Use of acylphosphine oxides and acylphosphonates as photoinitiators

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Results are presented which show that acylphosphine oxides are more efficient photoinitiators than acylphosphonates for the curing of acrylates and unsaturated polyesters, and that their efficiency is further increased by adding amines. The performance of these initiators was compared with two commercial photoinitiators 2,2-dimethoxy-2-phenylacetophenone and benzoin methylether. From these studies it was concluded that the acylphosphonates cannot be considered as useful photoinitiators for the production of surface coatings. The value of laser nephelometry as a method for screening photoinitiators is underscored. Some of the limitations of this method and that of bulk polymerization are assessed.

(Keywords: laser nephelometry; bulk polymerization; thin film polymerization; acrylates; styrene)

INTRODUCTION

Photoinitiators can be classed into two categories[1–6], those involving Type 1 cleavage and others involving a bimolecular process leading to radicals capable of initiating polymerization.

Photoinitiator efficiency can be assessed in a number of ways, e.g. using solution polymerization monitored by laser nephelometry[7] and using bulk polymerization[8–12]. However, the results from these methods do not always give a good indication of the performance of the photoinitiator systems used in the ultraviolet (u.v.) curing of thin films[8]. For solution polymerization monitored by laser nephelometry the observed rate of reaction is determined by the rate of precipitation of polymer. The most suitable monomer for this technique has been established as trimethylolpropane triacylate (TMPTA). Not only does this material expose the effects of oxygen inhibition[13], but also, because it forms a highly cross-linked polymer, the amount of precipitation obtained closely reflects the extent of polymerization. Bulk polymerization studies employing the amount of precipitable polymer to show the extent of polymerization can give a false indication of photoinitiator efficiency. If the photoinitiating system leads to low molecular weight oligomers (e.g. because of the occurrence of efficient chain transfer) which are soluble in the solvents employed for precipitation a true impression of the photoinitiating efficiency will not be gained.

The percentage of oxygen present in the reaction mixtures leads to the reactions exhibiting induction periods[14] and also leads to inaccuracies in determining photoinitiator efficiency. The presence of oxygen slows down the initiation process by reducing the concentration of radicals available for the initiation of polymerization. Unless special precautions are taken, oxygen inhibition is a particularly important problem encountered in the production of surface coatings[11]. Both laser nephelometry and bulk polymerization examinations can be carried out with the exclusion of oxygen. In these cases the rate of polymerization primarily reflects the rate of chain propagation, which can be influenced by photoinitiator efficiency. The efficiency of the photoinitiator system is related to the time taken to reach the normal rate of polymerization. This time in deoxygenated systems is often extremely short and difficult to determine with any degree of accuracy.

We now report upon the use of these techniques to study acylphosphine oxides and acylphosphonates as initiators for polymerization of methyl methacrylate and an acrylate resin mixture, together with a preliminary study of a styrene system. A few comparisons are also made with conventional initiators, e.g. benzoin methylether (BME), benzil and 2,2-dimethoxy-2-phenylacetophenone (DMPA).

EXPERIMENTAL

Benzoin methylether (BME) (Aldrich) was recrystallized from hexane/ether, m.p. 47.1–47.4°C. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (Ciba-Geigy) was recrystallized from petroleum ether (boiling range 60–80°C), m.p. 65.4–65.7°C. Benzoin isopropylether (BIPE) (Aldrich) was recrystallized from hexane, m.p. 77.2–78.2°C. Benzil and triphenylphosphine sulphide (Aldrich) were used as received. 1,1-Diphenylethylene (DPE) (Merck) was fractionated before use; the middle fraction, b.p. 79–80°C (at 30 Pa) was used in these experiments. 2,2,6,6-Tetramethylpiperidinoxyl (TMPO) and *N*-methyl-diethanolamine (*N*-MDEA) (Aldrich) were used as received. Methyl methacrylate (MMA) and styrene (STY) (Aldrich) were used as received without further

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purification (the amount of inhibitor in the monomers is substantially less than the amount of photoinitiator employed).

The resins used (all from Synthese b.v.) included a low molecular weight prepolymer, the epoxydiacrylate of Setacure AP 570 (26.6 wt%) in polyethyleneglycol (200) diacrylate (73.4 wt%) and Setacure AP 571, which is an unsaturated polyester (53 wt%) in Setacure AM 554, a polyethertriacrylate, (47 wt%).

Benzene, methanol and petroleum ether (boiling range 60–80°C) (BDH) and propan-2-ol (Baker) were used as received.

Synthesis

2,4,6-Trimethylbenzoyldiphenylphosphine oxide (TM-BPO), 2,6-dimethoxybenzoyldiphenylphosphine oxide (DMBPO) and pivaloyldiphenylphosphine oxide (PDPO) have been described previously[16]. 1,1-di(*p*-tolyl)ethylene (DTE) was available from previous studies[17].

Benzoyldimethylphosphonate (BDMP) and benzoyldiethylphosphonate (BDEP) were synthesized according to the reported procedure[18].

2,4,6-Trimethylbenzoyldiethyl phosphonate (TMBEP) was prepared by stirring continuously 2,4,6-trimethylbenzoyl chloride (12.0 g, 0.065 mol) at 0°C under nitrogen in a flask equipped with a dropping funnel, condenser and magnetic stirring assembly. Freshly distilled triethyl phosphite (11.5 g, 0.069 mol) was added dropwise over 20 min. The reaction mixture was allowed to warm up gradually to room temperature and then it was heated over an oil bath (at 80°C) with continuous stirring for one hour. The residual oil was distilled using a Vigreux column, giving the final product (15.3 g, 83%, b.p. 204–206°C at 47 Pa[18]).

2,4,6-Trimethylbenzoyldimethyl phosphonate (TM-BMP) m.p. 47.7–48.2°C was prepared similarly giving 65% yield.

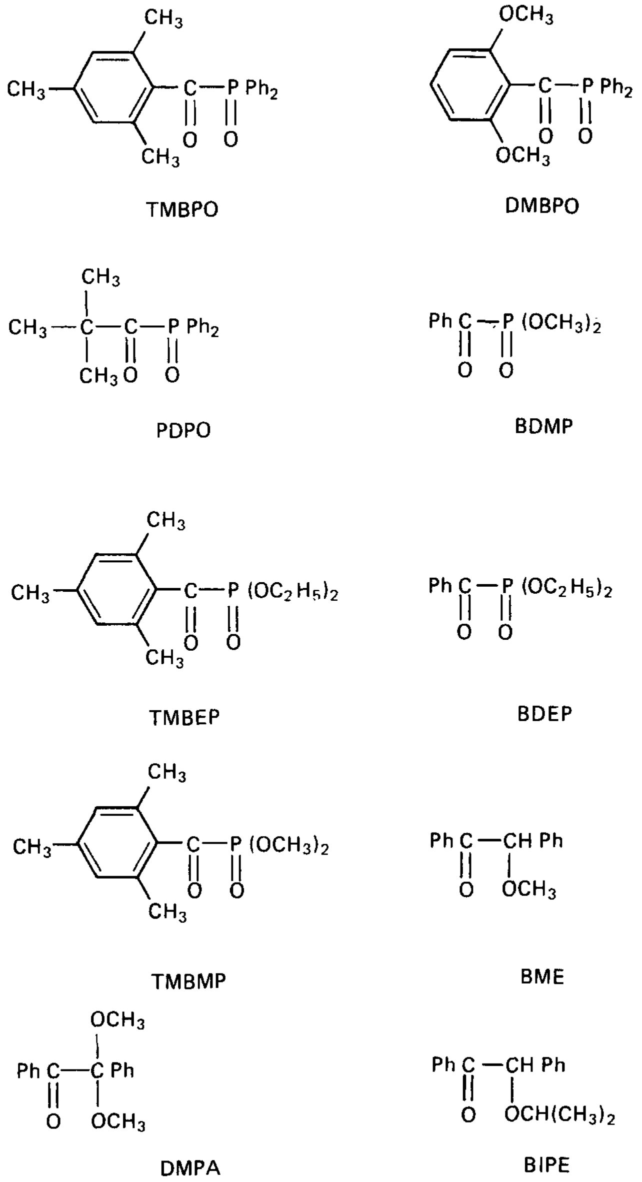
The structure of the photoinitiators is shown in *Scheme 1.*

Solution polymerization as monitored by laser nephelometry

The apparatus used to monitor the polymerization of trimethylolpropane triacrylate (TMPTA), a trifunctional monomer, was set up as previously described[7]. In such an investigation the laser beam passes through a 4 × 1 cm^2 polystyrene cuvette (Witeg) containing the monomer solution to be examined exposed to the atmosphere. The He–Ne laser (632.8 nm) was adjusted to obtain a linear response of the photodiode when the intensity of the laser beam was decreased by interposing neutral density filters. When the TMPTA solution containing photoinitiator is exposed to the u.v. radiation of a high pressure mercury lamp (90 W) encased in a spectral lamphouse (supplied by Ealing), a translucent white gel appears due to the formation of a cross-linked polymer which is insoluble in propan-2-ol. With the increasing turbidity of the irradiated sample the laser beam is attenuated and the intensity of the transmitted light detected by the photodiode drops rapidly. The curves which are recorded by this device will then directly reflect the kinetics of the polymerization process[7].

The photopolymerization of the monomer solution (prepared by dissolving 10 g of TMPTA in 1 l of propan-2-ol) by the photoinitiators was complete within a few seconds. The rate of polymerization, R_p(est), was estimated from the slope of the curves plotted on the chart recorder using a calibration curve obtained previously by plotting the amount of polymer formed (as determined by gravimetry) against time (measured in seconds).

The photoinitiating efficiency of each photoinitiator was determined under a variety of conditions. Initial investigations were conducted using photoinitiator concentrations of 10^{-2} mol l^{-1} in monomer solution. In other reactions the effect of adding tertiary amine (2×10^{-2} mol l^{-1}) and triphenylphosphine sulphide (1×10^{-2} mol l^{-1}) was investigated. Radical scavengers ditolylethylene (DTE), diphenylethylene (DPE) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) were used as possible inhibitors of the polymerization. The solutions were prepared while maintaining a constant photoinitiator concentration of 10^{-2} mol l^{-1} and an increasing radical scavenger concentration from 1×10^{-3} mol l^{-1} to 4×10^{-3} mol l^{-1}.



Scheme 1 Structure of the photoinitiators

Table 1 Comparison of the efficiency of various photoinitiators assessed by solution polymerization monitored by laser nephelometry[a]

	Induction period (s)			Rate of polymerization ($10^3\,s^{-1}$)		
Photoinitiator	No additive	*n*-MDEA[b]	TPPS[c]	No additive	*N*-MDEA	TPPS
1 BIPE	35.52	–	–	3.48	–	–
2 DMPA	14.00	12.60	20.40	4.18	3.96	3.59
3 BME	28.35	23.60	34.60	4.10	4.92	2.57
4 TMBPO	2.01	2.10	1.12	4.65	6.13	3.96
5 DMBPO	2.02	1.26	2.20	4.24	5.16	3.03
6 BDMP	39.80	89.00	43.90	3.16	2.24	1.37
7 BDEP	114.00	0	0	0.87	0	0
8 TMBEP	54.40	18.60	57.30	4.31	0.98	2.89
9 TMBMP	51.70	36.00	–	2.53	2.32	–

[a] Photoinitiator concentration $10^{-2}\,mol\,l^{-1}$ in TMPTA solution (10 g of TMPTA in $1\,dm^{-3}$ of propan-2-ol)
[b] *N*-methyldiethanolamine (*N*-MDEA) concentration ($2\times10^{-2}\,mol\,l^{-1}$)
[c] Triphenylphosphine sulphide concentration ($1\times10^{-2}\,mol\,l^{-1}$)

Table 2 Effect of radical scavengers on photopolymerization induced by TMBPO monitored by laser nephelometry[a]

Radical scavenger concentration ($10^{-3}\,mol\,l^{-1}$)		Induction period (s)	Rate of polymerization ($10^3\,s^{-1}$)
DPE[b]	1	2.70	4.32
	2	4.43	3.59
	3	5.93	2.72
	3.6	6.68	2.04
DTE[c]	1	3.36	3.45
	2	5.05	2.84
	3	6.90	2.43
	4	9.24	2.00
TMPO[d]	1	3.36	3.36
	2	4.32	3.10
	3	6.00	2.49
	4	6.60	2.39

[a] Photoinitiator TMBPO ($1\times10^{-2}\,mol\,l^{-1}$ concentration in TMPTA solution)
[b] 1,1-diephenylethylene
[c] 1,1-ditolyethylene
[d] 2,2,6,6-tetramethylpiperidin-1-oxyl

Bulk polymerization of methyl methacrylate and styrene

A general procedure was followed for each photoinitiator or photoinitiator–amine system. The photoinitiator ($2.5\times10^{-4}\,mol\,l^{-1}$) was dissolved in MMA (20 g). Triethanolamine ($1.25\times10^{-3}\,mol\,l^{-1}$), if used, was added to the mixture and thoroughly mixed. The solution was irradiated in a stoppered Pyrex tube (280 × 13 mm) in duplicate and the tube was rotated around a water-cooled medium pressure mercury lamp (Applied Photophysics Ltd, 450 W). On completion of the irradiation over a timed period, the solution was syringed into a flask containing petroleum ether (boiling range 60–80°C, 100 cm^3), which was vigorously agitated throughout the addition. The precipitated polymer was collected on a pre-weighed sinter, washed with petroleum ether and dried in a vacuum desiccator to constant weight.

Variations upon the precipitation technique were tried. Method A is that described above. Method B required that the irradiated solution was dissolved in benzene before being syringed into a flask containing methanol at −5°C. Method C also required the irradiated solution to be dissolved in benzene, but the solution was syringed into petroleum ether at −5°C.

Photoinitiated polymerization of thin films

This method has been previously described in detail[19].

RESULTS

Solution polymerization monitored by laser nephelometry

Initially, comparisons were made between the acylphosphine oxides, acylphosphonates and commercial photoinitiators to determine their initiating efficiency (*Table 1*). *N*-Methyldiethanolamine and triphenylphosphine sulphide were added to assess their synergistic values. The results are also shown in *Table 1*.

Attempts to elucidate if the observed induction periods were due to the trapping of photoproduced radicals were made by adding increasing concentrations of conventional radical scavengers to the monomer solution containing TMBPO photoinitiator. The results are shown in *Table 2*.

Bulk polymerization of methyl methacrylate (MMA) and styrene

A second series of comparisons between the acrylphosphonates, acylphosphine oxides and commercial photoinitiators was made. The initiating efficiency and the percentage polymerization after 30 min were measured in both MMA and styrene. *N*-methyldiethanolamine and triphenylphosphine sulphide were added to assess their synergistic value; the results are shown in *Table 3*.

Photoinitiated polymerization of thin films

A comparison was made of the effectiveness of the acylphosphonates, acylphosphine oxides and commercial photoinitiators (with added synergist) for the u.v. curing of epoxy–acrylate and unsaturated polyester thin films. The results (*Table 4*) show the optimal curing efficiency obtained using the amine synergists selected from earlier investigations[19]. Cure speeds are recorded in metres per minute (speed of the moving belt) and in seconds (length of time for which the sample was irradiated).

DISCUSSION

Solution polymerization monitored by laser nephelometry

The results obtained show that there is a remarkable difference between the initiation efficiency of acylphosphine oxides and acylphosphonates. The latter show very large induction periods (*Table 1* entries 6, 7, 8

Table 3 Comparison of the bulk polymerization of vinyl monomers using various photoinitiators[a]

Photoinitiator	Rate of polymerization ($10^4 s^{-1}$)	Yield of polymer[b] (%)	Rate of polymerization ($10^4 s^{-1}$)	Yield of polymer[c] (%)	Rate of polymerization ($10^4 s^{-1}$)	Yield of polymer[d] (%)
1 BME	0.67	11.37	–	–	–	–
2 BIPE	0.60	10.19	–	–	–	–
3 BENZIL	0.02	0.43	–	–	–	–
BENZIL/*N*-MDEA	0.22	3.84	–	–	–	–
4 TMBPO	1.22	19.66	0.62	10.65	0.87	14.51
TMBPO/*N*-MDEA	1.34	21.50	–	–	–	–
TMBPO/TPPS	1.15	18.74	–	–	–	–
5 DMBPO	1.18	19.17	0.86	14.27	0.96	15.85
DMBPO/*N*-MDEA	1.31	20.96	–	–	–	–
DMBPO/TPPS	1.28	20.57	–	–	–	–
6 BDEP	0.01	0.27	0.0	0.0	–	–
BDEP/*N*-MDEA	0.33	5.82	0.27	4.73	–	–
7 BDMP	0.02	0.38	0.00	0.00	0.02	0.32
BDMP/*N*-MDEA	0.37	6.38	0.41	7.19	0.32	5.51
8 TMBEP	0.53	9.12	–	–	–	–
TMBEP/*N*-MDEA	0.43	7.47	–	–	–	–
9 DMPA[e]	–	–	0.05	0.98	0.08	1.44
10 TMBPO[e]	–	–	0.20	3.52	0.21	3.65

[a] Concentrations: photoinitiator $= 2.5 \times 10^{-4}$ mol l^{-1}; *N*-methyldiethanolamine (*N*-MDEA) $= 1.25 \times 10^{-3}$ mol l^{-1}; triphenylphosphine sulphide (TPPS) $= 5 \times 10^{-4}$ mol l^{-1}
[b] Method A
[c] Method B
[d] Method C
[e] Styrene used instead of methyl methacrylate

Table 4 Effectiveness of various photoinitiators for u.v. curing of oligomeric mixes

	Epoxy–acrylate[a] cure speed		Unsaturated polyester[b] cure speed	
Photoinitiator	(m min^{-1})	(s)	(m min^{-1})	(s)
1 TMBPO	16	0.60	1	9.60
2 DMBPO	12	0.80	4	2.40
3 BDMP	0.4	24.00	1	9.60
4 BDEP	0.4	24.00	2	4.80
5 TMBEP	2	4.80	2	4.80
6 TMBMP	0.4	24.00	2	4.80
7 DMPA	14	0.68	2	4.80
8 DMPA[c]	1	9.60	1	9.60
7 TMBPO[c]	1	9.60	0.6	14.40

[a] Epoxy–acrylate resin contains 3% photoinitiator and 6% *N*-methyldiethanolamine
[b] Unsaturated polyester resin contains 4% dimorpholinopropane and 3% photoinitiator
[c] 3% Photoinitiator samples in the absence of amine

and 9). This difference cannot solely be explained on the basis of the difference in absorption properties of the two types of material[20]. The following equation relates the rate of initiation, R_I, to the inhibitor concentration, [In], and the measured inhibition period, t_i:

$$R_I = \frac{[In]}{t_i}$$

In all the reactions, the inhibitor is atmospheric oxygen, which is present to a similar extent in all the reaction mixtures. The oxygen is responsible for the induction period by virtue of its capacity to scavenge initiating and propagating radicals, and not to quench the excited triplet states of photoinitiators, which are known to be very short lived. Our recent finding[22] that both acylphosphine oxides and acylphosphonates induce photo-oxidative desulphurization at pentacovalent phosphorus attests to the fact that the initiators produce radicals which are scavenged by oxygen. Because of the similar reaction conditions, an order of reactivity can be obtained for the initiators from the observed induction periods using the relationship

$$R_I \propto \frac{1}{t_i}$$

The results are shown in *Table 1*.

It must be stressed that this order of reactivity was derived assuming that each compound absorbs the same amount of light, which in fact is not the case[20]. However, the purpose of the investigation using laser nephelometry was to establish the approximate efficiency of the photoinitiators under conditions closely associated to those employed in the u.v. curing process, which uses a polychromatic light source (which is also a mercury arc lamp) and is susceptible to the inhibiting effect of oxygen. Thus the measurement of induction periods is useful and from these (despite the assumptions, which lead to a tolerable level of inaccuracy) the order of reactivity can be expressed as follows:

TMBPO ∼ DMBPO > BDMP > TMBMP > TMBEP >
> BDEP

If the other photoinitiators are included, the order of reactivity becomes:

TMBPO ∼ DMBPO > DMPA > BME > BIPE >
BDMP > TMBMP > TMBEP > BDEP

The addition of amine appeared to have little perceptible effect upon the polymerization initiated by the acylphosphine oxides (*Table 1* entries 4 and 5) whereas with the benzoylphosphonates (*Table 1* entries 6 and 7) the effect of amines was unpredictable. With substituted acylphosphonates the amine reduces the induction period but, surprisingly, the rate of polymerization, especially for TMBEP, is reduced (*Table 1* entries 8 and 9). The effect may be due to the amine participating in a chain transfer process, thereby leading to low molecular weight polymers and consequently less precipitation of polymer. For the benzoylphosphonate BDEP, the amine added inhibited polymerization for the duration of the experiment. (*Table 1* entry 7). The method does not allow us to assess whether any polymerization has occurred during this period to give low molecular weight oligomers which are soluble in the propan-2-ol. With the conventional photoinitiators, 2,2-dimethoxy-2-phenylacetophenone and benzoin methylether, the effect of added amine was not particularly dramatic, which is in accord with initiation by the Type 1 process (*Table 1* entries 2 and 3). The effect of added triphenylphosphine sulphide was also investigated since it is known that this compound reacts with peroxy radicals, and therefore its addition should lead to a more rapid depletion of oxygen in the reaction mixture. Surprisingly the added sulphide had no beneficial effect, but rather the reverse. It is conceivable that the sulphide is acting as a trap for photoinitiating radicals although the precise mechanism for this process is unclear[23].

That the observed induction period is due to trapping of photoproduced radicals is shown by the results obtained by adding conventional radical scavengers, for example, ditolylethylene, diphenylethylene and 2,2,6,6-tetramethylpiperidin-1-oxyl to the reaction mixtures (*Table 2*). Increasing the concentration of these radical scavengers in the reaction mixture led to an increase in the induction period, with the rates of polymerization being similar. Increasing the concentration of the scavengers also decreased the amount of polymer formed. This is to be expected if under the conditions of the experiment the initiator is completely consumed due to the presence of scavengers, which will lead to fewer radicals being produced that can initiate polymerization. In addition, a consideration of the relative concentrations of the scavengers compared with TMPTA leads to the conclusion that the photogenerated radicals react far more efficiently with the scavengers than the TMPTA. It is interesting to note that DPE is slightly less efficient as a scavenger than DTE. This can be attributed to the former giving a radical adduct which can react via the free *para* position of the phenyl groups with other radicals, e.g. growing radical chains[24,25].

Bulk polymerization of methyl methacrylate and styrene

The bulk polymerization results showed yet again that added amine had little effect upon the amount of polymer formed when the acylphosphine oxides were used as initiators (*Table 3* entries 4 and 5). The amount of measurable polymer formed was dependent, however, on the solvent used to precipitate the polymer (*Table 3*). In all cases the amount of precipitate formed was less when methanol was used instead of petroleum ether for this purpose. This result probably stems from the greater solubility of the lower molecular weight oligomers in methanol than in petroleum ether.

The effect of added amine was more marked with the substituted acylphosphonate (*Table 3* entry 8) than with the acylphosphine oxides (*Table 3* entries 4 and 5), but the most dramatic effect was with the benzoylphosphonates (*Table 3* entries 6 and 7). In the last case the amount of precipitated polymer was vastly increased by adding amine. This result may be due to the benzoylphosphonate abstracting hydrogen from the amine in preference to intramolecular hydrogen abstraction[26,27] to give an α-aminoalkyl radical which is capable of initiating polymerization. Benzoin methylether, not surprisingly, was found to be an efficient initiator for polymerization although there is a discernable induction period (*Table 3* entry 1). In accordance with previous findings, benzil is a remarkably inefficient initiator, but the effect of added amine improves its performance substantially (*Table 3* entry 3). This improvement stems from the benzil reacting with the amine via a hydrogen abstraction, to give α-aminoalkyl radicals capable of initiating polymerization.

The efficiency of the polymerization of styrene by an acylphosphine oxide was also studied and it can be seen from the results that the efficiency is similar to that obtained with 2,2-dimethoxy-2-phenylacetophenone (*Table 3* entries 9 and 10).

Photoinitiated polymerization of thin films

All three types of organophosphorous compounds initiated the cure of acrylate films with varying degrees of efficiency. The acylphosphine oxides led to cure at speeds of approximately 1 m min^{-1} or 9.6 s, but their efficiency was increased by the addition of amine (*Table 4* entries 1, 2 and 9). Since added amine had little effect on the bulk polymerization initiated by the acylphosphine oxides and on the solution polymerization monitored by laser nephelometry, the beneficial effect of added amines in the u.v. curing tests must be due to their decreasing the efficiency of oxygen inhibition.

The acylphosphonates proved to be less efficient initiators than the acylphosphine oxides, curing at speeds of less than 0.5 m min^{-1} or 19.2 s, which is in agreement with the findings of Schnabel *et al.*[27] However, their performance is improved by the addition of amines (*Table 4* entries 5 and 6) and this can be ascribed to the amines reducing oxygen inhibition and also increasing the efficiency of production of initiator radicals. The high gloss epoxy–acrylate films produced were very coloured. The films cured using the acylphosphine oxides were a lighter brown/yellow colour than those cured by the acylphosphonates. The latter were probably darker in colour due to their longer exposure to u.v. light. It was not possible to distinguish clearly between the unsaturated polyester films cured using an acylphosphine oxide or an acylphosphonate. All of the polyester films produced by these organophosphorus compounds were of high gloss, clear and only very slightly coloured.

After bulk polymerization investigations to determine the efficiency of styrene polymerization using an acylphosphine oxide and 2,2-dimethoxy-2-phenylacetophenone (*Table 3* entries 9 and 10), a more extensive study was undertaken of the curing of unsaturated polyesters in styrene using various organophosphorus compounds as photoinitiators. From *Table 4* it can be seen that the unsaturated polyester system cures slowly and that even some acylphosphonates give a cure rate similar to the best acylphosphine oxide. This is no doubt due to the propagation reaction determining the cure speed rather than the efficiency of the photoinitiator.

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