

The Synthesis and Characterization of a Novel Photoinitiator for UV – LED PhotoCuring System

Pang Yulian¹, Yangyang Xin¹, Shizhuo Xiao², Zou Yingquan^{1*}

(1. College of Chemistry, Beijing Normal University, 100875 Beijing, China; 2. Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 100190 Beijing, China)

A novel photoinitiator for UV-LED photocuring has been prepared which contain 3,4-ethylenedioxythiophene (EDOT) units. This compound has been fully characterized by ¹H-NMR, IR and UV spectra. In addition, the study of the photosensitive performance of the synthesized photoinitiator has been carried out by Real-time Fourier Transform Infrared Spectroscopy (RT-IR). And the results show that this new photoinitiator's absorption spectra can well match with the emission spectra of UV-LED source and in the meanwhile it also has good thermal stability, good storage stability in UV-curable formations and high photoinitiating activity.

Introduction

UV-LED curing technology is attracting increasing attention in the field of photo- polymerization application because of its advantages of energy saving, environmental protection and hygiene, and it will be widely used with the development of photocuring technology. However, UV-LED lights as photocuring radiation light sources also have some disadvantages, such as narrow emission band and low power, which can slow the photocuring speed. And these weaknesses of UV-LED lights bring some challenges to the traditional photoinitiators, that is, most traditional photoinitiators are inapplicable to UV-LED photocuring system. So far, for most traditional photoinitiators, their optimal absorption wavelengths range from 300 nm to 370 nm, which can not match with the irradiation scope of commonly used UV-LED lights ranging from 365 nm to 405 nm. Therefore, in order to make UV-LED lights successfully applied to photocuring system, some specific photoinitiators

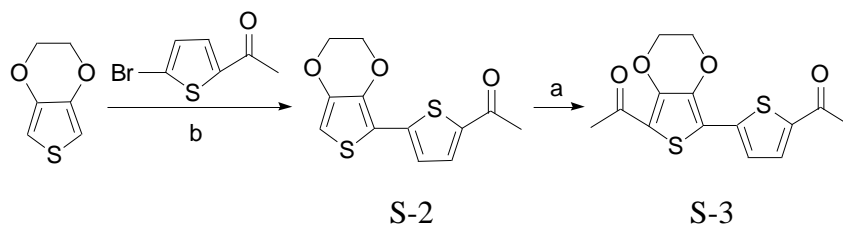
that can be well-matched with UV-LED lights and that have high light absorbability and high photoinitiating activity must be developed. [1]

In this paper, a novel photoinitiator contain 3,4-ethylenedioxythiophene (EDOT) units and bearing acetyl thienyl group and an acetyl group was synthesized, In addition, the study of the photosensitive performance of the synthesized photoinitiator was then carried out.

Experimental

Materials

3,4-ethylenedioxythiophene (EDOT) was purchased from Shanghai Adamas, 2-Acetyl-5-bromothiophene, Tetrakis (triphenylphosphine)palladium, Palladium diacetate was purchased from Alfa Aesar. Diphenyl ketone, Isopropyl Thioxanthone was received as a gift from Hubei Gurun technology Company. The other reagents and solvents were purchased from Beijing Lanyi.



Scheme 1. Synthesis of S-2 and S-3

Synthesis of S-2

Put KOAc(29.40 g, 0.3 mol) and TBAB(32.24 g, 0.1 mol) into 500 mL flask with DMF(200 mL), after the mixing, then added EDOT (14.24 g, 0.1 mol), 2-Acetyl-5-bromothiophene (20.50 g, 0.1 mol) and Pd(OAc)₂(2.24 g, 0.01 mol) into the mixture, Stirred for 6h at 80 °C. Then purified the mixture, got the intermediate products S-2, which is the pale yellow, the yield is 40%.
¹H-NMR(400MHz, CDCl₃) δ 2.55(s, 3H), 4.25-4.27(dd, 2H), 4.36-4.38(dd, 2H), 6.34(s, 1H), 7.18-7.19(d, 1H), 7.58-7.59(d, 1H).

Synthesis of S-3

Put S-2(3.22 g, 0.01 mol) into 250 mL flask with 100 mL CH₂Cl₂, after the mixing, added acetic anhydride(1.02 g, 0.01 mol) with 19ml CH₂Cl₂, after the mixing, added Stannic chloride pentahydrate(2.61 g, 0.01 mol) with acetonitrile(50 mL), Stirred for 6h at 25 °C. Then purified the mixture, got the intermediate products S-3, which is the pale yellow, the yield is 60%.
¹H-NMR(400MHz, CDCl₃) δ 2.54(s, 3H), 2.56(s, 3H), 4.42-4.43(dd, 2H), 4.44-4.45(dd, 2H), 7.33-7.34(d, 1H), 7.60-7.61(d, 1H).

Solubility

The solubility of S-3 is tested in Chloroform, dichloromethane, N-

methyl-2-pyrrolidone, vinyl pyrrolidone, hydroxyl ethyl acrylate (HEA), hydroxyl ethyl methacrylate (HEMA), ethyl acetate, ethanol, tetrahydrofuran, toluene, diethylene glycol ether, acetonitrile, acetone. Put the S-3 into solvent above until it can't be dissolved.

Thermal stability

Test the thermal stability of S-3 with TGA Q2000, the heating rate is 10°C/min.

UV spectrum

Put S-3 into acetonitrile, the concentration is 1.05×10⁻⁴mol/L (32.22ppm, 1ppm=1mg/L), test the UV spectrum by UV-2450 UV-Vis spectrophotometer.

Photopolymerization

The photopolymerization experiments are tested in the Real-time FT-IR. Contrasted S-3 with Diphenyl ketone, Isopropyl Thioxanthone, the monomer is hydroxyl ethyl methacrylate(HEMA), the concentration of Photoinitiator is 0.02%. The photosensitive formulations were deposited between two KBr plates for irradiation with the Hg lamps. The evolution of the double bond content of HEMA were continuously followed by real time FTIR spectroscopy at about 1630cm⁻¹.

The final conversions can be evaluated from the area of these peaks according to: $DC(\%) = [1 - (A_t - A_0)] \times 100\%$, Where A_0 and A_t stand for the area of the peak before irradiation and at a given time t respectively.

Results and discussion

The solubility of S-3 are not good in the solvent above. Further the solubility of S-3 in the Chloroform, dichloromethane, N-methyl-2-pyrrolidone, vinyl pyrrolidone are better than in the hydroxyl ethyl acrylate (HEA), hydroxyl ethyl methacrylate (HEMA), ethyl acetate, ethanol, tetrahydrofuran, toluene, diethylene glycol ether, acetonitrile, acetone.

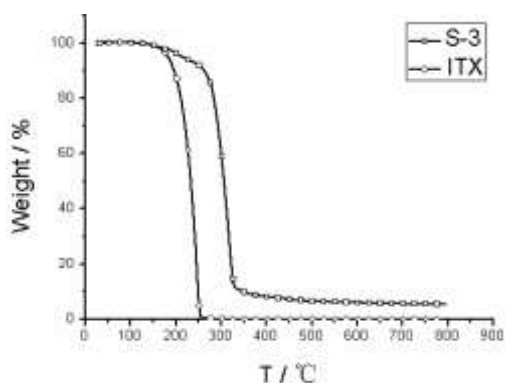


Fig. 1 TG of S-3 and ITX

Fig.1 demonstrated the decomposition temperature of S-3, ITX are 316 °C, 245 °C respectively. The thermal stability of S-3 is better than ITX.

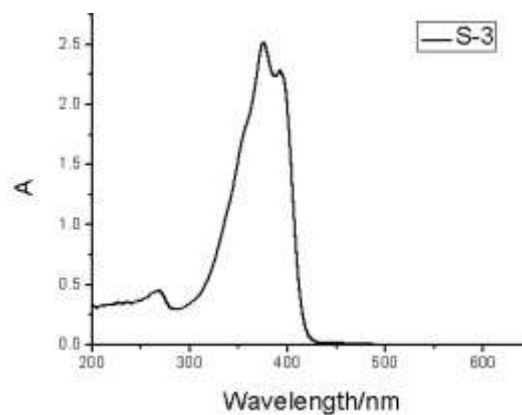


Fig. 2 UV spectrum of S-3

Fig.2 demonstrated the maximum absorption wavelength of S-3 is 375nm, molar extinction coefficient is $2.79 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, and S-3 have strong absorption between 365-405nm. So S-3 can match UV-LED.

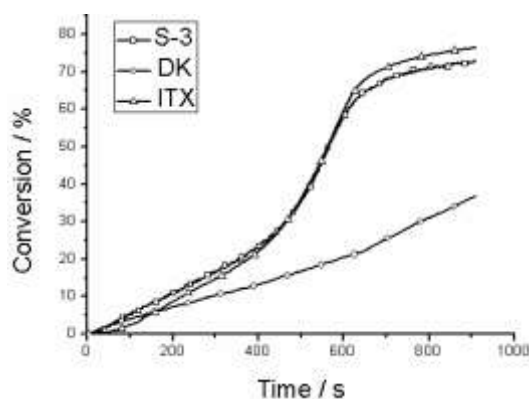


Fig.6 Conversion of double bond of HEMA initiated by S-3, DK, ITX

Fig.6 demonstrated that the conversion of HEMA initiated by S-3 is over 70%, which is the same as ITX when then concentration of photoinitiator is 0.02%, but the conversion of HEMA initiated by DK is about 40%. So the photoinitiator efficiency of S-3 is close to ITX.

Conclusions

In this paper, a novel photoinitiator is synthesized. The results show that this new photoinitiator's absorption spectrum can well match with the

emission spectra of UV-LED lights and in the meanwhile it also has good thermal stability and high photoinitiating activity. However, the new synthesized photoinitiator has low solubility in commonly used organic solvents and polymerization monomers. So in order to have it well used in UV-LED photocuring system, furthermore tuning its molecular structure need to be carried out to improve its solubility.

Acknowledgement. The authors thank Hubei Gurun Technology Company for providing the photoinitiators and the financial support.

References and Notes

[1] Koji Arimitsu. Latest progress and prospects of UV/EB curing technology [J]. News Lett. 2014 (6): 2-6.