

Phenanthroline-based Fe(II) complexes as photocatalysts for polymerization reactions

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Resumo/Abstract

RESUMO - O uso da luz em síntese química permite maior controle reacional, menor consumo energético e condições mais brandas, promovendo processos mais sustentáveis. Esta pesquisa visa o desenvolvimento de fotoiniciadores com complexos de ferro(II) coordenados a ligantes derivados da fenantrolina, aplicáveis em Fotopolimerização Radicalar Livre (FRP). O ferro é abundante, de baixo custo, baixa toxicidade e biocompatível, sendo uma alternativa promissora a metais mais tóxicos e menos acessíveis. A fenantrolina, por sua vez, é um ligante bidentado rígido e versátil, com propriedades fotoquímicas favoráveis e potencial de modificação estrutural. A metodologia inclui a síntese e caracterização dos ligantes e complexos, além da análise de propriedades espectroscópicas, fotoquímicas e eletroquímicas. A eficiência será avaliada em reações induzidas por LEDs, com monitoramento por FTIR. Também serão investigadas correlações entre a estrutura dos complexos e sua atividade fotoiniciadora, visando a racionalização do processo e o aprimoramento do desempenho fotocatalítico.

Palavras-chave: Ferro(II), fenantrolina, polimerização radicalar livre, fotoquímica, luz visível.

ABSTRACT - The use of light in chemical synthesis offers enhanced reaction control, reduced energy consumption, and milder conditions, promoting more sustainable processes. This research aims to develop photoinitiators based on iron(II) complexes coordinated with ligands derived from phenanthroline, applicable in Free Radical Photopolymerization (FRP). Iron(II) is abundant, low-cost, low-toxicity, and biocompatible, making it a promising alternative to more toxic and less accessible metals. Phenanthroline is a rigid, bidentate, and versatile ligand with favorable photochemical properties and potential for structural modification. The methodology includes synthesis and characterization of ligands and complexes, along with analysis of spectroscopic, photochemical, and electrochemical properties. The photoinitiator efficiency will be evaluated in LED-induced polymerization reactions, monitored by FTIR. Correlations between complex structure and photoinitiating activity will also be investigated, aiming to rationalize the process and enhance photocatalytic performance.

Keywords: Iron (II), phenanthroline, free radical photopolymerization, photochemistry, visible light.

Introduction

Photopolymerization reactions are considered green technology due to their low energy consumption, moderate temperature requirements, and absence of volatile organic compounds. These features make photopolymerization highly attractive for industries such as coatings, paints, adhesives, and microelectronics. Free Radical Polymerization (FRP) has revolutionized the field by enabling rapid polymer curing without the need for high temperatures. Its fast reaction rates and energy efficiency make FRP a sustainable and effective choice for a wide range of applications, including coatings, 3D printing, adhesives, dental and medical materials, textiles, and electronics.

Metal-based photoinitiators such as iridium (Ir) and ruthenium (Ru) complexes are highly efficient due to their strong visible light absorption, enabling the use of affordable LED light sources. Other metals like iron (Fe), platinum (Pt), nickel (Ni), zinc (Zn), and copper (Cu) are

also explored, but challenges remain in developing low-cost, effective photoinitiators.

Iron-based complexes have gained attention as photocatalysts in photopolymerization due to their abundance, low cost, biocompatibility, and low toxicity. Beyond these advantages, iron is widely recognized as an eco-friendly alternative, making these complexes especially promising for sustainable applications. Their use can reduce reliance on noble metals traditionally employed in these processes, enhancing both the economic and environmental viability of new photoinitiator systems.

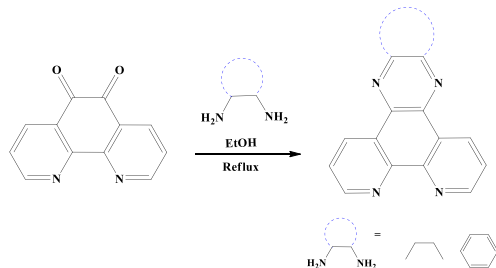
Experimental

Synthesis of the phenanthroline ligands

The ligands were prepared by adding a solution of ethylenediamine or o-phenylenediamine (7.5 mmol) in ethanol dropwise to a solution of 1,10-phenanthroline-5,6-dione (5 mmol) in ethanol (20 mL). The mixture was refluxed with stirring for 4 hours. After the reaction, the

solution was vacuum-concentrated, and the resulting solid recrystallized from methanol.

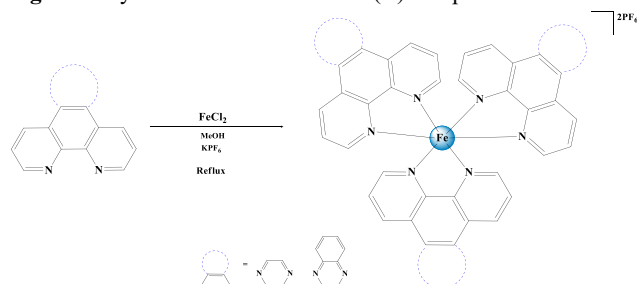
Figure 1. Synthesis reaction of the phenanthroline ligands.



Synthesis of the iron complexes

The synthesis of the Fe(II) complexes was carried out by adding FeCl₂ (1 mmol) to a methanolic solution of the ligand (3.3 mmol) under stirring for 15 minutes. A methanolic solution of KPF₆ (2 mmol) was then added, and the mixture was refluxed for 24 hours. After cooling to room temperature, the resulting precipitate was collected by filtration and washed with cold methanol.

Figure 2. Synthesis reaction of the Fe(II) complexes.



Free radical photopolymerization (FRP)

For FRP reactions, the formulations were prepared by combining the complexes (PC), di-tert-butyl-diphenyl iodonium hexafluorophosphate (Iod), ethyl dimethylaminobenzoate (EDB), and trimethylolpropane ethoxylate triacrylate (TMPETA). The reaction progress was continuously monitored in situ using a Perkin Elmer Frontier FTIR spectrometer. Photopolymerization was triggered by irradiation under LED 365 nm and 390-405 nm.

Results and Discussion

The ligands were characterized by Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (¹H NMR), ultraviolet-visible (UV-Vis) spectroscopy. Then, the complexes were characterized by FTIR, UV-Vis and fluorescence spectroscopy.

Free radical photopolymerization (FRP)

As shown in Table 1, the FRP of TMPETA was performed at room temperature under LED365 and 390-405 nm irradiation, employing a three-component system comprising the photocatalyst (PC), IOD, and EDB under various conditions.

Table 1. Results of FRP conditions under LED365 and 390 nm, at room temperature.

PC	PC/EDB/IOD (w%/w%/w%)	Conv. (%) at 365 nm	Conv. (%) at 390-405 nm
-	0/1/1	66	16
-	0/2/2	44	48
-	0/3/3	57	56
Fe(o-Ph)	0.2/2/2	69	67
Fe(o-Ph)	0.2/3/3	75	73
Fe(Et)	0.2/3/3	72	67

Conclusion

In summary, the ligands and their corresponding Fe(II) complexes were characterized through a combination of analytical techniques, including FTIR, ¹H NMR, UV-Vis spectroscopy, and fluorescence.

These complexes were able to catalyst the FRP of TMPETA in the presence of the additives IOD and EDB under 365 nm and 390-405 nm irradiation. In addition, the Fe(o-Ph) complex exhibited the best performance in FRP reactions of TMPETA, where a conversion of 75% and 73% was achieved in 365 nm or 390-405 nm LED irradiation.

Acknowledgments

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