A study of the photodecomposition products of an acylphosphine oxide and 2,2-dimethoxy-2-phenylacetophenone

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The photodecomposition of 2,4,6-trimethylbenzoyldiphenylphosphine oxide and 2,2-dimethoxy-2-phenylacetophenone was investigated under normal ultra-violet curing conditions. The rate of formation and the identity of the many photodecomposition products produced by each photoinitiator were similar, whether amines (triethylamine or *N*-methyldiethanolamine) were present or not. Experimental evidence indicates that the role of amines is predominantly one of oxygen scavenger. It was also established that the shelf-life (stability) of the photoinitiator 2,4,6-trimethylbenzoyldiphenylphosphine oxide is short when present in an epoxydiacrylate/*N*-methyldiethanolamine ultra-violet curable formulation. The decomposition products identified indicated that this is due to the occurrence of transesterification and hydrolysis reactions.

(Keywords: model environment; curing efficiency; shelf-life; photodecomposition; dinonyl phthalate; 1,5-pentanediol)

INTRODUCTION

Curing efficiency and shelf-life are two of the more important criteria considered in the selection of photoinitiators for ultra-violet-curable formulations. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TMBPO)[1-3] and 2,2-dimethoxy-2-phenylacetophenone (DMPA)[4] are photoinitiators that undergo a Norrish type 1 cleavage reaction to produce initiating free radicals, and for this reason do not require amine synergists for the photopolymerization of acrylates or other vinyl monomers. However, earlier investigations utilizing these photoinitiators have shown that, in order to achieve efficient cure speeds, it is necessary to add a tertiary amine[5,6]. It was recently reported[7] that the addition of amines to an acrylate formulation containing photoinitiators reacting by the type 1 cleavage mechanism accelerated the rate of polymerization. This was attributed to the amines scavenging non-chain-propagating oxygen-containing radicals. This finding concurs with those obtained in our earlier investigations[5]. From these investigations[5,6], which included photocuring in the absence of air, the role of amine was attributed to be predominantly one of an oxygen scavenger.

We now report upon a study of the photodecomposition of photoinitiators TMBPO and DMPA in two different model environments. The model environments, 1,5-pentanediol and dinonylphthalate, are non-polymerizable viscous materials and were used to simulate typical u.v.-curing formulations. Examination of the photodecomposition products obtained from both photoinitiators in the presence and absence of the tertiary amines, *N*-methyldiethanolamine and triethylamine, were made in order to determine if the photogenerated radicals reacted with the amine. Results are also reported of an investigation into the shelf-life (stability) of TMBPO when incorporated into an epoxydiacrylate/*N*-methyldiethanolamine u.v.-curable formulation.

EXPERIMENTAL

Instrumentation

The mass spectra were recorded on a Finnegan MAT 212 (EI) mass spectrometer interfaced with a Varian 3700 gas chromatograph using a temperature programme (range 70–230°C at a rate of 10°C min^{-1}). The separations were performed on a 15 m fused silica column (wide bore 1.5 μm) containing DB-5 (95% dimethyl polysiloxane, 5% diphenyl polysiloxane) with helium as the carrier gas.

The high-performance liquid chromatography (h.p.l.c.) experiments were carried out on a Waters Modular Liquid Chromatography System equipped with model 6000A pumps and the Wisp 710B Automatic Sample Processor. System control, quantification and reporting was carried out by the Waters 840 Chromatography Station. A Kratos Spectroflow 757 u.v.-absorbance detector ($\lambda = 254$ nm) was used. All separations were carried out on a Bakerbond C4 column.

The gas–liquid chromatography (g.l.c.) experiments were carried out on a Varian 3700 Gas Chromatograph with a flame ionization detector as above. The separations were performed on a 15 m fused silica column (internal diameter 0.32 mm) containing DB-5, with nitrogen as the carrier gas.

The u.v. curing experiments were carried out as

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Table 1 The percentage photodecomposition of TMBPO in dinonyl phthalate in the presence and absence of *N*-methyldiethanolamine, under u.v. curing conditions[a]

	Cure speed ($m\ min^{-1}$)	Residual TMBPO (%)	
		No amine	With amine
(1)	60	71.01	54.21
(2)	50	63.21	52.42
(3)	40	53.01	44.28
(4)	30	37.48	29.81
(5)	20	18.23	19.86
(6)	10	3.17	5.10
(7)	8	2.34	2.68
(8)	6	2.74	0
(9)	4	0	0
(10)	2	0	0

[a] TMBPO concentration, 3 wt%; *N*-methyldiethanolamine concentration, 6 wt%; film thickness, 20 μm; substrate, paper

described previously[5]. Cure speed (speed of the moving belt) is recorded in metres per minute and is equivalent to a specific irradiation time, recorded in seconds.

Materials

2,4,6-Trimethylbenzaldehyde, 2.4.6-trimethylbenzoic acid, diphenylphosphinic acid, benzaldehyde, acetophenone, methyl benzoate, benzoic acid, biphenyl, benzophenone, benzil, triethylamine and *N*-methyldiethanolamine (N-MDEA), all from Janssen Chimica, were used as received. Dinonyl phthalate (from Merck), methyl methacrylate and 1,5-pentanediol (from Aldrich) were used as received.

2,2-Dimethoxy-2-phenylacetophenone (from Ciba-Geigy) as recrystallized from petroleum ether (boiling range, 60–80°C) and has a melting point range of 65.4–65.7°C. 2,4,6-Trimethylbenzoyldiphenylphosphine oxide was available from previous studies[3].

The resin used (from Synthese BV) was a low-molecular-weight prepolymer, the epoxydiacrylate of Setacure® AP 570 (26 wt%) in polyethyleneglycol (200) diacrylate (PEGDA) (73.4 wt%).

The substrate used in all irradiations was satinized paper and the coatings were applied using an Erichsen rod to give a film thickness of 20 μm.

Experiment (1): examination of the photodecomposition of TMBPO in dinonyl phthalate

A solution of TMBPO in dinonyl phthalate was prepared by dissolving 1.29 g (3 wt%) of the photoinitiator in 40.00 g of dinonyl phthalate. The solution was applied to satinized paper using an Erichsen rod to give a 20 μm thick film. The paper was passed through the u.v. curing apparatus. The belt speed was controlled and the extent of decomposition examined for a variety of known belt speeds. After 'curing', the coating was scraped from the substrate and then subjected to analysis. The experiments were carried out in duplicate using freshly prepared solutions and analysed directly after the irradiation.

Primary h.p.l.c. analysis. The coating, dissolved in methanol (h.p.l.c. grade), was separated by a gradient elution programme, in which the gradients were established between two degassed eluents. Eluent A consisted of acetonitrile/water (vol. ratio 70:30) and eluent B consisted of acetonitrile/water (vol. ratio 90:10). A linear gradient was formed from 100% of A to 100% of B over a period of 5 min. The flow rate was 1 ml min^{-1}.

From this examination the extent to which the photoinitiator had decomposed was determined and thereby the amount of TMBPO decomposed as a function of irradiation time assessed. The results are shown in *Table 1*.

In order to identify the reaction products, another sample was prepared as before and 'cured' at a speed of 2 m min^{-1}. This was then analysed as follows.

Secondary h.p.l.c. analysis. The instrumentation used was as previously described. The cured coating was dissolved in methanol (h.p.l.c. grade) and applied to the column. Gradients were established between two degassed eluents. Eluent A consisted of acetonitrile/water/phosphoric acid (vol. ratio 30:70:0.1) and eluent B consisted of acetonitrile/water/phosphoric acid (vol. ratio 90:10:0.1). A linear gradient was formed from 100% of A to 100% of B over a period of 15 min. The flow rate was 1 ml min^{-1}. In order to identify the products detected, the retention times of a number of possible products (authentic samples) were determined. Where a match between the retention time of one of these authentic samples and a product was obtained, a chromatogram was run in which the reaction mixture was spiked with the authentic sample. The observation of simultaneous elution of the authentic sample and product was taken as indicative evidence for the identity of the product. Further confirmation of these assignments was sought using other analytical methods. The major products were identified as being diphenylphosphinic acid, 2,4,6-trimethylbenzoic acid and 2,4,6-trimethylbenzaldehyde.

Gas chromatography–mass spectrometry. The reaction mixture was applied to a 15 m fused silica column. Significant peaks in the g.c.–m.s. trace were examined in detail, i.e. the fragmentation patterns were recorded. The major products were identified as being 2,4,6-trimethylbenzaldehyde and 2,4,6-trimethylbenzoic acid. In addition the mass spectral data suggested that methyl diphenylphosphinate[8] (*m/z* 232 [30, M^+], 231 (80, M^+-1], 202 [13, $(C_6H_5)_2POH^+$], 199 [50, $(C_6H_5)_2PO^+-21$], 155 [44, C_6H_5–$C_6H_6^+$], 152 [25, $(C_6H_4)_2^+$], 77 [100, $C_6H_5^+$], 51 [60, $C_4H_3^+$]) and methyldiphenylphosphine oxide (*m/z* 216 [31, M^+], 215 [88, M^+-1], 201 [76, $(C_6H_5)_2PO^+$], 152 [21, $(C_6H_4)_2^+$], 77 [100, $C_6H_5^+$], 51 [91, $C_4H_3^+$]) were formed. The formation of the latter two products is somewhat surprising and could be indicative of the participation of methyl radicals generated from what is presently an unknown source.

Experiment (2): examination of the photodecomposition of TMBPO in dinonyl phthalate in the presence of an amine

A solution of TMBPO in dinonyl phthalate was prepared by dissolving 1.20 g (3 wt%) of the photoinitiator and 2.40 g (6 wt%) of the amine *N*-methyldiethanolamine (N-MDEA) in 40.00 g of dinonyl phthalate. The examination of this freshly prepared solution, made in order to determine the extent to which the photoinitiator had decomposed under the conditions described in experiment (1), was determined. The amount of TMBPO decomposed (in the presence of amine) as a

Table 2 The percentage photodecomposition of DMPA in dinonyl phthalate in the presence and absence of *N*-methyldiethanolamine, under u.v. curing conditions[a]

	Cure speed (m min⁻1)	Residual DMPA (%)	
		No amine	With amine
(1)	60	74.14	78.50
(2)	50	71.02	73.27
(3)	40	66.49	69.40
(4)	30	59.54	62.13
(5)	20	39.52	48.39
(6)	10	12.84	20.73
(7)	8	11.73	13.49
(8)	6	6.48	10.14
(9)	4	4.86	2.76
(10)	2	0	0

[a] DMPA concentration, 3 wt%; *N*-methyldiethanolamine concentration, 6 wt%; film thickness, 20 μm; substrate, paper

function of irradiation time was assessed as soon as the irradiations were completed. The results are shown in *Table 1*.

In order to identify the reaction products, another sample was prepared. This sample consisted of 1.20 g (3 wt%) of TMBPO photoinitiator and 2.40 g (6 wt%) of the amine triethylamine (TEA) dissolved in 40.00 g of dinonyl phthalate. Examination and analysis of the photodecomposition products were performed under similar conditions and methods as employed in experiment (1). H.p.l.c. and g.c.–m.s. indicated that the following products were formed: 2,4,6-trimethylbenzaldehyde, 2,4,6-trimethylbenzoic acid, diphenylphosphinic acid, methyl diphenylphosphinate and methyldiphenylphosphine oxide.

Experiment (3): examination of the photodecomposition of DMPA in dinonyl phthalate

A solution of DMPA in dinonyl phthalate was prepared by dissolving 1.20 g (3 wt%) of the photoinitiator in 40.00 g of dinonylphthalate. An examination of the extent to which the photoinitiator decomposed under the experimental conditions described in experiment (1) was determined. The amount of DMPA decomposed as a function of irradiation time was assessed. The results are shown in *Table 2*.

In order to identify the reaction products, another sample was prepared as before. Examination and analysis of the photodecomposition products were performed under similar conditions and methods as employed in experiment (1). H.p.l.c. analysis and g.c.–m.s. showed the following compounds to be produced: benzoic acid, methyl benzoate, methyl anisoate, methyl 4-benzoylbenzoate and methyl 2-benzoylbenzoate. In addition, minute amounts of benzaldehyde, benzophenone, benzil, acetophenone and biphenyl were produced. Needless to say, the origin of some of these compounds is obscure, but the identification of the isomeric methyl benzoylbenzoates is beautiful confirmatory evidence for the correctness of the assignments made in an earlier study using the technique of chemically induced dynamic nuclear polarization[9].

Experiment (4): examination of the photodecomposition of DMPA in dinonyl phthalate in the presence of an amine

A solution of DMPA in dinonyl phthalate was prepared by dissolving 1.29 g (3 wt%) of the photoinitiator and 2.40 g (6 wt%) of N-MDEA in 40.00 g of dinonyl phthalate. An examination of the extent to which the photoinitiator decomposed under the experimental conditions described in experiment (1) was determined. The amount of DMPA decomposed (in the presence of amine) as a function of irradiation time was assessed. The results are shown in *Table 2*.

In order to identify the reaction of products, another sample was prepared as described in experiment (2), except that the photoinitiator in this case was DMPA. Examination and analysis of the photodecomposition products were performed under similar conditions and methods as employed in experiment (1). H.p.l.c. and g.c.–m.s. analysis showed that the presence of amine had little effect upon the product distribution, which was similar to that observed in the previous experiment.

Experiment (5): examination of the photodecomposition of TMBPO in 1,5-pentanediol

A solution of TMBPO in 1,5-pentanediol was prepared by dissolving 1.20 g (3 wt%) of the photoinitiator in 40.00 g of 1,5-pentanediol. The photodecomposition of the initiator TMBPO was investigated in detail in order to identify the photodecomposition products yielded. Analysis was performed under the same conditions, using the same methods and instrumentation as described in experiment (1) (second subsection only). A representative chromatogram is shown in *Figure 1a*.

Experiment (6): examination of the photodecomposition of TMBPO in 1,5-pentanediol in the presence of amine

A solution of TMBPO in 1,5-pentanediol was prepared by dissolving 1.2 g (3 wt%) of the photoinitiator and 2.40 g (6 wt%) of TEA in 40.00 g of 1,5-pentanediol. This solution was investigated as described above in experiment (5). A representative chromatogram is shown in *Figure 1b*.

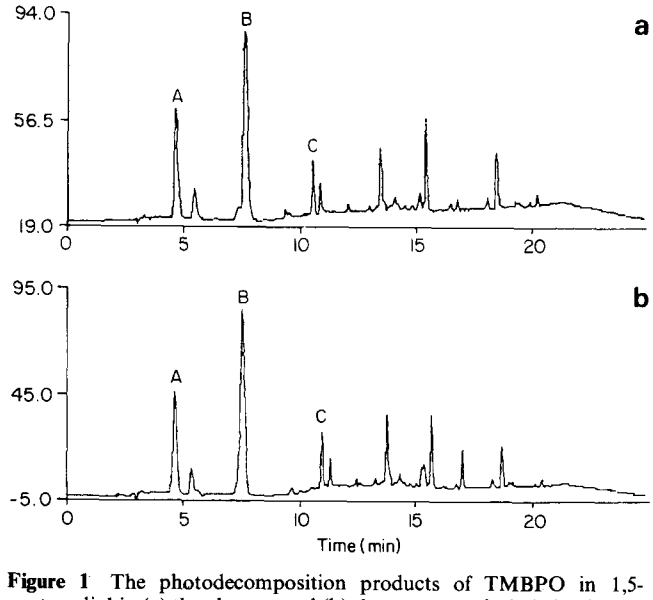


Figure 1 The photodecomposition products of TMBPO in 1,5-pentanediol in (a) the absence and (b) the presence of triethylamine, as identified by h.p.l.c.: **A**= diphenylphosphinic acid; **B**=2,4,6-trimethylbenzoic acid; **C**=2,4,6-trimethylbenzaldehyde

Table 3 The effect of shelf-life stability on the cure speeds for TMBPO and DMPA photoinitiators in a *N*-methyldiethanolamine/epoxydiacrylate u.v.-curable formulation[a]

Age of sample (h)	Cure speed ($m\ min^{-1}$)	
	TMBPO	DMPA
2	20	20
26	16	20
50	1	20

[a] DMPA and TMBPO concentrations, 3 wt%; *N*-methyldiethanolamine concentration, 6 wt%; film thickness, 20 μm; substrate, paper

Experiment (7): examination of the photodecomposition of DMPA in 1,5-pentanediol

A solution of DMPA in 1,5-pentanediol was prepared by dissolving 1.20 g (3 wt%) of the photoinitiator in 40.00 g of 1,5-pentanediol. This solution was investigated as described in experiment (3) and the products as found by h.p.l.c. analysis were found to be similar to those obtained in experiment (3).

Experiment (8): examination of the photodecomposition of DMPA in 1,5-pentanediol in the presence of amine

A solution of DMPA in 1,5-pentanediol was prepared by dissolving 1.20 g (3 wt%) of the photoinitiator and 2.40 g (6 wt%) of TEA in 40.00 g of 1,5-pentanediol. This solution was investigated as described above in experiment (7) and the product distribution as observed by h.p.l.c. analysis found to be similar to that obtained in experiment (7), i.e. the presence of amine has little effect.

Experiment (9): examination of the shelf-life of epoxydiacrylate formulations containing TMBPO

During preliminary investigations of the curing efficiency of both TMBPO and DMPA in the presence and absence of *N*-methyldiethanolamine in an epoxydiacrylate resin[5], it was clearly apparent that the cure speed of the TMBPO/*N*-methyl diethanolamine formulation deteriorated after 24 h. A detailed investigation of the shelf-life stability of TMBPO was performed. Formulations were prepared by dissolving 0.30 g (3 wt%) of TMBPO and 0.6 g (6 wt%) N-MDEA in 10.00 g of Setacure® AP 570/PEGDA (200) resin, and were stored in brown glass bottles in a box at room temperature (20°C). The results are shown in *Table 3*. After four days the TMBPO formulation was analysed by g.l.c. However, the chromatograms obtained were too complicated to allow unambiguous analysis.

Experiment (10): examination of the shelf-life of expoxydiacrylate formulations containing DMPA

A detailed investigation of the shelf-life stability of DMPA was also performed as described in experiment (9). The formulations were prepared by dissolving 0.30 g (3 wt%) of DMPA and 0.60 g (6 wt%) N-MDEA in 10.00 g of Setacure® AP 570/PEGDA (200) resin, and were stored as described in experiment (9). Examination of the cure speed (by the usual curing methods) as the age of the prepared formulation increased was determined, the results being shown in *Table 3*. As the curing efficiency remained constant over a period of days, further analysis was considered unnecessary.

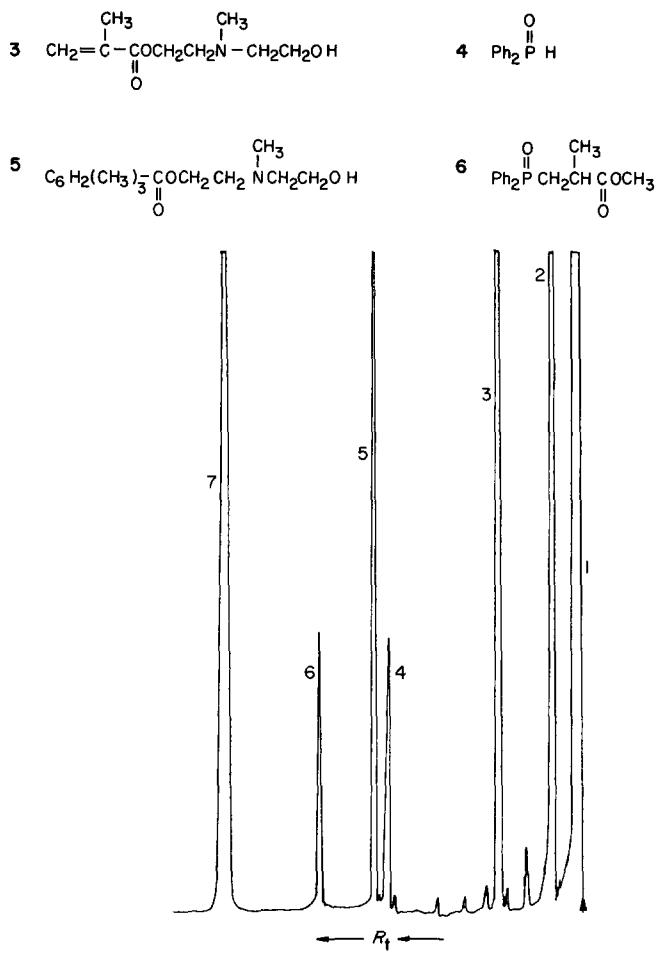


Figure 2 The decomposition products of TMBPO in methyl methacrylate monomer containing *N*-methyldiethanolamine as identified by g.l.c. and m.s.: **1** = methyl methacrylate; **2** = *N*-methyldiethanolamine; **3**–**6** are shown on the figure; **7** = 2,4,6-trimethylbenzoyldiphenylphosphine oxide

Experiment (11): examination of the stability of TMBPO in a mixture of methyl methacrylate and N-*methyldiethanolamine*

The u.v. curing formulation described in experiment (9) was replaced by one containing methyl methacrylate (MMA) monomer, to enable identification of the decomposition products. The sample to be investigated was prepared as described previously in experiment (9), but using MMA instead of the epoxydiacrylate resin. This was stored in a brown glass bottle, in a box at room temperature, maintaining a dark environment continually. The decomposition of the photoinitiator in the dark environment was followed daily by g.l.c. analysis, as described in experiment (9), the products being identified by comparison with authentic samples. At this point, only the starting materials MMA, N-MDEA and TMBPO could be identified by comparison. A representative chromatogram is shown in *Figure 2*.

After a period of 10 days, the decomposition mixture was analysed by mass spectrometry as before in experiment (9). *Figure 2* shows the structures of the products **3** to **6**, identified by mass spectrometry[9]:

3 165 [2, $M^+ - 18$], 156 [25, $M^+ - 31$], 113 [90, $CH_2{=}C(CH_3)CO_2CH_2CH_2^+$], 88 [100, $CH_2{-}N(CH_3)CH_2CH_2OH^+$]

4 202 [35, M^+], 201 [100, $(C_6H_5)_2PO^+$], 183 [38, $(C_6H_4)_2P^+$], 155 [11, C_6H_5–$C_6H_6^+$], 152 [17, $(C_6H_4)_2^+$], 77 [55, $C_6H_5^+$], 51 [62, $C_4H_3^+$]

5 265 [0.01, M^+], 234 [10, $M^+ - 31$], 147 [100, $(CH_3)_3C_6H_2CO^+$], 119 [20, $(CH_3)_3C_6H_2^+$, 88 [100, CH_2–$N(CH_3)CH_2CH_2OH^+$]

6 302 [3, M^+], 287 [12, $M^+ - 15$], 271 [10, $M^+ - 32$], 243 [8, $M^+ - CO_2CH_3$], 215 [58, $(C_6H_5)_2P(O)CH_2^+$], 201 [100, $(C_6H_5)_2P^+$], 183 [12, $(C_6H_4)_2P^+$], 155 [33, C_6H_5–$C_6H_6^+$], 77 [82, C_6H_5], 51 [40, $C_4H_3^+$]

This mass spectral fragmentation pattern compares favourably with that reported[10] for $(C_6H_5)_2P(:O)CH_2CH_2CO_2CH_3$.

DISCUSSION

Investigation of the photodecomposition of TMBPO and DMPA

Previous reports have shown[5,11] that the photocuring efficiency of 2,4,6-trimethylbenzoyldiphenylphosphine oxide (TMBPO) in clear coatings is less efficient in the absence of amine than that exhibited by 2,2-dimethoxy-2-phenylacetophenone (DMPA). The rate of photodecomposition of both TMBPO and DMPA photoinitiators, in the presence and absence of tertiary amine, was investigated in a model environment selected to mimic a clear u.v.-curable coating. From *Table 2* it can be seen that the addition of an amine does not accelerate the photodecomposition of DMPA. Since the type 1 cleavage process leads to DMPA having a very short triplet lifetime[4], it is not surprising that the excited initiator does not react with the amine in a bimolecular reaction. By way of contrast, *Table 1* shows that there is an effect of added amine upon the photodecomposition of TMBPO. The addition of amine led to a rather sharp increase in the rate of decomposition at the faster belt speeds, levelling off at the slower belt speeds. That the effect of added amine influences the type 1 cleavage process of TMBPO is unlikely when one considers the short triplet lifetime of the acylphosphine oxide[1]. The slight increase in the rate observed may be accounted for by the occurrence of non-photochemical processes involving nucleophilic attack by photoproducts, e.g. hydroperoxides, upon the acylphosphine oxide. Another possible decomposition mechanism could be via an S2 reaction in which the photoproduced radicals, e.g. peroxy radicals, induce the decomposition of the oxide. Comparing the rate of decomposition of the two photoinitiators purely on a weight-to-weight basis and ignoring the fact that their absorption properties in the 300–400 nm wavelength region are different[5], one would conclude that the faster decomposition rate of the acylphosphine oxide should make it the more efficient photoinitiator for the polymerization of acrylates. In reality, DMPA is the more efficient photoinitiator despite its poorer light-absorption characteristics.

These results suggest that although the TMBPO undergoes rapid photodecomposition under u.v. curing conditions, not all the photogenerated radicals participate in initiating polymerization. It is conceivable that the phosphorus-centred radicals are rapidly scavenged by oxygen, thereby reducing their potential to initiate polymerization. This rationalization is supported by an earlier report[5], where in the absence of oxygen the acylphosphine oxides were found to be good photoinitiators for the curing of acrylate resins. The scavenging of acyl and phosphorus-centred radicals by oxygen is currently under investigation[12]. Similarly a recent investigation of the effect of amine synergists on the photoinitiated polymerization of an air-saturated diacrylate resin supported the supposition that certain amines are capable of sustaining a radical chain process for oxygen scavenging[7].

Examination of the photodecomposition of DMPA and TMBPO in both the presence and absence of triethylamine give identical reaction products as judged by h.p.l.c. and g.l.c. analyses. This finding clearly indicates that the photoinitiators do not interact with the amine and that the photogenerated radicals are also not scavenged by the amine. If this had been the case, the yield of aldehydes derived from the acyl radicals should have been increased by the presence of amine.

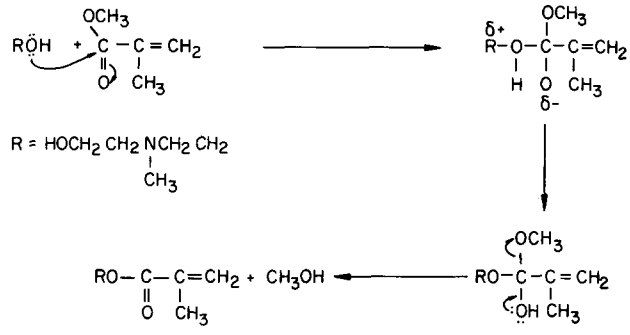
From the results, which show identical reaction products in the presence and absence of amine, and considering those from earlier reports[5] where u.v. curing was performed in the absence of air, the possibility of an α-aminoalkyl radical generated via the reaction of primary radicals with the amine being solely responsible for improving the curing efficiency so dramatically is unlikely. Thus the combined results suggest that the beneficial role of amines in u.v.-curable formulations is predominantly one of an oxygen scavenger[13].

Decomposition of a TMBPO u.v.-curable formulation

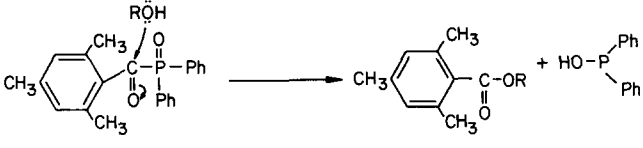
When selecting the components to constitute a u.v.-curable formulation, the storage stability or shelf-life of the prepared mixture is considered to be an important criterion. Contaminants present in the resin, following manufacture, or already present in the storage container used, will greatly reduce the stability, as will heat and light. Chemically labile photoinitiators, added amines or alcohols may also reduce the stability of the formulation.

A series of investigations was carried out to ascertain the shelf-life (stability) of a u.v.-curable formulation containing TMBPO and *N*-methyldiethanolamine. Experimental evidence presented shows that the curing efficiency of this u.v.-curable formulation was lost over a period of 3 days. The results are presented in the chromatogram (*Figure 2*), which shows the four decomposition products generated in the prepared formulation. Identification by g.l.c. analysis and mass spectroscopy showed the products to be the result of direct and indirect nucleophilic attack by N-MDEA upon the methyl methacrylate monomer and the photoinitiator, TMBPO.

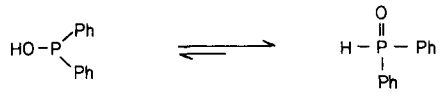
The identity of products (MMA, N-MDEA and TMBPO) was established by comparison with authentic samples and confirmed by mass spectrometry to be the original components of the formulation. The decomposition product **3** was identified by mass spectrometry and is most likely formed by a transesterification process:



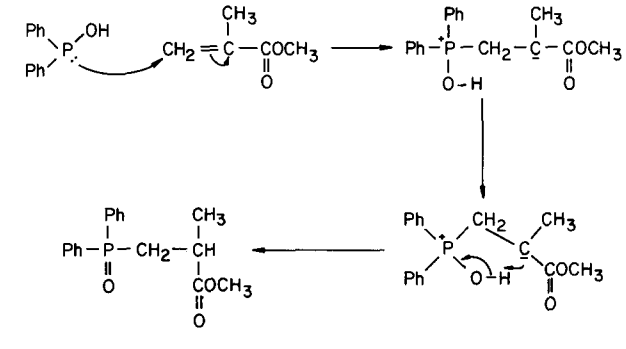
The formation of product **5** arises as a result of a nucleophilic attack by N-MDEA upon the photoinitiator, TMBPO. The aminoalcohol attacks the electron-deficient carbonyl group to give product **5** and diphenylphosphinous acid:



The diphenylphosphinous acid will readily tautomerize to give product **4** (diphenylphosphine oxide), with the equilibrium lying towards the formation of the phosphine oxide:



The predominance of the pentavalent form (**4**) of the diphenylphosphine oxide is expected on the account of its ability to undergo $d\pi$–$p\pi$ bonding, thus increasing the stability of its structure. However, the diphenylphosphinous acid will also show nucleophilic character by attacking the methyl methacrylate monomer, resulting in the formation of product **6** via a Michael addition reaction:



These product studies demonstrate the deleterious effect of including an aminoalcohol* in u.v.-curable formulations containing the acylphosphine oxide, TMBPO.

CONCLUSIONS

The investigations show that both TMBPO and DMPA photodecompose efficiently in the presence and absence of amine, and that the role of amine in the u.v.-curable formulation is predominantly that of an oxygen scavenger. It has been shown[5] that in the absence of amines the curing efficiency of these photoinitiators is poor. An additional problem came to light when the shelf-made stability of TMBPO was discovered to be poor in u.v.-curable formulation containing N-MDEA, as a result of the nucleophilicity of the amine, which attacked the photoinitiators and acrylate monomer. Whilst in the case of TMBPO and DMPA the effect of added amine serves to accelerate polymerization and cure speeds, without noticeable reduction in the surface properties and severe yellowing, it has been discovered that it will participate in the reduction of the shelf-life of a TMBPO-formulated resin used in this investigation. However, one should only use N-MDEA as a synergist with acylphosphine oxides with due care, and it would appear advisable to use unsubstituted tertiary amines to overcome the side-reactions associated with the reactivity of the hydroxyl groups.

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* Recent experiments indicate that the reactions described may be special to amino alcohols