R = n-alkyl, or alkyl substituted by hydroxy and/or alkoxy groups to provide excellent solubility in coatings

R' = H, CH$_3$, OH
to tune absorption spectrum

R'' = H, CH$_3$, OR

2

R, R' = optional
R'' = alkyl

3   4   5

and torsional modes of the molecule are responsible for the extremely rapid and effective radiationless deactivation.

Another promising new class of UV absorbers, the 2-(2-hydroxyphenyl)-1,3,5-triazines 2 [4] is being investigated and developed for application in coatings, plastics, and color photographic paper.

Such UV absorbers exhibit very high performance and thermal stability. They can be made liquid by appropriate choice of the substituents R, R', and R''. The liquid form is preferred for automotive coatings.

3. Adjustment of New Hindered Amine Light Stabilizers (HALS) to Future Technologies

HALS compounds have been known for more than 30 years. Commercially available HALS are based on 2,2,6,6-tetramethylpiperidine (3, R = H, R' = H).

HALS 3 (R = H, CH$_3$) as well as its nitroxyl radical 4 and the N-alkoxyamine 5, both produced from 3 during photooxidative degradation of polymers, are all extremely effective free-radical scavengers [5] and stabilizers for plastics and

coatings. Compatibility and long-term retention are obtained by adjustment of R'.

Migration of post-added traditional HALS 3 amd attachment of functionalized new HALS (e.g. R, R' = unsaturated groups) to the polymer are both subjects of current investigations. In the latter case copolymerization or grafting techniques are applied, e.g. grafting during extrusion ('reactive processing'). Polymer-bound photo-stabilizers outperform traditional products in special new applications such as polymer blends or systems in extractive environments.

4. Conclusion

Polymers and coatings of extended lifetime require light stabilizers of increased performance. New products offer better protection due to their superior efficiency and their ability to remain in the substrate.

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Recent Developments in Radical Photoinitiator Chemistry

Allan F. Cunningham, Vincent Desobry, Kurt Dietliker*, Rinaldo Hüsler, and David G. Leppard
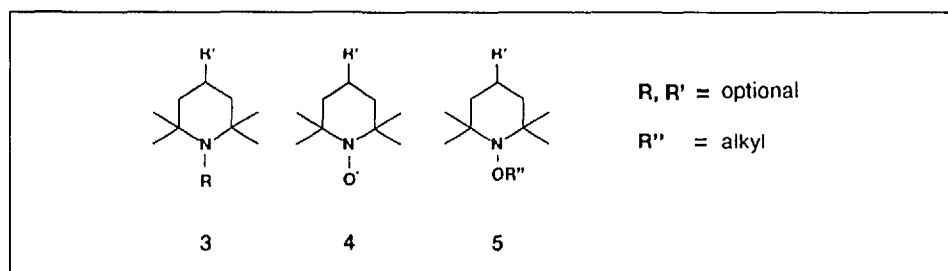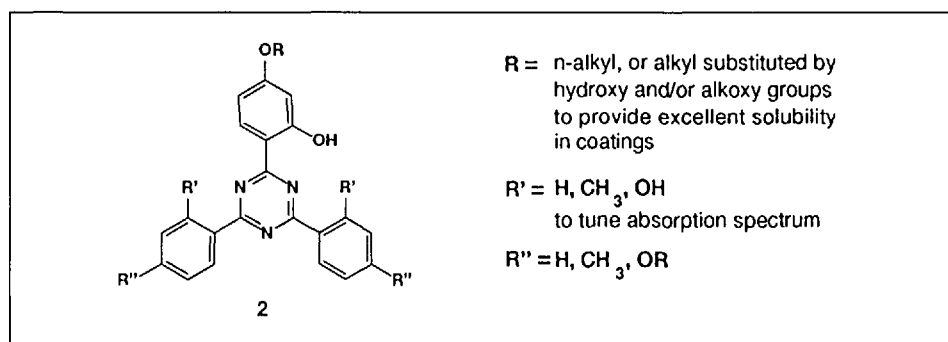
Abstract. Radiation curing is an established technology used in many industrial manufacturing processes. New applications and technical specifications stimulate the continuous development of tailor-made photoinitiators which can efficiently meet specific requirements. A new class of radical photoinitiators, bisacylphosphine oxides (BAPO), give four initiating radicals per photoinitiator molecule and undergo photobleaching of the low-energy absorption band. These features make the compounds highly efficient for radiation curing of highly opaque white pigmented systems, thick coatings, or fiber-reinforced formulations.

1. Introduction

Light-induced polymerization is the basis of important advanced technologies, since it is among the most efficient methods capable to achieve fast and extensive curing of multifunctional oligomers and monomers. Highly reactive systems are cured within a fraction of a second upon exposure to intense UV radiation or laser beams, transforming the liquid resin into a strongly cross-linked solid polymer without the need of additional heat [1].

These features translate into technical advantages which made radiation curable coatings one of the most rapidly develop-

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Polymers and coatings of extended lifetime require light stabilizers of increased performance. New products offer better protection due to their superior efficiency and their ability to remain in the substrate.

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Abstract. Radiation curing is an established technology used in many industrial manufacturing processes. New applications and technical specifications stimulate the continuous development of tailor-made photoinitiators which can efficiently meet specific requirements. A new class of radical photoinitiators, bisacylphosphine oxides (BAPO), give four initiating radicals per photoinitiator molecule and undergo photobleaching of the low-energy absorption band. These features make the compounds highly efficient for radiation curing of highly opaque white pigmented systems, thick coatings, or fiber-reinforced formulations.

1. Introduction

Light-induced polymerization is the basis of important advanced technologies, since it is among the most efficient methods capable to achieve fast and extensive curing of multifunctional oligomers and monomers. Highly reactive systems are cured within a fraction of a second upon exposure to intense UV radiation or laser beams, transforming the liquid resin into a strongly cross-linked solid polymer without the need of additional heat [1].

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ing fields in the entire coating industry. Firstly, radiation-curable coatings need less – if any – additional solvents and are thus of ecological interest. Secondly, this coating technology exhibits a number of economic advantages such as compact curing installations, high productivity because of the high cure speed, and, most important, energy savings compared to conventional thermal curing. Energy is usually only needed to initiate the curing process which is operated at the temperature achieved by the reaction heat and the IR emission of the irradiation source. The excellent properties of the coatings thus obtained allow their use in surface protection or printing applications on various materials such as paper, wood, plastic and metal.

Another feature of the light-induced polymerization is the possibility for image-wise irradiation through a mask or by a laser direct-imaging process. This technique allows the production of high-resolution relief images needed in applications such as printed circuit board production, printing plates, or stereolithography [2].

Common to all these technologies is the use of a suitable photoinitiator. This compound produces upon absorption of light of suitable wavelengths highly reactive photoproducts, capable of initiating a polymerization reaction. The development of new high performance photoinitiators which can meet the requirements of newly emerging applications is, therefore, a major goal for industrial research in the field of radiation curing.

Radical photopolymerization has found most widespread technical use so far, although the specific features of cationically polymerizing systems lead to increasing use of these systems. Accordingly, photoinitiator research in industry during the last years has mainly focused on the development of UV and visible photoinitiators for radically polymerizing systems, and a variety of radical photoinitiators are commercially available [3].

2. Photoinitiators for Clear Coatings and Pigmented Systems

Some of the most efficient, commercially available photoinitiators for radical polymerization, which find widespread use in various industrial applications, are shown in *Fig. 1*. A common feature of all these compounds is the acetophenone structure. Upon irradiation, they undergo a *Norrish* type-I cleavage, producing a benzoyl and a substituted alkyl radical. Both radicals can initiate the polymerization of ethylenic C=C bonds, albeit with different efficiency.

The main features of these initiators are high quantum yields for radical formation, the formation of highly reactive radicals, adequate solubility in the resins, and high thermal and chemical stability [3]. Each of the compounds has been developed to match the requirements of a specific range of technical applications. As an example, the short triplet lifetime of 1 allows its use in the presence of monomers such as styrene, which efficiently quench the triplet state of other photoinitiators. The structures of the solid photoinitiator 2 or the liquid compound 3 prevent the formation of yellowish photoproducts and make these compounds especially suitable for applications in clear coatings where no yellowness is tolerated. Compound 4 contains the same photoreactive group as 3, but the additional substituent on the aromatic nucleus allows further chemical reactions on the primary OH group and improves secondary properties, such as compatibility with aqueous systems and the volatility of the compound.

The curing of clear coatings can be achieved with high efficiency using these compounds, since the formulations are transparent in the near UV where these photoinitiators have sufficient absorption. Formulations containing additional components, which absorb or scatter the light of these wavelenghts, are more difficult to cure. Examples are clear coatings containing UV absorbers for improved out-door weatherability, fiber reinforced plastics, or pigmented systems such as colored coatings or printing inks. Since these components compete with the photoinitiator for the incident light, compounds such as 1–4 are not efficient in these systems. The curing of these systems remains a major challenge in radiation curing, and most efforts in photoinitiator research during the last years have, therefore, been devoted to the development of photoinitiators for these applications.

A way to overcome the limitations of photoinitiators 1–4 is to shift their absorption spectra to longer wavelengths, where sufficient light is available [4]. This concept has been realized with the introduction of α-amino-ketone photoinitiators 5 and 6 (*Fig. 2*) [5][6].

The absorption maxima of these compounds is red-shifted by the introduction of suitable substituents on the aromatic nucleus (*Fig. 3*). The character of the low-
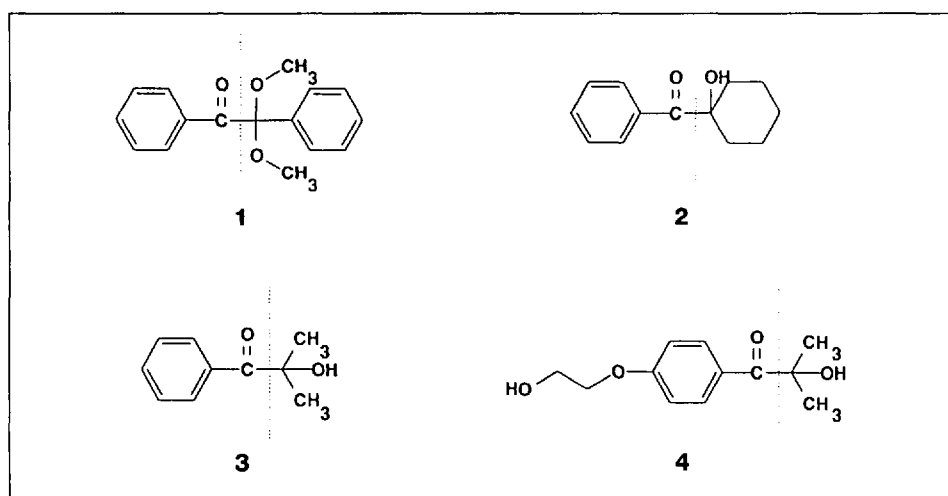

Fig. 1. *Photoinitiators for clear coatings, printing plates, and water-borne systems.* The dotted lines indicate the site of photoinduced cleavage.
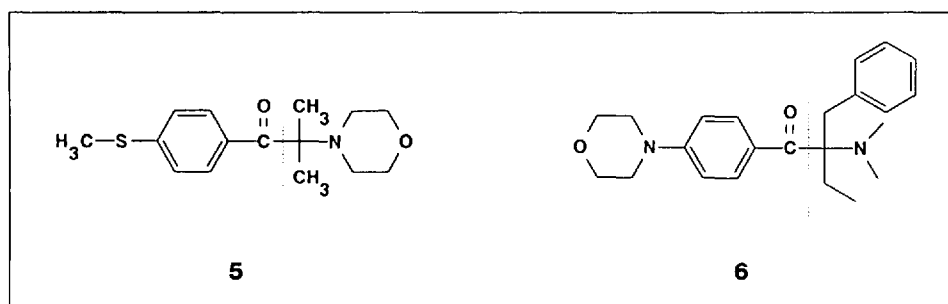

Fig. 2. *Photoinitiators for pigmented systems and resist applications.* The dotted lines indicate the site of photoinduced cleavage.
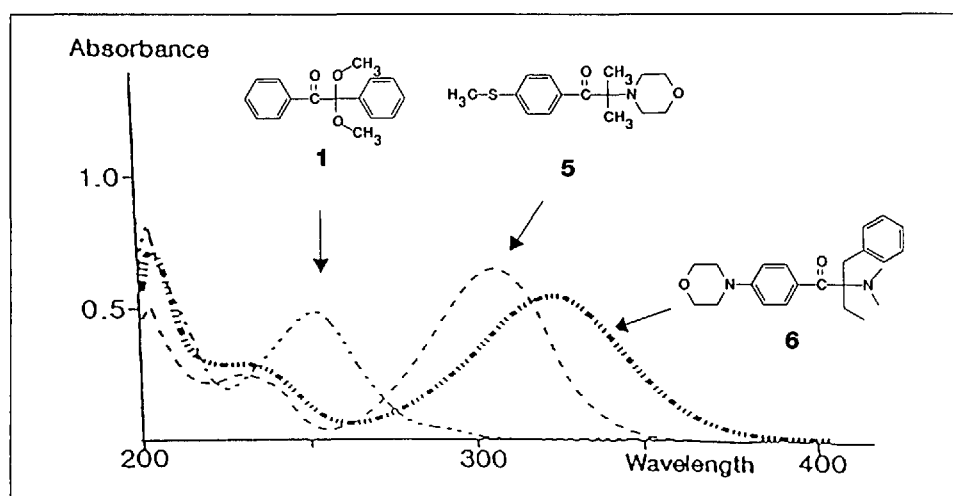
Fig. 3. *Absorption spectra of photoinitiators* **1**, **5**, *and* **6**

Fig. 4. *New BAPO photoinitiator for pigmented systems.* The dotted lines indicate the sites of photoinduced cleavage.

energy absorption band gradually changes from a nπ* transition, as found, *e.g.*, in compound **1**, to a typical charge-transfer band in **6**. This change in the character of the lowest excited triplet state influences the photochemical reactivity; however, if the substituent at the α-position is a suitable amino group, the efficiency to undergo α-cleavage can be tuned to be similar to that of compounds **1–4**.

More important than the position of the main absorption band in the spectra of compounds **5** and **6** is the fact that these absorptions extend well up into the visible part of the spectrum, thereby allowing for sufficient light absorption in the presence of most types of pigments. These photoinitiators are thus highly efficient in pigmented systems.

The absorption of the photoinitiator or its photoproducts at the blue end of the visible spectrum imparts, however, yellowness to the cured formulation. This is the case for both α-amino-acetophenones **5** and **6**. These photoinitiators are, therefore, successfully used in different colored coatings, inks or resist materials, where a slight yellowness is either of no concern or outweighed by the color of the pigment. They can, however, not be used in applications such as white-pigmented coatings or inks, where yellowness is not tolerated.

3. Development of New Photoinitiators for White-Pigmented Systems and Thick Layers

Rutile-type titanium dioxide, preferentially used as a pigment in white coatings due to its high hiding power, acts as an efficient screen for the light of all wavelengths below 380 nm. A photoinitiator, efficient in the presence of this pigment, has, therefore, to absorb sufficient light of

wavelengths longer than 380 nm, while its photoproducts must not absorb light in the same region. Accordingly, the design of a new photoinitiator which can fulfill both requirements was necessary.

The principle of photobleaching is known for a variety of compounds. Photoinitiators using a dye as chromophor often undergo a change in color during the irradiation, and titanocenes are another example of visible photoinitiators showing this effect [7]. The bleaching does, however, usually not result in colorless

products, which is of little concern in application areas for these initiators, such as the fabrication of printing plates or resists.

A photoinitiator useful in white pigmented system must, however, undergo complete bleaching of the absorption at the blue end of the visible spectrum, resulting in colorless products. A first class of photoinitiators which fulfills these requirements are monoacylphosphine oxides (MAPO) [8], which were introduced some years ago. The increasing demand
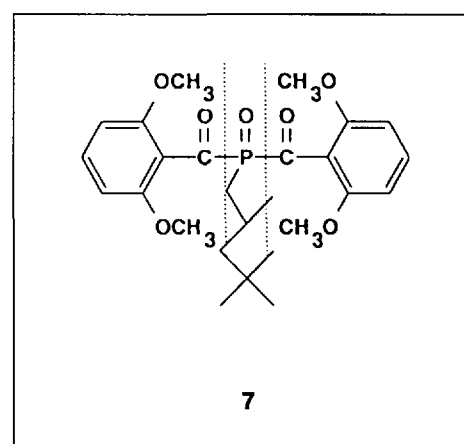
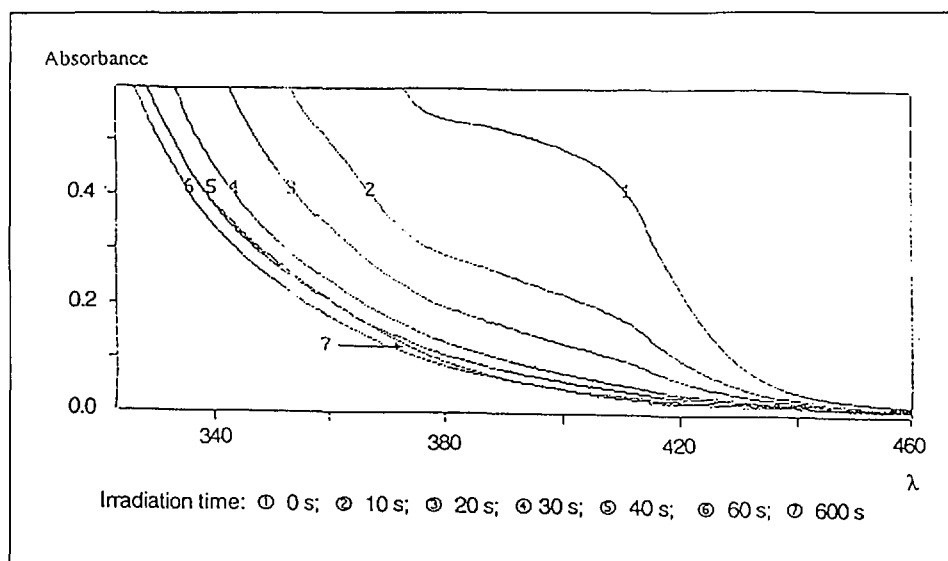Scheme. *Photopolymerization Initiated by BAPO Photoinitiator* **7**
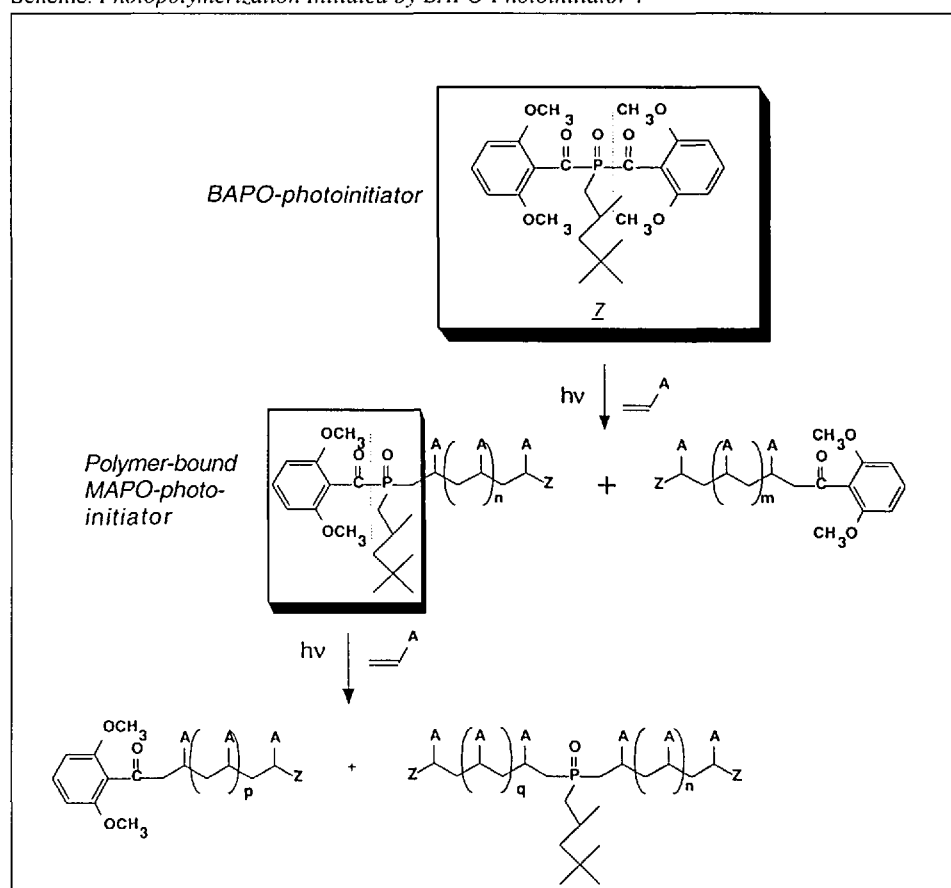
Fig. 5. *Photo-bleaching of BAPO photoinitiator* 7 *during irradiation in the presence of an excess methyl* tert-*butylacrylate*

for better hiding power of the coating required, however, the development of a new and more efficient photoinitiator, which allows the curing of formulations containing a higher pigment loading and higher film thicknesses. Research following these lines resulted in the recent introduction of new bisacylphosphine oxide (BAPO) photoinitiators. The structure of the compound 7, which has been commercialized this year as part of an optimized blend with the α-hydroxy ketone 3, is shown in *Fig. 4*.

The photochemistry of these compounds has been studied using CIDNP-NMR spectoscopy, preparative irradiation, and trapping techniques [9]. It was unequivocally shown that the photoinitiator undergoes cleavage of the C–P bond from a triplet state to give a benzoyl and a phosphinoyl radical. Both radicals efficiently initiate the polymerization reaction (*Scheme*). The phosphinoyl radical is converted into a polymer-bound monoacylphosphine oxide (MAPO) group, which, in turn, is a photoinitiator moiety and undergoes a second photoinduced cleavage reaction. A second pair of initiating radicals is thereby formed which also contribute to the initiation of polymerization. The BAPO photoinitiator, therefore, produces four initiating radicals in a stepwise process, twice as much than other α-cleavage photoinitiators which can only undergo one cleavage reaction. This high radical yield explains the high reactivity of this photoinitiator found in various applications.

Bisacylphosphine oxides have low energy absorption bands in the range of 380–420 nm ($\varepsilon = 600$ l/mol·cm), which are attributed to interactions between or-

bitals on the carbonyl and the phosphinoyl groups. The absorption of compound 7 in the range of 350–450 nm is shown in *Fig. 5* (curve 1). Since the C–P bond is cleaved in the photochemical reaction (*Scheme*), the chromophore responsible for the long-wavelength absorption is destroyed. This results in the photobleaching shown in *Fig. 5*. Most important for applications in white pigmented systems is the fact that no new photoproducts absorbing in the visible are formed.

The high performance of this photoinitiator was shown in different applications [9], where coatings with higher pigment loadings or higher film thickness could be cured than with the hitherto available photoinitiators.

An additional advantage of the photobleaching is the fact that the optical density of the formulation in the range where the bleaching occurs diminishes during the curing process. The thickness of the resin layer that can be cured by irradiation is usually limited by the fact that light can only penetrate into the formulation to a depth determined by the photoinitiator absorption. The diminishing optical density of formulations containing the photobleaching initiator 7 allows the light to penetrate continuously into deeper layers. Formulations of several cm thickness can thus be completely cured with the new BAPO photoinitiator.

4. Conclusions

The continuous demand for photoinitiators which can meet the requirements of new applications in the coating and imaging technology has provided a major stim-

ulus for the development of new photoinitiators over the past years. As a consequence, radiation curing became an established technique in applications which were regarded as not being feasable for this technology some years ago. An example is the curing of highly pigmented white coatings, which has become an industrially useful process with the introduction of suitable photoinitiators.

This development will continue in the future. On the one hand, the technical and economical advantages of radiation curing, as well as the increasing limitations of allowed amounts of volatile organic compounds, will initiate a change from other curing methods using solvent-based systems to this technology. On the other hand, new applications requiring photoinitiators with new properties are steadily emerging, and the demand for more efficient photoinitiators for existing markets will continue. The design and development of new tailor-made compounds, which can cope with both the technical and ecological demands, is, therefore, a continuing challenge for industrial research.

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