Liquid bis-acylphosphine oxide (BAPO) photoinitiators

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Abstract

Bis-acylphosphine oxide (BAPO) photoinitiators (PIs) have been used extensively for high TiO2 loading UV ink and sunlight curing applications due to its superb photo speed. However, BAPO's low solubility and low dissolution speeds in oligomers compared to mono acylphosphine oxide creates difficulties for the formulator to use. Therefore, a liquid BAPO which can be easily blended into UV system would be a desired product in the UV Curing Industry. A liquid BAPO that had the same photo speed as a solid BAPO was commercialized during late 1990's, but was discontinued several years ago for unknown reasons. Since then only diluted liquid BAPO is commercially available in the market. A novel liquid BAPO with a freezing point below -20°C and exhibits photo speed comparable to the solid BAPO will be introduced. Herein, its chemical structure and reaction mechanism will be discussed in great details.

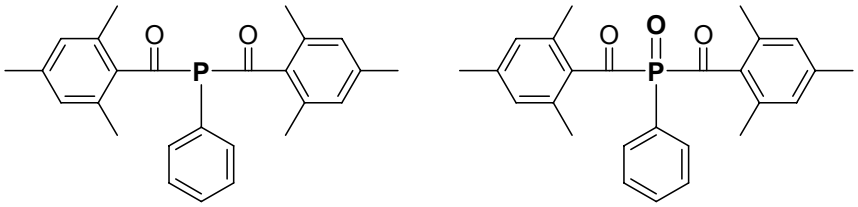
Introduction

Bis-acylphosphine oxide (BAPO) is a very potent photoinitiator (PI) in light-induced polymerization of the ethylenically unsaturated compounds. It has a higher extinction coefficient than acyl phosphine oxides such as TPO or TPO-L and thus usually leads to superb photo speed. However, due to BAPO's symmetric chemical structure, its poor solubility in a variety of monomers and oligomers seriously limits its use in some applications. To further explore the scope of BAPO, the development of liquid bis-acylphosphine oxides or the derivatives with comparable photoactivity is highly desirable. In this presentation, a liquid mixture (LMBAPO) of bis-acylphosphine (BAP) and bis-acylphosphine oxideis (BAPO) is shown to be as effective as a solid BAPO.

The New Liquid BAPO

LMBAPO: LMBAPO has the structures shown in Scheme 1 below.

Scheme 1: LMBAPO Structures



The composition of LMBAPO is determined to be about 1:1 mixture of BAPO and BAP by HPLC. The UV absorption spectrum of LMBAPO compared to TPO and BAPO is shown in Figure 1.

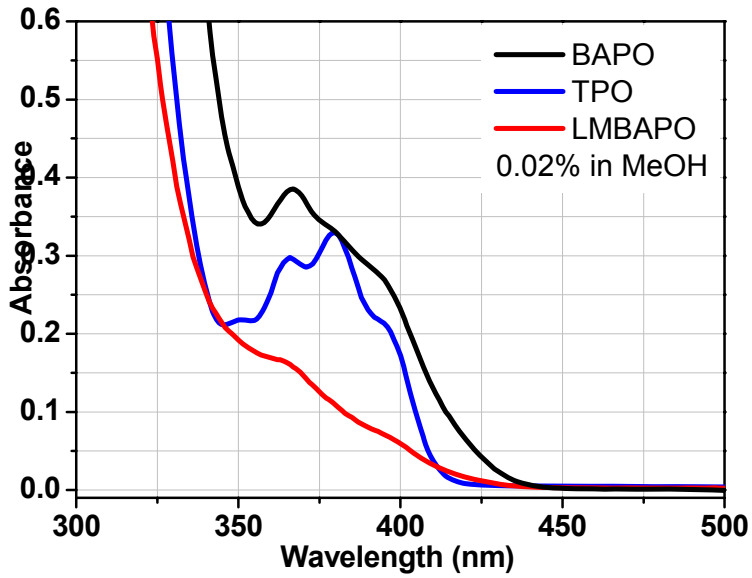


Figure 1. UV Absorption of LMBAPO, BAPO and TPO

The absorption spectrum of LMBAPO shows similar broad shoulders to BAPO at 350-400 nm. Even the absorption of LMBAPO is not as strong as TPO and BAPO; it is proposed to be oxidized to BAPO and results in same or comparable absorption intensity of BAPO.

Liquid form photoinitiators provide below advantages over their powder form counterparts.

1. Easy to handle
2. High resin and pigment compatibilities
3. No crystallization problem
4. No fine dust hazards

LMBAPO is a yellow liquid and has remained liquid at -20 ^{o}C for more than three months. The typical physical properties of LMBAPO are listed in Table 1.

Table 1: Physical Properties of LMBAPO

Item	Description
Appearance	Yellow liquid
Viscosity	1650 @20 ^{o}C
Color(Gardner)	3.0. (10% in Toluene)
Freezing point	<-20 ^{o}C
Density	1.14 g/cm^3 @20 ^{o}C

Solubility of LMBAPO v.s. BAPO

The solubility of LMBAPO and BAPO in a variety of solvents and monomers is compared and collected in Table 2. As shown in table 2, LMBAPO is more soluble than BAPO in most commonly-used solvents and monomers. In addition, BAPO containing solutions usually crystallize easily at room temperature, which is not the case for LMBAPO even at a lower temperature.

Table 2: Solubility Property of LMBAPO v.s. BAPO

	BAPO[a]	LMBAPO
Acetone	14	>30
n-Butyl acetate	6	>30
Toluene	22	>50
HDDA	5	>30
IBOA	5	>30
TMPTA	5	>30
TPGDA	5	>30

[a]: Data is obtained from Ciba Specialty Chemicals (BASF).

Photoactivity of LMBAPO

The photoactivity of LMBAPO is compared to BAPO and TPO in 50% TiO2 loading UV ink. The test results on PVC sheet are shown in Table 3. For thin film (10 μm), the tape adhesion test indicates that solid BAPO is slightly better than LMBAPO. However for thick film (150 μm), LMBAPO is much superior to TPO and BAPO. The reasons for the discrepancy of photoactivity of LMBAPO v.s. BABO in thin and thick UV coatings are not clear. Theoretically the lifetime of BAPO upon UV radiation is shorter than BAP. For thick coating, if the loading of BAPO is not high enough to trigger the curing of all the monomers and oligomers, the adhesion on the substrate will become poor. To the contrary, BAP can be oxidized to BAPO smoothly and thus still can release active radical initiators after multiple exposures.

Table 3: Photoactivity Comparison of LMBAPO v.s. BAPO

Ink UV white[a]	100	100	100
184[b]	3	3	3
TPO[c]	1		
BAPO		1	
LMBAPO			1
Total	104	104	104
Rel. Cure Speed (10 μm on PVC sheet)	68 m/min×2	68 m/min×1	68 m/min×1
Tape adhesion		◎[d]	
Gloss	◎	◎	◎
Rub resistance		◎	◎
Rel. Cure Speed (150μm on PVC sheet)	20 m/min×6	20 m/min×4	20 m/min×2
Tape adhesion			◎
Gloss	◎	◎	◎
Rub resistance		◎	◎

[a]: TiO_2 loading: 50%

[b]: Available from Chitec Technology Co. as Chivacure 184

[c]: Available from Chitec Technology Co. as Chivacure TPO

[d]: ◎ Superior

Conclusion

We have presented a new photoactive mixture of bisacylphosphine and bisacylphosphine oxide, LMBAPO. It is a low-viscosity liquid which is devoid from the drawbacks of BAPO. Besides, the photoactivity is comparable or even better than solid BAPO, especially for thick coatings. Since LMBAPO is the precursor of BAPO, it is more cost-effective than BAPO from the point of view of synthesis. Currently it is the most valuable alternative for BAPO in ink and coating industry. We are focusing on the development of a revolutionary new liquid BAPO derivative which will be disclosed in the near future.