Development of Ni(II) Complexes Based on Thiosemicarbazides as Photocatalysts in Free-Radical Photopolymerization

Poliana C. Mello [1*](IC), Naralyne M. Pesqueira [1](PG), Douglas H. N. Santos [1](PG), Beatriz E. Goi [1](PQ), Valdemiro P. Carvalho-Jr [1](PQ)

[1]São Paulo State University (Unesp), School of Technology and Sciences, Presidente Prudente, SP, 19060-900, Brazil.

***Email: poliana.campagnoli@unesp.br**

Abstract

Developing efficient and cost-effective photoinitiating systems that operate under mild conditions remains a key challenge in light-driven polymerization. In particular, the development of systems based on low-cost metal complexes has gained attention as a promising strategy to replace expensive transition metals such as ruthenium or iridium. In this context, monometallic Ni(II) complexes of the type [Ni(N,N,S-tsc)(4-aminopyridine)] (**Ni^{Me}** and **Ni^{Ph}**), incorporating tridentate ligands derived from thiosemicarbazides, were synthesized. These complexes were characterized using various spectroscopic techniques, and their catalytic activity was evaluated in free-radical photopolymerization (FRP) reactions. This study investigates the role of light in modulating the reactivity of these nickel-based systems, aiming to elucidate their catalytic performance and contribute to the development of new transition-metal photocatalysts for applications in homogeneous catalysis.

Keywords: nickel, thiosemicarbazides, photocatalyst, photopolymerization, LED

Introduction

Free-radical photopolymerization (FRP) offers significant advantages over thermal polymerization, including fast reaction rates at room temperature, lower energy consumption, and the absence of volatile organic compounds, making the process more sustainable(1). The use of LEDs and low operational costs also contribute to its widespread application in paints, adhesives, coatings, medicine, dental materials, microelectronics, and 3D printing. FRP is initiated by photoinitiators (PIs) or photoinitiating systems (PISs) that generate reactive species upon light exposure(1).

Recent advances involve three-component systems in which regenerable PIs act as photoredox catalysts (PCs), enabling reduced initiator loadings and low light intensities while enhancing photosensitivity(1,2). To improve FRP performance, new systems based on novel Ni(II) complexes bearing thiosemicarbazides ligands were developed. These complexes were evaluated as photocatalysts for the FRP of TMPETA in combination with the additives Iod and EDB(1) (Figure 1).

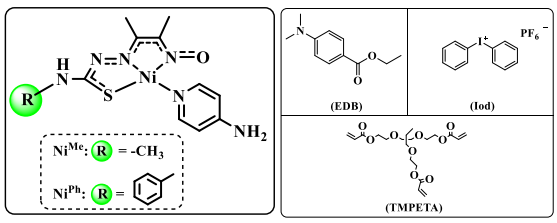

Figure 1. Photocatalysts, additives and monomer used in FRP reactions.

Experimental

Synthesis of Ni(II) complexes

The ligands H_2L^{Me} and H_2L^{Ph} were synthesized according to procedures reported in the literature(2). The synthesis of the complexes [Ni(N,N,S-TSC)(4-aminopyridine)] (**Ni^{Me}**) and [Ni(N,N,S-TSC)(4-aminopyridine)] (**Ni^{Ph}**) was carried out through 1:1 reactions between $[NiCl_2(PPh_3)_2]$, MeCN, and the appropriate ligand, followed by the addition of 4-aminopyridine and three drops of Et_3N (Figure 2).

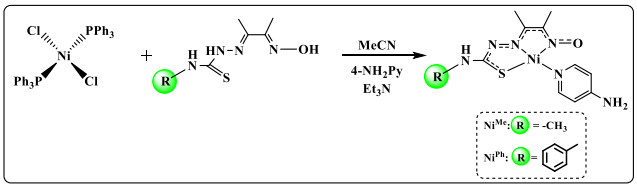

Figure 2. Synthesis of **Ni^{Me}** and **Ni^{Ph}**.

FRP reactions

The free-radical photopolymerization of TMPETA was performed using three-component systems comprising Ni(II) complexes, iodonium salt (Iod), and ethyl dimethylaminobenzoate (EDB). Formulations were prepared with a monomer-to-initiator mass ratio of 0.2%/3%/3% (w/w/w) for Ni/Iod/EDB systems. These mixtures were then applied as laminates approximately 75 µm thick. Photopolymerization was conducted under LED@365 nm and 390–405 nm at 25 °C. The consumption of C=C bonds was monitored by FTIR at 1635 cm^{-1}.

Results and Discussion

Ni(II) complexes were synthesized via equimolar reactions between $[NiCl_2(PPh_3)_2]$ and the corresponding ligands in MeCN. These complexes were thoroughly characterized using spectroscopic techniques and investigated as photocatalysts in FRP reactions.

^{1}H NMR characterization

For **Ni^{Me}** and **Ni^{Ph}** complexes, the signals appeared as doublets around 8.00 and 6.50 ppm, corresponding to the aromatic ring of the amine, and a singlet near 6.80 ppm associated with the NH_2 group, confirming the coordination of the ligands to nickel. For **Ni^{Me}**, a singlet attributed to the methyl group was observed around 2.8 ppm (Figure 3).

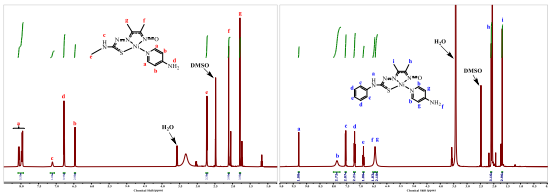

Figura 3. ^{1}H NMR of **Ni^{Me}** and **Ni^{Ph}** in DMSO- d^6.

UV-Vis characterization

The UV-Vis spectra of the Ni(II) complexes in DMSO at 25 °C exhibited high-energy bands at $\lambda \approx 260$ nm, attributed to spin-allowed intraligand (IL) transitions ($n \rightarrow \pi$) from the TSC ligands (Figure 4). The low-energy absorption bands around 390 nm observed in Ni(II) complexes may correspond to ligand-to-metal charge transfer (LMCT) transitions. The bands around 550 nm are likely associated with metal-to-ligand charge transfer (MLCT) transitions [$d\pi(Ni) \rightarrow \pi(TSC)$](3).

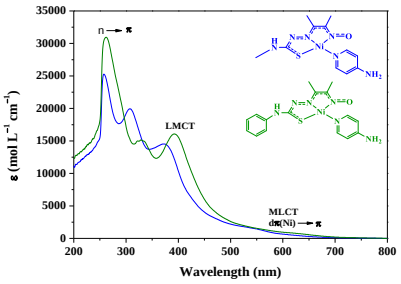

Figure 4. UV-Vis spectra of **Ni^{Me}** and **Ni^{Ph}** in DMSO at 25 °C. $[Ni^{II}] = 2.5 \times 10^{-5}$ mol L^{-1}.

Free Radical Photopolymerization (FRP)

The FRP of TMPETA was carried out using a three-component system composed of Ni(II) complexes, Iod, and EDB under LED@365 and LED@390–405 nm. The photopolymerization conditions for the Ni(II)/Iod/EDB system were 0.2%/3%/3%, 0.2%/2%/2%, and 0.1%/1%/1% w/w/w under LED@365 nm and 390-405 nm (Table 1). Ni(II) complexes exhibited good performance under 365 nm irradiation, achieving final conversions ranging from 30% to 78% within 1200s (Table 1). **Ni^{Me}** exhibited superior catalytic activity compared to **Ni^{Ph}**, achieving higher final conversions in shorter times (Table 1). These results can be attributed to the higher absorptivity of **Ni^{Me}** at these wavelengths (Figure 4). Additionally, the optimal condition was 0.2%/3%/3% under LED@365 nm (Figure 5), where the Ni(II) complexes showed the best performance in FRP (>75% at 600s).

Table 1. Final conversions of TMPETA after 1200 s under different photoinitiating systems and LED irradiation wavelengths.

PC	PC/Iod/EDB	Conv.(%) at 365 nm	Conv.(%) at 390-405 nm
Ni^{Me}	0.1%/1%/1%	76	0
Ni^{Me}	0.2%/2%/2%	53	50
Ni^{Me}	0.2%/3%/3%	76	63
Ni^{Ph}	0.1%/1%/1%	0	0
Ni^{Ph}	0.2%/2%/2%	30	0
Ni^{Ph}	0.2%/3%/3%	78	56

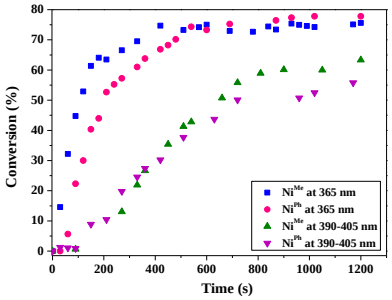

Figure 5. Conversion of TMPETA vs irradiation time under LEDs (at 365 or 390-405) in laminate, with Ni(II)/Iod/EDB.

Conclusions

Ni^{Me} and **Ni^{Ph}** were successfully synthesized and characterized using spectroscopic techniques. In FRP reactions, **Ni^{Me}** exhibited superior catalytic activity, achieving higher conversions in shorter times under LED irradiation, which can be attributed to its enhanced absorption properties compared to **Ni^{Ph}**.

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