \mathrm{AO}_2^{\cdot} \qquad \text{Step 9}$$

$$\mathrm{AO}_2^{\cdot} + \mathrm{AH} \xrightarrow{k_{\mathrm{OOH}}} \mathrm{AOOH} + \mathrm{A}\cdot \qquad \text{Step 10}$$

Scheme 3

where I = photoinitiator, $\mathrm{R}\cdot$ = radical initiator, M = monomer, $\mathrm{P}_n^{\cdot}$, $\mathrm{P}_m^{\cdot}$ = polymer radicals, P_n, P_m, P_{n+m}, $\mathrm{P}_n\mathrm{H}$ = polymers, $\mathrm{A}\cdot$ = aminyl radical and AH = aliphatic or aromatic amine.

Steps 1–6 involve the standard initiation, propagation, and termination process of free radical polymerization. Steps 7, 9 and 10 show the radical chain oxygen scavenging mechanism. A radical $\mathrm{A}\cdot$, produced by hydrogen abstraction of a labile amine hydrogen (A–H) by a polymer radical $\mathrm{P}_n^{\cdot}$, reacts with oxygen to generate a peroxy radical ($\mathrm{AO}_2\cdot$). The peroxy radical abstracts a hydrogen from a second amine to give a hydrogen peroxide plus an aminyl radical. The sequence represented in steps 9 and 10 is then repeated with up to 15 oxygen molecules[7] being consumed for each aminyl radical produced in step 7. As shown in step 8, the aminyl radical may add to the monomer M and reinitiate the polymerization process.

Figure 2 shows exotherm curves for the photopolymerization of HDODA with the DOB photoinitiator. For exotherms recorded on both the thin-foil unit (*Figure 2a*, air-saturated) and d.s.c. (*Figure 2b*, nitrogen-saturated), as the concentration of DMEA increases, H_{max} increases and T_{max} decreases. This is in contrast to results for the BIPE photoinitiated system where addition of DMEA (*Figure 1b*) retards the polymerization of nitrogen-saturated HDODA. *Figures 3–6* show plots of H_{max} and T_{max}^{-1} (recorded on the thin-foil and d.s.c. exotherm units) *versus* weight per cent of DMEA. In each case, H_{max} and T_{max}^{-1} which are indicative of the relative overall polymerization rate[16], increase with concentration. Similar results are shown for the photopolymerization of HDODA (air-saturated and nitrogen-saturated) with triethylamine (TEA) added to the system (*Figures 7–10*). Apparently, tertiary amines in general, and specifically those with readily abstractable hydrogen atoms such as DMEA and TEA, are quite effective in accelerating the rate of the DOB-initiated polymerization of HDODA even in nitrogen-saturated samples. Consequently, it must be concluded that *Scheme 3* cannot account for the efficiency of the DOB/amine combination in non-oxygenated samples (*Figures 2b, 5, 6, 9* and *10*) and probably does not fully explain the dramatic increases in rate experienced in air-saturated HDODA (*Figures 2a, 3, 4, 7* and *8*).

Our results for the DOB/amine-initiated photopolymerization of HDODA in the absence (d.s.c.) and presence (thin-foil) of oxygen can be explained in light of the photochemical/photophysical behaviour of DOB. Unlike benzophenone, DOB undergoes an α-cleavage process in the absence of hydrogen-donating molecules (*Scheme 2*). While this α-cleavage process ($k_\alpha = 1.6 \times 10^6\ \mathrm{s}^{-1}$ in ref. 17) is quite slow compared with the α-cleavage rate for BIPE ($k_\alpha \gg 5.0 \times 10^9\ \mathrm{s}^{-1}$, ref. 18), it is nonetheless capable of generating reactive radicals to initiate the free radical polymerization process. However, with only DOB present the free radical polymerization is slow and gives a very poor yield of polymer. This can be seen by examination of *Figure 2a* (0 wt%) and *Figure 2b* (0 wt%). There is evidence in the literature[19,20] that photolysis of DOB in the presence of hydrogen-donating species generates the ketyl radical and subsequently the pinacol (*Scheme 2*). In order to confirm a similar mechanism for the generation of radical species in the DOB/amine system, two sets of experiments were conducted. First, photolysis of DOB (0.06 M) in benzene with 0.12 M TEA present yielded a white product which was identified as the pinacol. This, of course, provides irrefutable evidence for the ketyl radical intermediate proposed in *Scheme 2*. The second set of experiments deal with the laser flash photolysis of a benzene solution of DOB in the presence of TEA and will be presented in considerable detail as it contains valuable information about the rate of interaction between DOB* and TEA. *Figure 11* shows the transient absorption spectrum of DOB in deoxygenated benzene from 340 to 560 nm recorded 70 ns after firing the laser ($\lambda_{ex} = 351$ nm). In accordance with the results of Amirzadeh *et al.*[20], we assign the broad transient from 380–560 nm with a maximum between 420 nm and 450 nm to the triplet–triplet absorbance of DOB. We defend this assignment as upon monitoring at 380 nm (or 535 nm) we obtain a single exponential decay with a lifetime of 699 (or 694) ns. The decay curves show essentially no deviation from an exponential decay function and strongly suggest that a

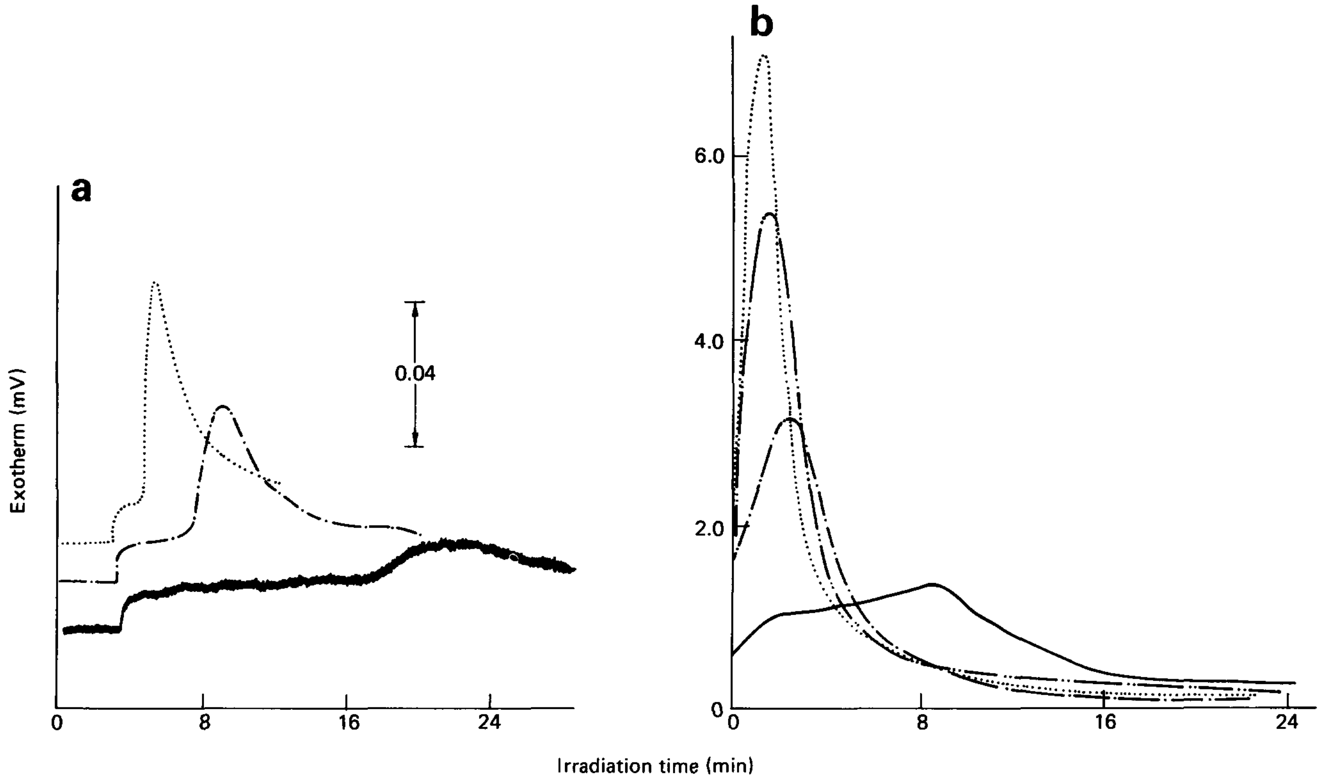


Figure 2 Exotherm curves for the DOB (0.2 wt% to monomer) initiated polymerization of HDODA with various concentrations of DMEA. (a) Thin-foil unit: —— (0 wt%), —·—· (2 wt%), ······ (8 wt%). (b) D.s.c. ——(0 wt%), —·— (0.5 wt%), -··-·· (2.0 wt%), ······ (4.0 wt%)

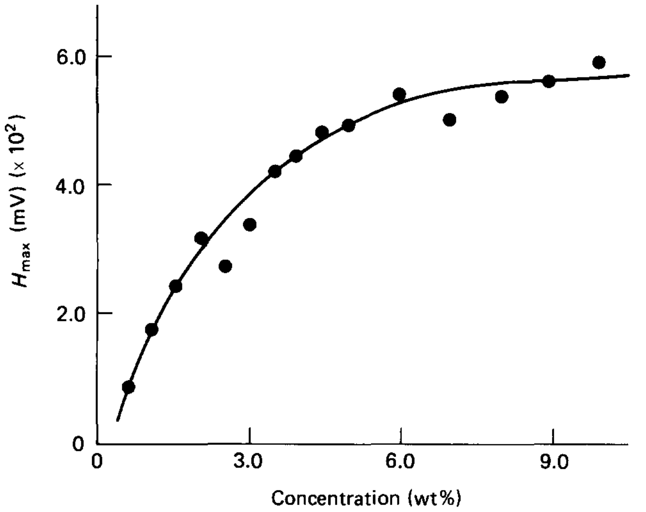


Figure 3 Plot of H_{max} *versus* DMEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of air-saturated HDODA (thin-foil unit)

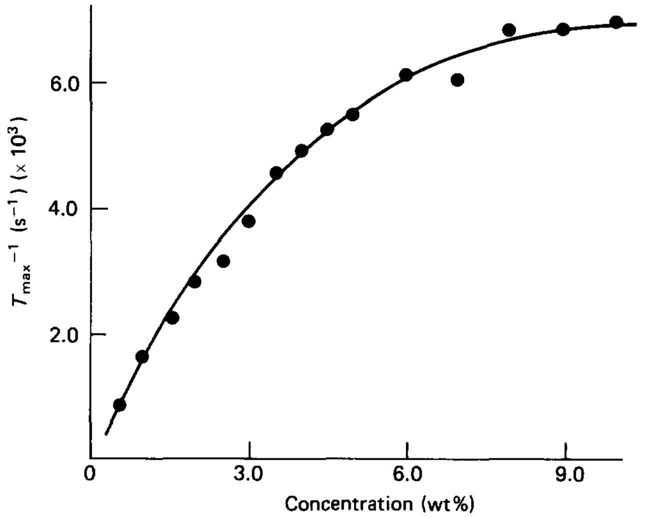


Figure 4 Plot of T_{max}^{-1} *versus* DMEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of air-saturated HDODA (thin-foil unit)

single species is primarily responsible for the major absorbance in these regions, especially on time scales well below 1 μs. The lifetimes for the decay curves at 380 and 535 nm are in agreement with a 770 ns lifetime reported in reference 20 for the triplet state of DOB photolysis obtained by laser flash. Additionally, both our results in the present paper and those of Amirzadeh *et al.*[20] are in excellent agreement with the results obtained by Lewis *et al.*[21] who predicted a lifetime of 830 ns in benzene by quenching the room temperature phosphorescence of DOB. Additional evidence for assignment of the 390–550 nm broad band absorbance in *Figure 11* to DOB triplet–triplet absorbance can be found in the laser flash photolysis results reported for acetophenone[22]. The maximum of the DOB triplet–triplet absorbance should be very close to the maximum of the triplet–triplet absorbance band of acetophenone since both have the same basic structure, PhCO–CH_2R where R is either –H (acetophenone) or –Ph(DOB). This is indeed the case as acetophenone (see ref. 22) and DOB have local maxima at approximately 415–430 nm. By contrast benzophenone and benzil, which have the general structure PhCO–R where R = –Ph and –COPh, have maxima at 535 and

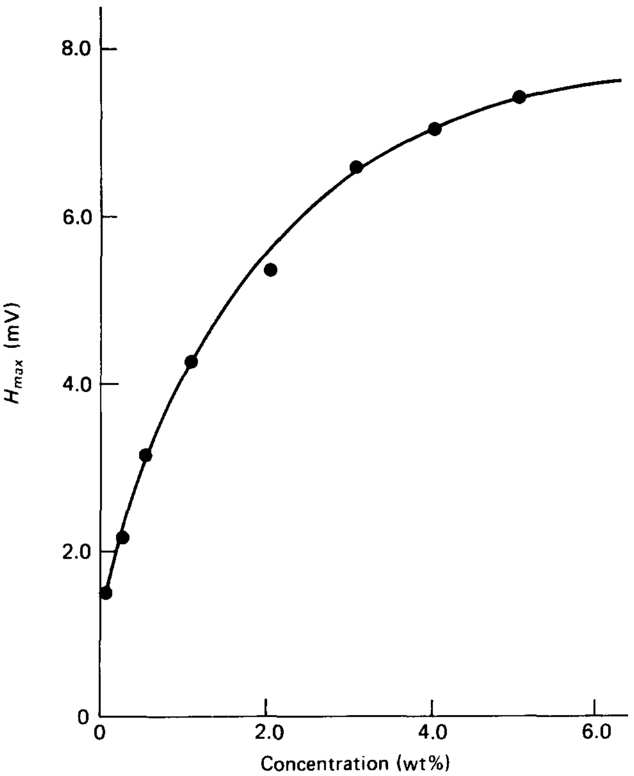


Figure 5 Plot of $H_{\max}$ *versus* DMEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of nitrogen-saturated HDODA (d.s.c.)

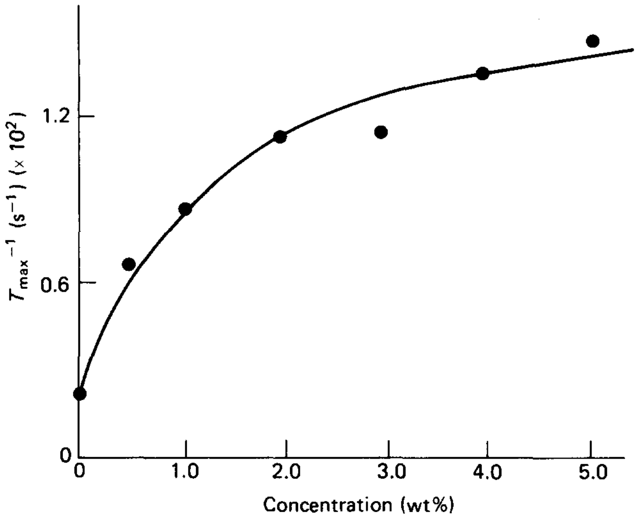


Figure 6 Plot of $T_{\max}^{-1}$ *versus* DMEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of nitrogen-saturated HDODA (d.s.c.)

500 nm, respectively. Thus, by analogy with acetophenone, it is clear that the transient spectrum in *Figure 11* can be attributed to DOB triplet–triplet absorbance. A word of caution should be extended here. We have noted that spectra taken for DOB in which fresh (non-photolysed by previous pulses from the laser) samples were not employed show a distinct peak with maximum around 500 nm which exactly matches the triplet–triplet absorbance of benzil (PhCO–COPh). This is not surprising since benzil, which has a rather pronounced triplet–triplet absorbance band, is produced as a minor ($\phi = 0.006$, ref. 21) component in benzene.

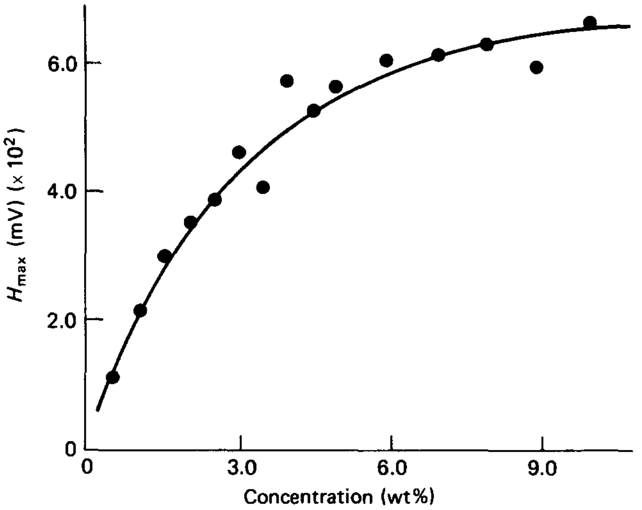


Figure 7 Plot of $H_{\max}$ *versus* TEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of air-saturated HDODA (thin-foil unit)

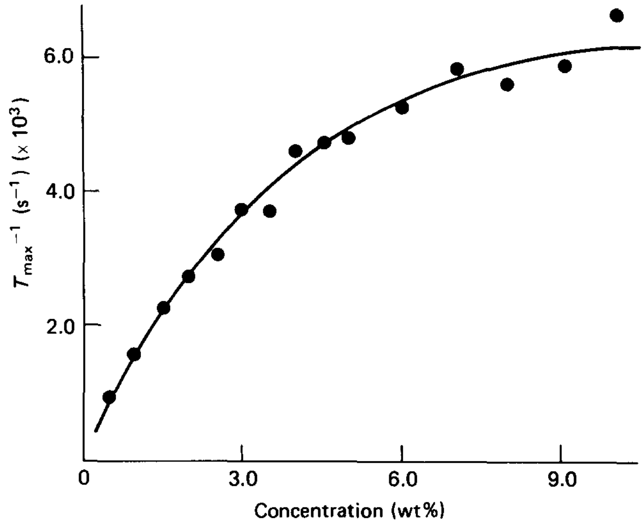


Figure 8 Plot of $T_{\max}^{-1}$ *versus* TEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of air-saturated HDODA (thin-foil unit)

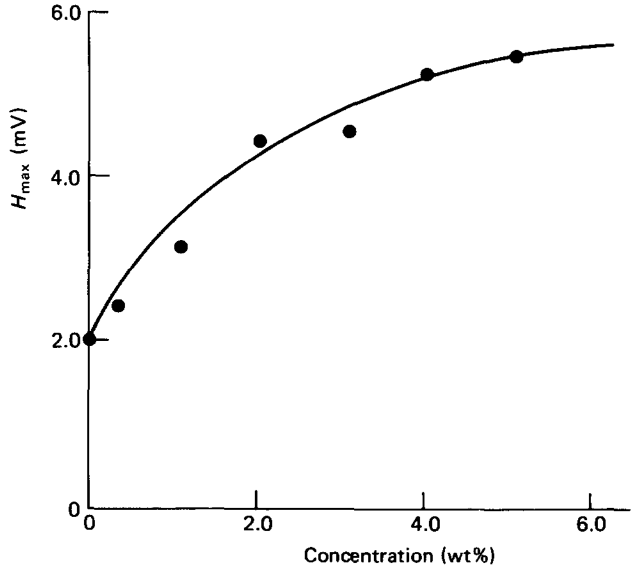


Figure 9 Plot of $H_{\max}$ *versus* TEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of nitrogen-saturated HDODA (d.s.c.)

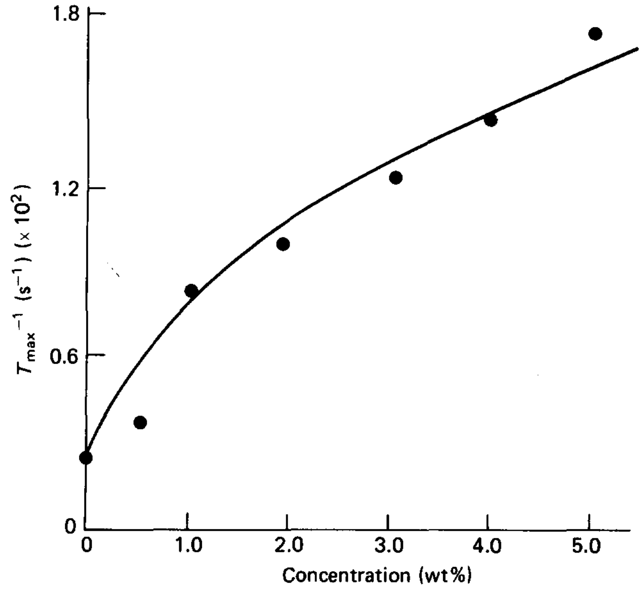


Figure 10 Plot of T_{max}^{-1} *versus* TEA concentration for the DOB (0.2 wt% to monomer) initiated polymerization of nitrogen-saturated HDODA (d.s.c.)

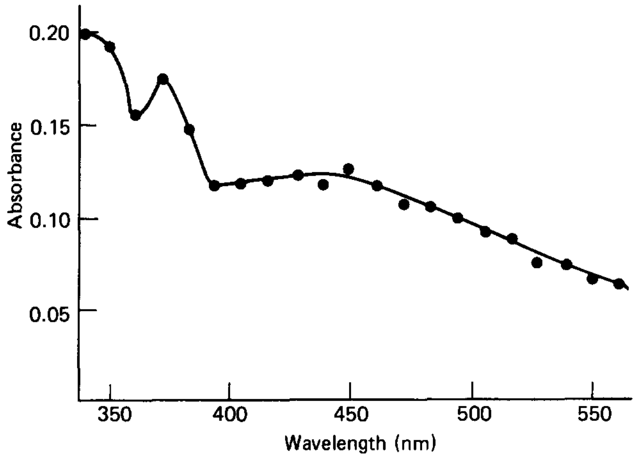


Figure 11 Transient absorbance spectrum (70 ns) of DOB in deoxygenated benzene ($\lambda = 351$ nm)

Figure 12 shows the transient absorbance spectrum (70 ns after firing laser) for DOB in the presence of TEA. At the concentration of TEA employed, the triplet–triplet absorbance of DOB* is replaced by an absorbance with a maximum around 400 nm which can most likely be attributed to the ketyl radical formed by DOB hydrogen abstraction from TEA (*Scheme 2*). In defence of this assignment, it should be noted that the peak absorbance in *Figure 12* at 400 nm is very similar to the absorbance maximum of the ketyl radical recorded upon photolysis of acetophenone in cyclohexane or ethanol[22]. In order to obtain the quenching rate constant for DOB* by TEA, decay curves of the transient at 535 nm were recorded for DOB* with increasing TEA concentration. The lifetimes reported for the DOB triplet state in *Table 1* were measured for the short-lived component of a two exponential decay function in the case of DOB/TEA solutions. Of course, as previously discussed, the decay of the transient for DOB* in benzene monitored at 535 nm with no TEA present fits a single exponential decay function with lifetime of 694 ns. Apparently the longlived component is due to the ketyl radical which has a lifetime well above 1 μs in benzene. The lifetime data from *Table 1* can readily be fit to a Stern–Volmer type equation as

$$\frac{\tau_0}{\tau} = 1 + k_q \tau_0 [Q]$$

where τ_0 = unquenched DOB triplet lifetime, τ = DOB lifetime in the presence of quencher Q, k_q = bimolecular quenching rate constant and [Q] = concentration of TEA (*Figure 13*). The rate constant k_q is 1.7×10^9 mol^{-1} s^{-1}, which is close to the diffusion-controlled quenching rate constant in benzene of 5.0×10^9 l mol^{-1} s^{-1}, and much

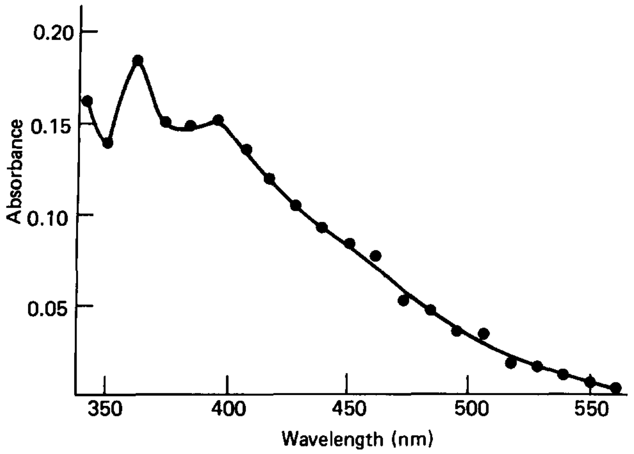


Figure 12 Transient absorbance spectrum (70 ns) of DOB in deoxygenated benzene ($\lambda = 351$ nm) in the presence of 7.2×10^{-3} M TEA

Table 1 Lifetimes for the DOB triplet state

TEA (mol l^{-1}) × 10^3	τ (ns)[a]	τ_0/τ
0.000	694	1.00
0.072	517	1.34
0.140	495	1.40
0.720	348	1.99
1.400	206	3.36
2.100	175	3.96

[a] Excited at 351 nm; observed at 535 nm

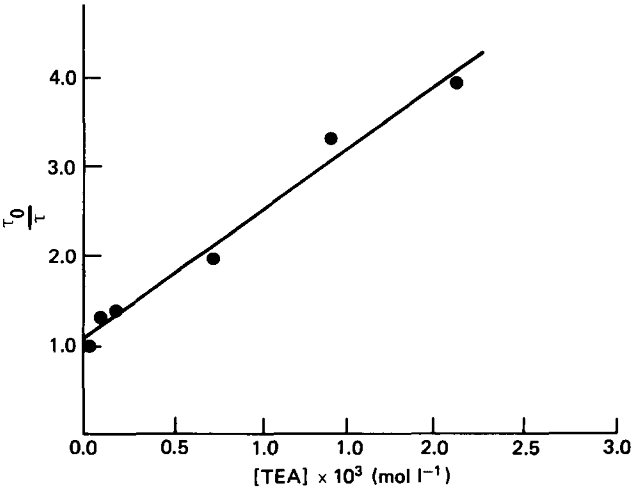


Figure 13 Stern–Volmer plot for quenching of DOB triplet by TEA

higher than the rate constants for quenching of DOB* by alkylthiols[20] and cyclic ethers[19] which have k_q values near $10^7\,\mathrm{l\,mol^{-1}\,s^{-1}}$. Apparently, aliphatic amines are especially effective in quenching the triplet state of DOB. The affinity of aliphatic amines for quenching benzophenone is well known[13-15]. Therefore it is not surprising that DOB/aliphatic amines, as reported here, are especially good initiator systems for the free radical polymerization of neat difunctional acrylates.

Finally, although the transient absorption spectrum of pure alkyl radicals, such as is expected to be generated by hydrogen abstraction from TEA, could not be detected by our experimental apparatus, it is nonetheless reasonable to expect that the TEA radical exists. Thus, in view of the large body of evidence[3,15,23] from the benzophenone/amine photoinitiator literature which identifies the amine radical as the primary initiating species for free radical polymerization, we conclude by analogy that the TEA as well as the DMEA radical is responsible for the polymerization of HDODA in our systems (*Figures 7–10*). Furthermore, it is quite obvious that the TEA and DMEA radicals are operative even in the presence of oxygen due to their expected reactivity and rapid diffusion rate.

One additional point is important in considering the production of the ketyl and TEA radicals. Since the inherent lifetime of unquenched DOB in a non-interactive solvent is less than 1 μs, one must ask by what mechanism do tertiary amines such as TEA compete with oxygen for reaction with excited DOB? Apparently, as in the case of benzophenone and amines[13-15], the triplet state of DOB forms an excited state complex or exciplex with the tertiary amine. The exciplex, which is stabilized by partial electron transfer, provides the structural arrangement required for hydrogen abstraction and subsequent ketyl radical formation (*Scheme 4*).

$$\mathrm{DOB} \xrightarrow{h\nu} (\mathrm{DOB})_1^* \xrightarrow{k_{\mathrm{isc}}} (\mathrm{DOB})_3^*$$

$$(\mathrm{DOB})_3^* + \mathrm{TEA} \underset{k_{\mathrm{ex}}^{-1}}{\overset{k_{\mathrm{ex}}}{\rightleftharpoons}} (\mathrm{DOB}^- - \mathrm{TEA}^+)^*_{\mathrm{exciplex}}$$

$$(\mathrm{DOB}^- - \mathrm{TEA}^+)^* \longrightarrow \underset{\substack{\text{ketyl}\\ \text{radical}}}{\mathrm{DOB}\bullet} + \mathrm{TEA}\bullet$$

$$2\,\mathrm{DOB}\bullet \longrightarrow \text{Pinacol}$$

$$\mathrm{TEA}\bullet + \mathrm{HDODA} \longrightarrow \text{Polymer}$$

Scheme 4

In summarizing the laser flash photolysis results, it is proposed that excited DOB readily interacts with TEA to form an exciplex intermediate resulting in the production of a ketyl radical and a TEA radical. It is the highly reactive TEA radical which initiates the free-radical polymerization of HDODA in air-saturated and nitrogen-saturated samples. It is concluded by inference that the DOB/DMEA system behaves in a manner similar to that of the DOB/TEA system.

In order to extend our results, the photopolymerization of HDODA in the presence of DOB and an amine functionalized methacrylate was conducted. It has recently been shown that *N,N*-dimethylaminoethyl methacrylate (DMAEMA) is an effective co-photoinitiator with benzophenone[24]. An exciplex mechanism, similar to the one shown in *Scheme 4*, was proposed to account for the reported effectiveness of the systems. *Figure 14* shows exotherms for the photopolymerization of HDODA in the d.s.c. (nitrogen-saturated) using the DOB/DMAEMA photoinitiator. Plots of H_{max} *versus* DMAEMA (wt%) are given in *Figures 15* and *16*. These results are very similar to those obtained for TEA and DMEA. The DMAEMA cosynergist has the added advantage of having a methacrylate functionality capable of participating in the polymerization process. This is indeed an important factor since amine cosynergists are notorious[5] for participation in a chain-transfer/retardation process which reduces the molecular weight and/or crosslink density of the polymer. By

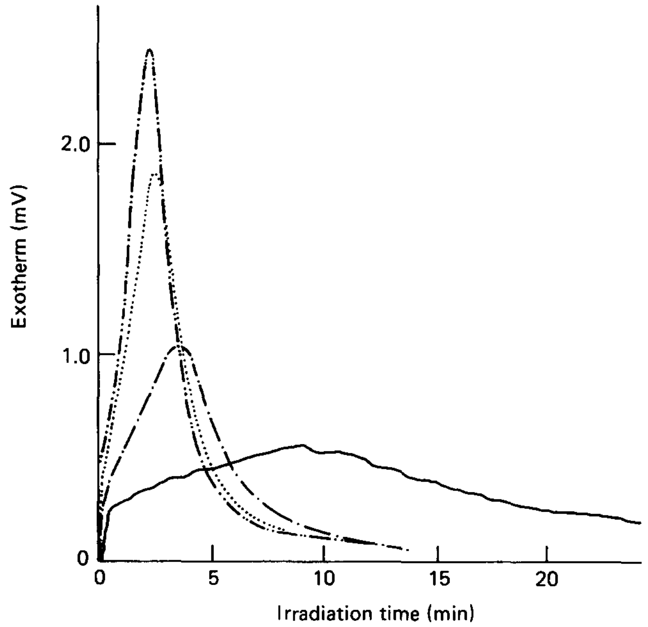


Figure 14 D.s.c. exotherm curves for the DOB (0.2 wt% to monomer) initiated polymerization of HDODA with various DMAEMA concentrations: —— (0 wt%), —·— (1 wt%), ······ (3 wt%), –··–·· (5 wt%)

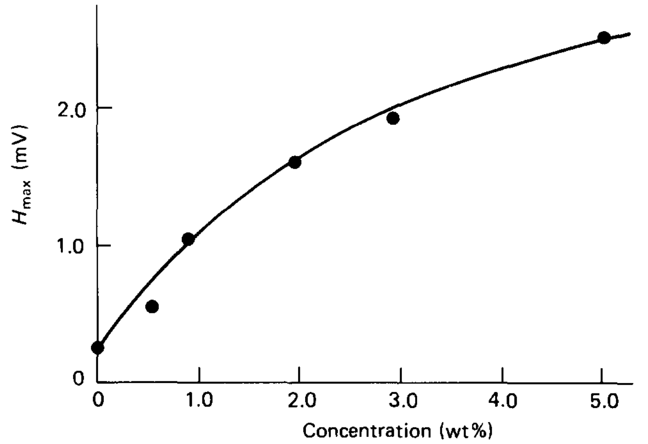


Figure 15 Plot of H_{max} *versus* DMAEMA concentration for the DOB (0.2 wt%) initiated polymerization of nitrogen-saturated HDODA (d.s.c.)

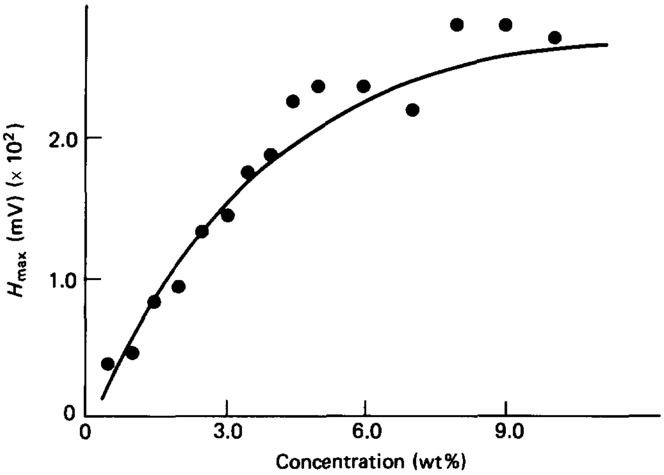


Figure 16 Plot of H_{max} *versus* DMAEMA concentration for the DOB (0.2 wt%) initiated polymerization of air-saturated HDODA (thin-foil unit)

'locking' the amine into the polymer matrix the deleterious effects of chain transfer are minimized[24,25].

CONCLUSIONS

This paper demonstrates the use of DOB and tertiary amine synergists as effective photoinitiator systems both in the absence and presence of oxygen. DOB and tertiary amines form excited state complexes or exciplexes which readily decompose to give a ketyl radical and an aminyl radical. The ketyl radical combines with a like species to give the corresponding pinacol leaving the amine radical to initiate the polymerization of a difunctional acrylate. In addition to the use of common tertiary amines such as TEA and DMEA, an amine-functionalized methacrylate (*N*,*N*-dimethylaminoethyl methacrylate, DMEMA) was also found to interact favourably with excited DOB to generate an effective radical initiator. DMEMA is a particularly important co-synergist since it can be polymerized into the polymer matrix through the methacrylate functionality, thus eliminating the reduction in crosslink density normally experienced when amines are present in free-radical polymerizations.

ACKNOWLEDGEMENTS

This research was supported by NSF Grant DMR 85-14414 (Polymers Program). We also wish to acknowledge the NSF for assistance in purchasing the nanosecond laser flash photolysis unit (Grant CHE-8411829, Chemical Instrumentation Program). An undergraduate scholarship awarded to M.C. by the Southern Society for Coatings Technology is also gratefully acknowledged.

REFERENCES

1 Pappas, S. P. and McGinnis, V. D. 'UV Curing Science and Technology' (Ed. S. P. Pappas), Technology Marketing Corporation, Connecticut, 1978, p. 1
2 Ledwith, A. *J. Oil Col. Chem. Assoc.* 1978, **61**, 105
3 Kinstle, J. A. *J. Rad. Cur.* 1974, **1**, 2
4 Carlblom, L. H. and Pappas, S. P. *J. Polym. Sci., Polym. Chem. Edn* 1977, **15**, 1381
5 Hoyle, C. E. and Kim, K. J. *J. Rad. Cur.* 1985, **12**, 9
6 Hoyle, C. E. and Kim, K. J. *J. Appl. Polym. Sci.* 1987, **33**, 2985
7 Decker, C. and Jenkins, A. D. *Macromolecules* 1985, **18**, 1241
8 Berner, G., Puglis, J., Kirchmayr, R. and Rist, G. J. *J. Oil Col. Chem. Assoc.* 1978, **61**, 105
9 Morgan, C. R. and Kyle, D. R. *J. Rad. Cur.* 1983, **10**, 4
10 Bergmann, A. and Hirshberg, Y. *J. Am. Chem. Soc.* 1943, **65**, 1429
11 Stocker, J. H. and Kern, D. H. *J. Org. Chem.* 1968, **33**, 1271
12 Fouassier, J.-P. and Merlin, A. *Makromol. Chem.* 1980, **181**, 1307
13 Cohen, S. G. and Litt, A. D. *Tetrahedron Lett.* 1970, **11**, 837
14 Guttenplan, J. B. and Cohen, S. G. *J. Am. Chem. Soc.* 1972, **94**, 4040
15 Sandner, M. R., Osborn, C. L. and Trecker, D. J. *J. Polym. Sci., Polym. Chem. Edn* 1972, **10**, 3173
16 Hoyle, C. E., Hensel, R. D. and Grubb, M. B. *Polym. Photochem.* 1984, **4**, 69
17 Heine, H.-G., Hartmann, W., Kory, D. R., Magyar, J. G., Hoyle, C. E., McVey, J. K. and Lewis, F. D. *J. Org. Chem.* 1974, **39**, 691
18 Heine, H.-G. *Tetrahedron Lett.* 1972, **47**, 4755
19 Fouassier, J.-P. and Merlin, A. *Can. J. Chem.* 1979, **57**, 2812
20 Amirzadeh, G., Kuhlmann, R. and Schnabel, W. *J. Photochem.* 1979, **10**, 133
21 Lewis, F. D., Hoyle, C. E., Magyar, J. G., Heine, H.-G. and Hartmann, W. *J. Org. Chem.* 1975, **40**, 488
22 Lutz, H. and Lindquist, L. *Chem. Commun.* 1971, **10**, 493
23 Vesley, G. A. *J. Rad. Cur.* 1986, **13**, 4
24 Jiang, G.-J., Shirota, Y. and Mikawa, H. *Polym. Photochem.* 1986, **7**, 311
25 Hoyle, C. E. and Kim, K. J. *Polymer* 1988, **29**, 18