Azo dye as photoinitiator for Free Radical Polymerization under LED irradiation

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Abstract

Photopolymerization is facing a revolution with the development of energy-efficient light sources, namely LEDs. With the ongoing efforts to develop photoinitiating systems outperforming the existing ones in terms of polymerization rates and monomer conversions, the search for new families of dyes that have not been investigated yet in the context of photopolymerization is still very active from the academic viewpoint.

In this context, **3-ethoxy-5-phenyl-azo** was synthesized and characterized using spectroscopic techniques and its effectiveness as a photoinitiator of the FRP reaction is being investigated under light conditions, starting with a 365 nm LED in the laminate condition, resulting in the system with the photoinitiator and the monomer: 3-ethoxy-5-phenyl-azo/TMPETA. Besides, in the tests performed, the dye demonstrated good efficiency.

Keywords: Azo dyes, organic photoinitiator, photopolymerization , organic photocatalyst, LED

Introduction

Photoredox catalysis under very soft irradiation (sunlight, house-hold flourescence or LED bulbs) is now well-know in organic synthesis. In very recente years, this method has also been introduced for the synthesis of polymers to initiate a free radical polymerization (FRP) (1). In this area, the photoplymerization reations is initiated using photoinitiators (PI, commonly organic PI) that generates reactive species (radicals, cations, anions, radical cations, acids, bases) and are consumed during the light exposure (2).

Besides, photopolymerization reactions are commonly presented as belonging to a green technology characterized by low electrical power input and energy requirements, low temperature operation and no volatile organic compounds release (solvent-free systems) (3).

To improve FRP performance, new systems based on azo dyes were developed. These compounds were evaluated as photoinitiators for the FRP of TMPETA. (3)

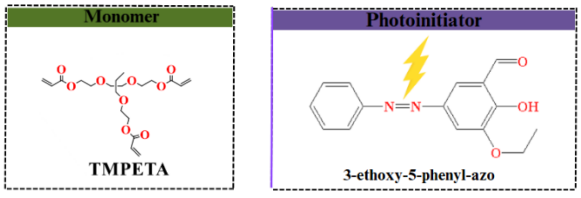

Figure 1. Monomer and photoinitiator that are used and FRP reactions.

Experimental

Synthesis of the 3-ethoxy-5-phenil-azo

The synthesis of the dye is divided into 2 parts: the first part forms the diazonium salt from aniline with HCl and $NaHCO_3$ (solution 1).

In the second part, the second reaction occurs, the aldehyde is added in another flask (solution 2) with NaOH, in this way, solution 2 is added to solution 1 and the coupling reaction occurs, forming the azo dye as can be seen in the figure 2.

Figure 2. Synthesis of 3-ethoxy-5-phenyl-azo

FRP reactions

Photopolymerization was performed using 2 components: 3-ethoxy-5-phenyl-azo/TMPETA with 3% of photoinitiator in 0.5 g of monomer. The system used was the laminate to place the photoinitiator and monomer solution. In addition, the LED used was 365 nm and the consumption of C=C bonds was monitored by FTIR at 1650 cm^{-1}.

Results and Discussion

The 3-ethoxy-5-phenyl-azo dye was analyzed by the following spectroscopy techniques: UV-Vis, ^{1}H NMR and was investigated as a photoinitiator in the FRP of TMPETA.

^{1}H NMR characterization

Initially, at 1.0 and 1.5 ppm, signals related to the ethoxy substituent are present, in which the first is associated with CH_3 and the second with CH_2. The signals presented at 7.80 and 7.90 are related to the H_2 present in the aromatic ring with the aldehyde group. There are three others that are related to the aromatic ring that comes from the azo coupling and that present values between 7.35 and 7.40 ppm. Finally, the last signals are related to the most acidic H_2 of the molecule that are related to the aldehyde group that present values at 11.5 and 10.2 ppm.

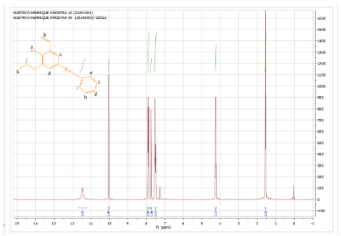

Figure 3. ^{1}H NMR of 3-ethoxy-5-phenyl-azo in $CDCl_3$

UV-Vis characterization

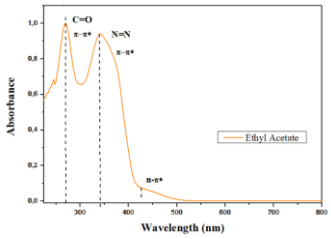

Figure 4. UV-Vis spectroscopy analysis in ethyl acetate

The electronic transitions π-π* and n-π were observed at 347 and 266 nm, respectively, for the concentration of 1.0×10^{-4} mol/L, and are associated with the N=N and C=O bonds.

Free Radical Photopolymerization (FRP)

The photopolymerization conditions for the 3-ethoxy-5-phenyl-azo/TMPETA system were performed under 3 conditions: 1%, 2%, and 3% of photoinitiator in wt to 0.5 g of monomer using a 365 nm LED.

The azo dye was efficient under all conditions, with the best performance at 3% due to the higher photoinitiator content, enabling greater radical generation via chromophore bond cleavage and reaching 80% conversion. Lower concentrations showed reduced conversion and delayed reaction onset due to fewer radicals formed.

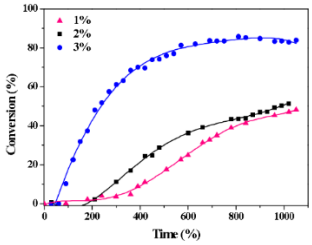

Figure 5. Conversion of TMPETA vs irradiation time under LEDs (at 365 nm) in laminate, with 3-ethoxy-5-phenyl-azo/TMPETA.

Conclusions

The 3-ethoxy-3-phenyl-azo was synthesized and characterized effectively using the spectroscopy techniques. Furthermore, the dye showed photoinitiating activity, achieving high conversion by breaking the chromophore bond that provides the radicals in the medium that initiate the polymerization reaction, in addition to its high absorption capacity.

Acknowledgments

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