A polymeric aminoketone type photoinitiator

Author: Dr. Chingfan Chris Chiu
Chitec Technology Co., Ltd.
Taiwan

Abstract

A novel polymeric photoinitiator (PI 3) based on aryl aminoketone structure and difuctional linker with molecular weight around 1,000-1,500 shows a comparable photospeed to traditional photoinitiator (PI 2) in various UV ink systems. PI 3 is in liquid form and is much less extractable before and after photo-curing compared to PI 2.

Introduction

Recently extractability and toxicity has become a concern among UV ink industries after the food giant Nestlé published its first recommended list of PIs in 2008. Surprisingly, 7 out of 10 top selling photoinitiators (PIs) in the UV ink industries were not recommended on this list. Furthermore, many new polymeric type PIs with molecular weight greater than 1000 were highlighted on the list due to its low toxicity and low extractability.

In 2004, Chitec had commercialized a novel polymeric photoinitiator (PI 1) as shown in figure 1, which was aimed for UV ink applications where liquid form and low odor are required. PI 1 is based on the aminoketone structure similar to the most widely used PI for UV ink (PI 2). PI 2 is a monomeric type PI and produces strong odor after curing as shown in figure 1. On the contrary, PI 1's fragmentation product after UV radiation has a low volatility and hence releasing low odor. Besides the advantage of low volatility, PI 1 is in liquid form at room temperature thanks to its unique polyester tail. PI 1 also shows significantly lower extractability compared to PI 2. Unfortunately, PI 1 suffers from low photospeed like most of the polymeric PIs do. In most cases, PI 1 has only 1/2 to 1/3 of PI 2's photospeed. PI 1 was therefore discontinued due to the combination of high cost disadvantage and inefficiency photospeed.

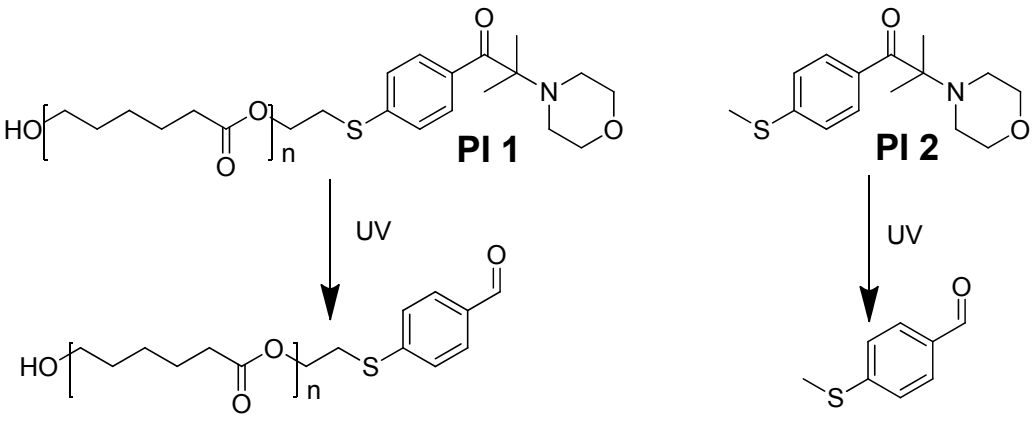
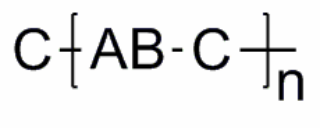


Figure 1. Fragmentation products of PI 1 and PI 2 after UV radiation.

The new Liquid Photoinitiator

Herein, we would like to introduce a neo polymeric photoinitiator (PI 3) which greatly improves the photospeed of PI 1 yet also retains its advantages such as low extractability. Its conceptual structure is shown below:



AB represents photoactive moiety and C represents the difunctional linker. The UV absorption spectrum of PI 3 is shown below in Figure 2.

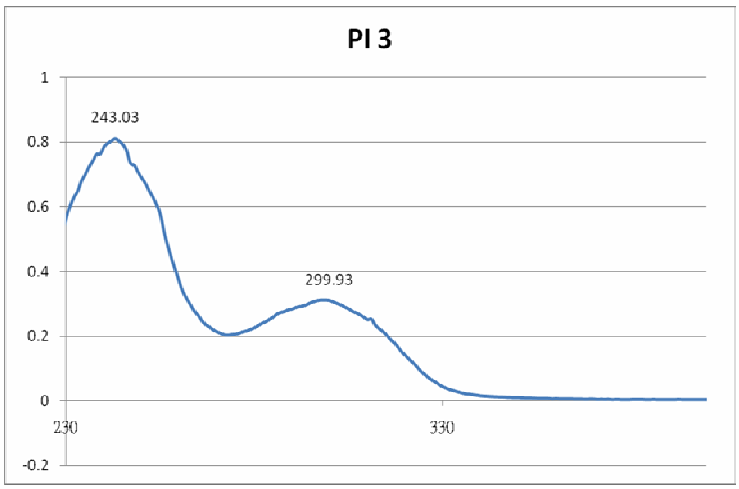


Figure 2: UV Absorption of PI 3

From the above UV spectrum, one of the two main absorption peaks for PI 3 is located at 300 nm which presents AB's π to π* absorption and is 6 nm blue-shifted compared to PI 2's λmax. The other peak at 243 nm is the absorption by the linker.

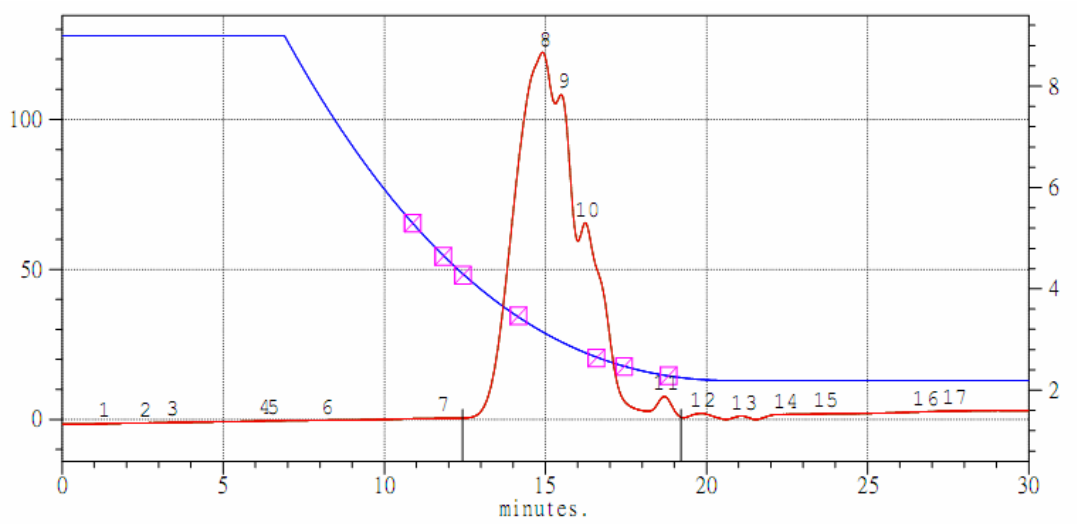


Figure 3. GPC result of PI 3.

PI 3's molecular weight is determined by GPC as shown in Figure 3. For this particular lot, PI 3's M_n is 908 and M_w is 1577 respectively, with a M_w/M_n ratio of 1.74. The typical physical properties of PI 3 are listed in Table 1.

Table 1: Physical Properties of PI 3

Item	Description
Appearance	Yellow to amber liquid
Viscosity	6850 cps
Molecular weight (M_w)	~1500
Density	1.118 g/cm^3 @ 20 ^{o}C

The appearance of PI 3 is a transparent amber viscous liquid. It is very soluble in most monomers and oligomers.

Table 2: Photoactivity Comparison- PI 2 vs. PI 3

Composition	Ink 1	Ink 2
Polyester tetra-acrylate	39.19	39.19
Aromatic Urethane Hexa-acrylate	10.05	10.05
Bisphenol-A epoxy Diacrylate	24.12	24.12
Propoxylated Glycerol triacrylate	15.07	15.07
Blue Pigment	3.72	3.72
IsopropilThioxanthone	1.24	1.24
4-Ethoxycarbonyl-N,N-dimethylaniline	2.48	2.48
PI 2	4.13	-
PI 3	-	4.13
Subtotal	100.00	100.00
thickness	10 µm	10 µm
photospeed(m/min)	150	150

Photoactivity and extractability of PI 3

Each UV ink shown in Table 2 was printed on PP film and cured. 0.15 g of each printed film was ground and was extracted with 10 g absolute ethanol at 60 °C for 7 hours. The extract was then filtrated and analyzed by GC (gas phase chromatography).

Table 3: Extractability Determination

Photoinitiators	**Extractability* %**
PI 2	> 40 %
PI 3	< 10 %

* Compared with non-cured sample

Conclusion

The novel polymeric PI 3 designed specifically for UV ink demonstrates similar photospeed as monomeric PI 2. In addition, PI 3 shows low extractability after UV radiation. Therefore, PI 3 is an ideal replacement for PI 2 on UV ink applications where low extractability and low migration are required.