

Novel Polymeric Photoinitiator and Sensitizer

Dr. Qingjin YAN^a, Wenchao ZHAO^a, Shidian HAN^a, John HUIBERTS^b

(a: Insight High Technology Co., Ltd. Beijing P.R.China;

b: IGM Resins B.V., the Netherlands)

E-mail: yan@iht.com.cn

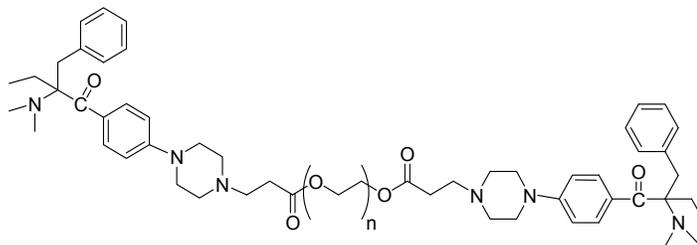
Abstract : Two novel compounds of di-functional piperazine based alpha-aminoacetophenone and acetophenone have been introduced to apply in ultraviolet curing coatings and inks as free radical type I photoinitiator and sensitizer respectively with the property of extremely lower odor, lower migration and higher curing speed.

1. Introduction

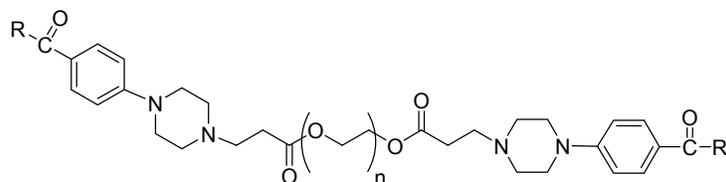
UV-curing technology has been industrialized since 1970's, and has been developed rapidly for more than 30 years as people have been paying more and more attention on environmental protection. Although UV curing system is environment friendly, small molecular photoinitiators still have some disadvantages. For instance: ①the residue of photoinitiators in cured film or the migration of photolysis fragments of photoinitiators may lead to toxicity. ②In addition, photolysis fragments for most of these photoinitiators have some odor since the molecular weight of them is relatively low.. These kinds of problems have limited the development of applications of photocured products in sanitation and food package materials. The development concept of bonding low molecular weight photoinitiator to polymer chains or incorporating polymerizable groups into low molecular weight photoinitiator would solve these problems and bring the new prosperity of UV industry.

Insight High Technology Co., Ltd (IHT) and IGM Resins B.V (IGM) had reported two polymeric free radical type II photoinitiators with lower migration, lower odor, and robust curing properties^[1,2].

In this article, two novel polymeric free radical type I photoinitiators, polymeric piperazine based alpha- amino acetophenone (Polymeric 910) and polymeric piperazine based acetophenone (PPA)^[3], are introduced and systematically investigated on their curing speed, solubility, migration and odor compared to corresponding photoinitiators with lower molecular weight. The chemical structures of the two photoinitiators are as below (Scheme 1 and 2) :



Scheme 1. Polymeric piperazine based alpha- amino acetophenone (Polymeric 910)



R = Me , Et.

Scheme 2. Polymeric piperazine based acetophenone (PPA)

2. Experiment section

1) Raw materials and formulations

Table 1 and 2 are the list of raw materials which used for photocuring coatings and inks formulations.

Table 1 raw materials for photocuring systems

Components	Formulation A	Formulation B	Manufacturer
6145-100	35	35	Eternal Chemical Industry
EO-TMPTA	30	30	TianJin TianJiao
HDDA	30	30	TianJin TianJiao
Irgacure 369	3.75	/	Ciba
Polymeric 910	/	5	IHT

Note: the parts of photoinitiator in the formulations are added in an amount equal to molar amount of photoinitiation reactive fragments.

Table 2 raw materials for photocuring pigmented systems

Components	Formulation C	Formulation D	Formulation E	Formulation F
6311-100	66	66	66	66
EO-TMPTA	20	20	20	20
Jet Black 250	10	10	10	10
PPA	/	3	/	2
Irgacure 369	/	/	3	1
ITX	1	1	1	1
Triethanolamine	3	/	/	/

2) Test methods

a) Gel conversion

The coating is applied on glass sheet by wire wound rod (thickness of film is 45 μ m), and soaked in acetone for 72hrs after cured. The gel conversion is calculated by the following equation:

$$\text{gel\%} = \frac{\text{the weight of the film after dissolved}}{\text{the weight of the undissolved film}} \times 100\%$$

Curing condition: Lamp distance: 20cm; lamp power: 500W.

b) Evaluation of yellowing of the films ^[4, 5]

Color meter is usually used to measure Y_{id}. The equation regulated in USA material test standard ASTM D1925 is:

$$Y_{id} = \frac{(130.11X - 114.94Z)}{Y}$$

Tester : SC-80C automatic chroma difference meter (Beijing Kangguang Apparatus Co.,

Ltd.), Y_{id} is directly outputted (thickness of film is 45 μ m).

Curing condition: Belt speed:4m/min; lamp distance: 13cm; lamp power:1000 \times 2W.

c) Odor ^[6]

The coating is applied on PT paper by wire wound rod with a coating area being 1dm². After cured by UV-curing machine, it is kept at 60 $^{\circ}$ C for 30min. The odor is valued by a number from 0 to 5. The smaller of the value, the lower the odor.

Curing condition:

Belt speed: 4 m/min; lamp distance: 13cm; lamp power:1000×2W.

d)Migration ^[7]

The coating is applied on PT paper by wire wound rod with a coating area being 1dm². After the coating is cured by UV-curing machine, the films are placed in the simulating liquid of water and 3% acetic acid aqueous solution respectively and kept at 80°C for 2hrs. The amount of migration of photoinitiator is determined by HPLC.

Curing condition : belt speed: 4m/min, lamp distance: 13cm, lamp power:1000×2W.

e)Solubility

5.5g of Polymeric 910 or PPA is dissolved in 5g of HDDA, TPGDA, PEA, EO-TMPTA and TMPTA respectively. The solutions are heated to 60°C to be mixed uniformly and then placed at room temperature for 24hrs to observe whether there is precipitate. If there is no precipitate, the solubility is above 100.

The solubility of Irgacure 369 is determined by analyzing the content of initiator in supernatant of supersaturated solution at room temperature by NMR.

f) Hardness of film

Two high-pressure Hg lamps (80W/cm each) have a lamp distance of 13cm, and the thickness of tested film is 45µm. QYB pendulum hardness meter having amplitude of 5° is used for calculating relative hardness based on counts of glass board, which is equal to film counts/glass board counts.

Curing condition : belt speed: 4m/min, lamp distance:13cm, lamp power:1000×2W.

3. Results and discussion

3.1 polymeric piperazine based alpha- amino acetophenone (Polymeric 910)

3.1.1 IR and UV absorption

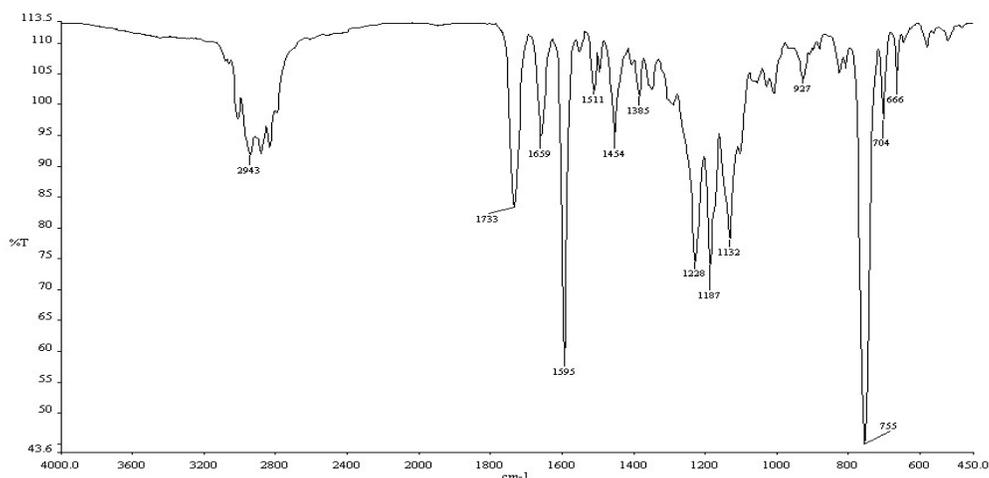


Figure 1. IR spectrum of polymeric piperazine based alpha- amino acetophenone (Polymeric 910)

Figure 1 is IR spectrum of polymeric piperazine based alpha- amino acetophenone. It shows that the peak at 3060cm^{-1} is assigned to the contraction vibration of C-H bond on phenyl ring, the peaks at 2943cm^{-1} , 2876cm^{-1} and 2792cm^{-1} are assigned to the contraction vibration of C-H bond in alkyl, the peak at 1733cm^{-1} is assigned to characteristic absorbance of $-\text{COO}$ group, the peak at 1647cm^{-1} is assigned to characteristic absorbance of C=O bond to benzene ring, and the peaks at 1595cm^{-1} , 1572cm^{-1} , 1511cm^{-1} are assigned to the skeleton inside vibration of phenyl ring.

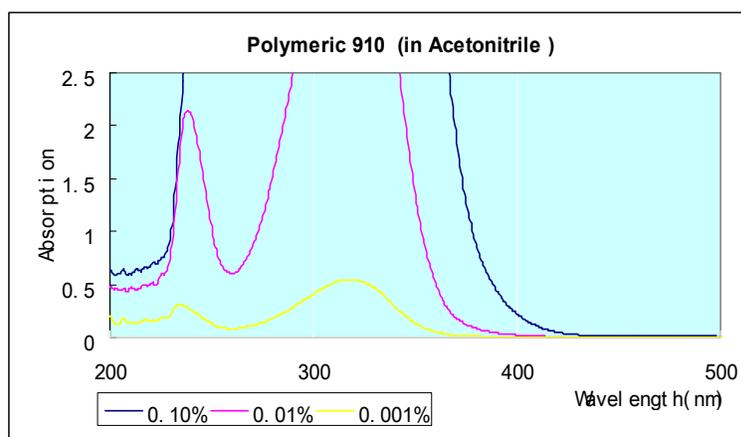


Figure 2. UV absorption spectrum of polymeric piperazine based alpha- amino acetophenone (Polymeric 910)

Figure 2 shows the UV absorption spectra of polymeric piperazine based alpha- amino acetophenone (Polymeric 910) in acetonitrile solution. From Figure 2 we can see that Polymeric 910 has relatively strong absorbance at 330nm and 240nm , consequently it is suitable for UV pigmented formulation and deep curing inks.

3.1.2 Gel conversion Rate of photocuring formulation

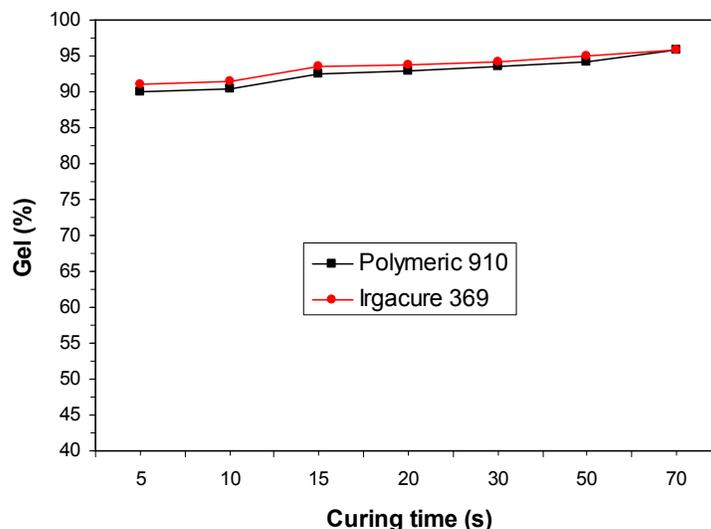


Figure 3. Effect of Polymeric 910 and Irgacure 369 on curing rate

Figure 3 shows effect of photoinitiators on curing rate. It can be seen that when the photoinitiator is added in an amount equal to the molar amount of photoinitiation reactive fragments, the initiation reactivity of Polymeric 910 is similar to small molecular weight Irgacure 369 .

3.1.3 Yellowing of cured film

Table 3 YID of different photocuring systems

formulations	YID
Polymeric 910	1.05
Irgacure 369	1.05

Table 3 showed the YID number of photocuring systems initiated by different photoinitiators, It can be seen that the yellowing extent of Polymeric 910 and Irgacure 369 are the same.

3.1.4 Hardness of cured films

Table 4 Hardness of different photocuring systems

formulations	Hardness
Polymeric 910	0.620
Irgacure 369	0.624

The cured film of Polymeric 910 has the similar hardness as that of Irgacure 369 formulation (table 4) . This is probably because that Polymeric 910 has substantially the same initiation reactivity as that of Irgacure 369, and thus the slight variation of formulation resulted from different amounts of Polymeric 910 and Irgacure 369 can be ignored.

3.1.5 Migration of the photoinitiators

Table 5 migration property of different photocuring systems

simulating liquid (water)		simulating liquid (3% acetic acid aqueous solution)	
Polymeric 910	Unable to detect Polymeric 910	Polymeric 910	Unable to detect Polymeric 910
Irgacure 369	Unable to detect 369	369	Unable to detect 369

From table 5 we can see that the migration amount of Polymeric 910 and Irgacure 369 is unable to detect.

3.1.6 Odor

Table 6 the odor level of different curing systems

formulations	Odor level
Polymeric 910	2
Irgacure 369	2

The cured films of both Polymeric 910 and Irgacure 369 have low odor (table 5) .

3.1.7 Viscosity-temperature curve and solubility

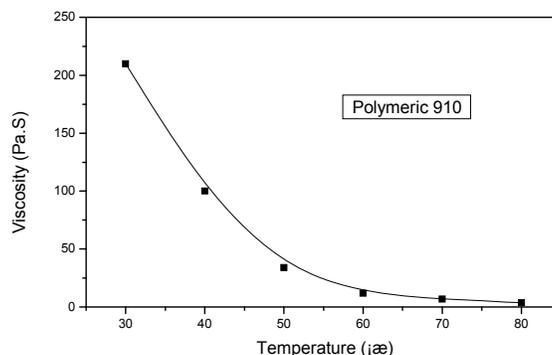


Figure 4. Viscosity-temperature curves of Polymeric 910

Figure 4 shows viscosity-temperature curve of Polymeric 910. Polymeric 910 has a high sensitivity to temperature since Polymeric 910 has large rigidity of molecular chains and high flow activation energy. Therefore, the viscosity of Polymeric 910 will decrease to a great extent when temperature increases slightly.

Table 7. Solubility of photoinitiators in different monomers

Solubility (20°C, g/100g)	HDDA	TPGDA	TMPTA	EO-TMPTA	PEA
Irgacure 369	10	6	5	5	15
Polymeric 910	>100	>100	>100	>100	>100

Solubility of Polymeric 910 is much higher than that of Irgacure 369 (table 7) , because Polymeric 910 is liquid substance performance and thus has better compatibility than Irgacure

369. The results means that polymeric 910 is very suitable in UV curing formulations with high viscosity and low monomer content, such as offset ink.

3.2 Polymeric piperazine based acetophenone photoinitiator (PPA)

3.2.1 Introduction

PPA, a polymeric piperazine based acetophenone sensitizer, can enhance and/or broaden UV absorption of Type II photoinitiators, and provide extremely efficient curing performance. PPA has good solubility and allows formulators to make stable photoinitiator blends with high reactivity. Higher level of preferred photoinitiators, e.g. 4-PBZ, can be held in solution. The shifted UV chromophore of PPA, enables the product to absorb more of the strongest emission wavelength from the medium pressure Mercury lamp at 313nm and 365 nm. The effect of PPA is most notable in black inks. The level of aminoacrylates in formulations containing PPA can be reduced, although some amine like EHA will still be required in the photoinitiator blend. PPA is a pale yellow liquid, and has no odor or known byproducts on curing. When used correctly, no migration is anticipated.

3.2.2 IR and UV absorption

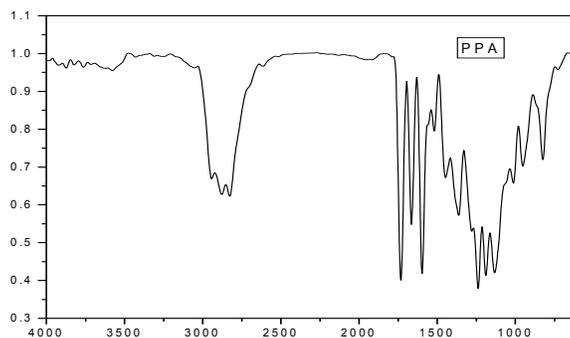


Figure 5. IR spectrum of Polymeric piperazine based acetophenone photoinitiator

Figure 5 is IR spectrum of polymeric piperazine based acetophenone(PPA). It shows that the peaks at 2951cm^{-1} , 2883cm^{-1} and 2824cm^{-1} are assigned to the contraction vibration of C-H bond in alkyl, the peak at 1734 cm^{-1} is assigned to characteristic absorbance of $-\text{COO}$ group, the peak at 1670 cm^{-1} is assigned to characteristic absorbance of C=O bond to benzene ring, and the peaks at 1593 cm^{-1} , 1521 cm^{-1} are assigned to the skeleton inside vibration of phenyl ring.

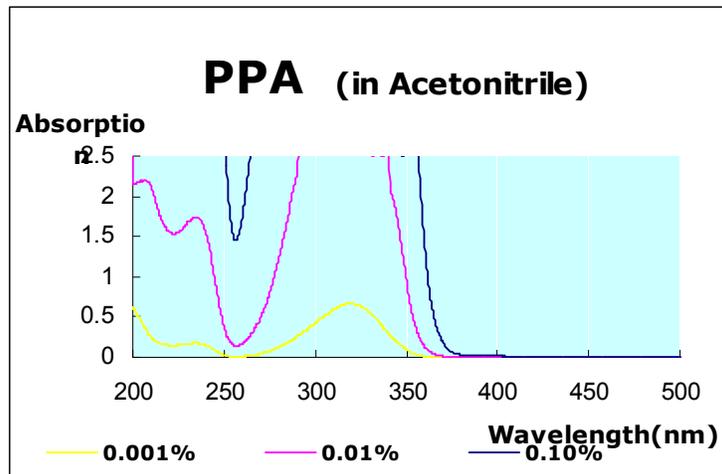


Figure 6 UV absorption spectrum of Polymeric piperazine based acetophenone photoinitiator

Figure 6 shows the UV absorption spectra of polymeric piperazine based acetophenone in acetonitrile solution. It can be seen from Figure 6 that PPA system has relatively strong absorbance at 332nm, thus it is suitable for pigment formulation and deep curing coatings and inks.

3.2.3 Viscosity-temperature curve and solubility

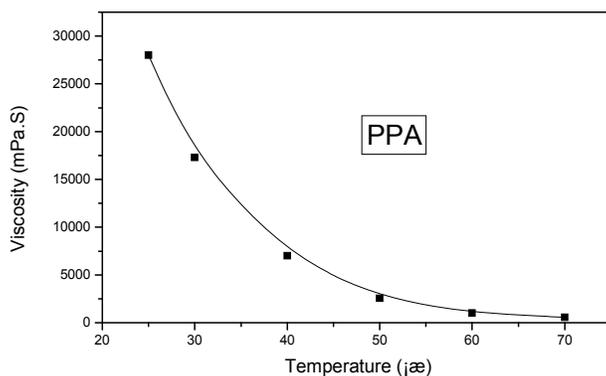


Figure 7. Viscosity-temperature curves of PPA

Figure 7 indicates viscosity-temperature curves of PPA. PPA has low viscosity and high sensitivity to temperature.

PPA is dissolvable with most of the UV-curable monomers and resins.

3.2.4 Hardness of cured films of photocuring pigmented inks formulation

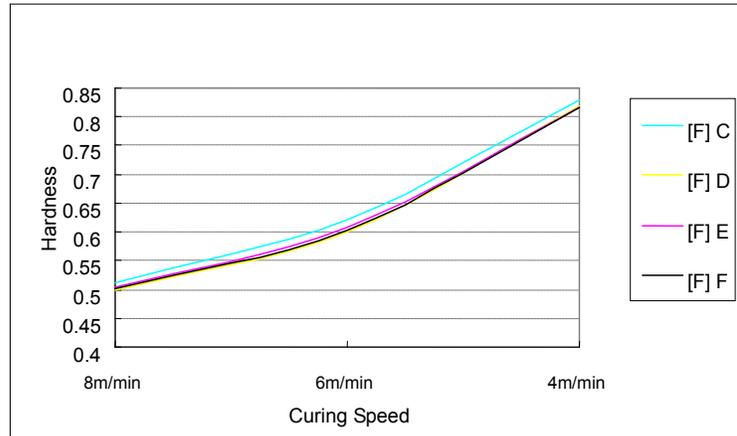


Figure 8. Hardness of cured films in the different pigmented formulations

From Figure 8 we can see that cured films in pigmented inks with PPA (Formulation D and F) have the similar hardness as that of Irgacure 369 (Formulation E) and triethanolamine (Formulation C). The results indicate that the curing performance of PPA in combination with ITX is similar to that of Irgacure 369 and triethanolamine.

4. Conclusion

Macromolecular photoinitiator, Polymeric 910 has the similar initiation reactivity, low odor and low migration as Irgacure 369, but has better compatibility with monomers as compared to Irgacure 369. Therefore, it is very suitable to apply in UV curing formulations with high viscosity and low monomer content, for instance, offset ink.

All kinds of free radical type II photoinitiators, such as benzophenone and thioxanthone derivatives, are effectively sensitized by PPA. Its high photoinitiating performance makes it especially suitable for pigmented UV curing systems, food packaging as well.

References

- [1] Han Shidian, et al, Proc. Radtech Asia 2005, p.61.
- [2] Frank Bertens, et al, Proc. Radtech Europe 2005. Volume I, p.471.
- [3] The two compounds were applied by Sun Chemical with patents of WO2005007637 and WO2005076074. IHT and IGM had gotten exclusive intellectual property license from Sun Chemical.
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- [6] Thomas Bolle. Proc. Radtech Asia 2003, p.172
- [7] European directive 89/109/EEC