Fe(III) complexes as photocatalysts for photopolymerization reactions, hydrogels preparation and copolymerization

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Resumo/Abstract

RESUMO - A polimerização ativada por luz oferece uma alternativa sustentável e energeticamente eficiente aos processos térmicos convencionais, ao reduzir significativamente o consumo de energia. Nesse contexto, os catalisadores à base de ferro se destacam por sua baixa toxicidade, baixo custo, abundância natural e biocompatibilidade, tornando-se excelentes candidatos para aplicações fotoquímicas sustentáveis. Este estudo investiga complexos de Fe(III) contendo ligantes de base de Schiff simétricos como fotocatalisadores para a Fotopolimerização Radicalar Controlada (CRP2) do acrilato de metila (MA). As reações foram realizadas sob irradiação de LED a 365 nm, utilizando um sistema tricomponente (Fe(III), EDB e Ph-Br), resultando em polimerizações eficientes e bom controle sobre a arquitetura molecular. A solubilidade em água desses complexos também permitiu a polimerização do 2-hidroxietil metacrilato (HEMA), originando hidrogéis com alto teor de água, características essenciais para aplicações biomédicas.
Além disso, esses sistemas foram empregados na síntese de copolímeros em bloco (PHEMA-β-PBA), demonstrando ainda mais a versatilidade dos fotocatalisadores à base de Fe(III) no desenvolvimento de materiais poliméricos avançados e sustentáveis.

Palavras-chave: ferro, bases de Schiff, polimerização radicalar fotocontrolada, solúvel em água.

ABSTRACT - Light-activated polymerization offers a sustainable, energy-efficient alternative to conventional thermal processes by significantly reducing energy consumption. In this context, iron-based catalysts stand out for their low toxicity, affordability, natural abundance, and biocompatibility, making them excellent candidates for green photochemical applications.
This study investigates Fe(III) complexes bearing symmetric Schiff base ligands as photocatalysts for the Controlled Radical Photopolymerization (CRP2) of methyl acrylate (MA). Reactions were carried out under 365 nm LED irradiation using a tricomponent system (Fe(III), EDB, and Ph-Br), achieving efficient polymerization and good control over molecular architecture. The water solubility of these complexes also enabled the polymerization of 2-hydroxyethyl methacrylate (HEMA), yielding hydrogels with high water content, essential features for biomedical applications.
Additionally, these systems were employed in the synthesis of block copolymers (PHEMA-β-PBA), further demonstrating the versatility of Fe(III)-based photocatalysts in the development of advanced, sustainable polymeric materials.

Keywords: *iron, Schiff bases, Photocontrolled Radical Polymerization, water-soluble.*

Introduction

Visible light has emerged as a powerful and sustainable energy source for driving chemical reactions, enabling the formation of well-defined macromolecules under mild, non-invasive conditions (1–6). In contrast to traditional thermal methods, photopolymerization proceeds at low temperatures and without solvents, making it particularly advantageous for polymerizing acrylates, methacrylates, and styrenes. This strategy is especially promising for hydrogel synthesis, offering a greener alternative to conventional solvent-based or thermally driven approaches (7-8).

Hydrogels—three-dimensional, water-rich polymer networks—exhibit high swelling capacity and biocompatibility, making them ideal for biomedical applications that mimic soft tissues.[7–9] Their photopolymerization, facilitated by water-soluble initiators and monomers, enhances process efficiency and environmental safety while reducing energy consumption.(6,8-9)

Block copolymers (BCPs), with their ability to self-assemble into ordered nanostructures, represent a significant advance over random copolymers, allowing for precise material design based on composition and thermal history (10).

In this context, iron-based catalysts stand out as a sustainable choice due to their low toxicity, affordability, biocompatibility, and natural abundance, key attributes for green photochemical applications (11). Iron(III) complexes exhibit diverse geometries, with Schiff bases standing out for their easy synthesis, thermal stability, and strong metal coordination (12-13)

To evaluate the photoinitiation efficiency of iron(III)-based systems in CRP2 under LED irradiation, two iron(III) complexes with symmetric Schiff base ligands were synthesized and tested as photocatalysts in a three-component system comprising acrylate monomers (MA, HEMA, or BA), phenacyl bromide (Ph-Br), and ethyl 4-(dimethylamino)benzoate (EDB).

Experimental

Synthesis of the Schiff base ligands

The Schiff base ligands (L1 or L2) were synthesized with salicylaldehyde or 3-ethoxysalicylaldehyde (2.5 mmol) and ethylenediamine (1.25 mmol) in methanol (20 mL) under reflux at 65 °C for 24 hours. Then, a yellow solid precipitated from the reaction, which was subsequently isolated by vacuum filtration and washed with cold methanol to afford the purified ligand.

Synthesis of the iron complexes

Schiff base ligands (L1 or L2) (2.5 mmol) were dissolved in a mixture of methanol (15 mL) and acetonitrile (20 mL) in the presence of triethylamine (0.2 mL), and the resulting solution was stirred at room temperature for 2 hours. The mixture was then transferred to a separate flask containing anhydrous $FeBr_3$ (2.5 mmol) and stirred overnight at ambient temperature. After completion, the solvent was removed under reduced pressure, affording a dark solid corresponding to FeL1 or FeL2. The crude product was isolated by filtration and washed thoroughly with cold isopropanol.

Atom Transfer Radical Photopolymerization (ATRP)

ATRP experiments were initiated by introducing the iron complex (FeL1 or FeL2) into a Schlenk flask equipped with a magnetic stir bar. Subsequently, the components ethyl 4-(dimethylamino)benzoate (EDB), phenacyl bromide (Ph-Br), and the deoxygenated monomer methyl acrylate (MA) were added under an inert atmosphere. The sealed flask was then irradiated at 25 °C in a photoreactor equipped with 365 nm LEDs (10 mW cm^{-2}). At predetermined time intervals, 0.1 mL aliquots of the reaction mixture were withdrawn for analysis. Monomer conversion was monitored by Fourier-transform infrared spectroscopy (FTIR), specifically following the decrease of the absorption band at 1635 cm^{-1} corresponding to the C=C bond. The same aliquots were subsequently diluted in tetrahydrofuran (THF, 1 mL) and analyzed by gel permeation chromatography (GPC) to determine the number-average molecular weight (Mn) and polydispersity index (Đ) of the resulting polymers.

Polymerized hydrogels preparation

Hydrogel polymerization was carried out by initially introducing the iron complex (FeL1 or FeL2) into a Schlenk flask equipped with magnetic stirring. The system was then charged with EDB, Ph-Br, and the deoxygenated monomer 2-hydroxyethyl methacrylate (HEMA), under an inert atmosphere. The reaction vessel was placed inside a photoreactor and subjected to irradiation using 365 nm LEDs (intensity in 10 mW cm^{-2}) at a constant temperature of 25 °C. At specific time points, 0.1 mL aliquots of the reaction mixture were collected and analyzed by FTIR spectroscopy to evaluate monomer conversion, with particular attention to the absorption band at 1635 cm^{-1}.

Copolymerization reactions

The copolymerization of HEMA and butyl acrylate (BA) was carried out using the iron complex (FeL1 or FeL2) as a photocatalyst, in the presence of EDB and Ph-Br as additives. The reaction was initiated by introducing the catalyst system into a Schlenk flask equipped with a magnetic stir bar, followed by the addition of 3 mL of deoxygenated HEMA. The mixture was placed in a photoreactor and irradiated with 365 nm LED (10 mW cm^{-2}) at 25 °C. After a defined irradiation period, 2.3 mL of BA were added to the reaction mixture to proceed with the copolymerization process. At specific time intervals, 0.1 mL aliquots were withdrawn to monitor monomer conversion via FTIR, focusing on the disappearance of the vinyl stretching band at 1635 cm^{-1}. The collected aliquots were subsequently diluted in 1 mL of THF and analyzed by GPC to determine the molecular weight distribution and dispersity of the resulting copolymers. Upon completion of the reaction, the polymeric materials were isolated by precipitation, followed by filtration and repeated reprecipitation to remove residual monomers and side products.

Results and discussion

The ligands were characterized by Fourier-transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^1H NMR), ultraviolet–visible (UV–Vis) spectroscopy, and cyclic voltammetry (CV). Then, the complexes were characterized by FTIR, MALDI-TOF mass spectrometry, UV–Vis and CV.

The emission spectra of Fe(III) complexes, with the addition of either EDB or Ph-Br, were measured at 350 nm in CH_2Cl_2 at 25 ºC. Quenching experiments were carried out for the complexes containing Ph-Br.

The photolysis of FeL1 and FeL2 was conducted in CH_2Cl_2 under steady-state conditions, with or without the additives (Ph-Br and EDB), and irradiated with 365 nm LED light for 30 minutes.

Atom Transfer Radical Photopolymerization (ATRP)

According to Table 1, the ATRP of MA was conducted using a three-component system composed of PC, Ph-Br, and EDB, under varying conditions using LED365 nm irradiation at room temperature.

Table 1. Results of MA photopolymerization conditions under LED365 nm, at room temperature.

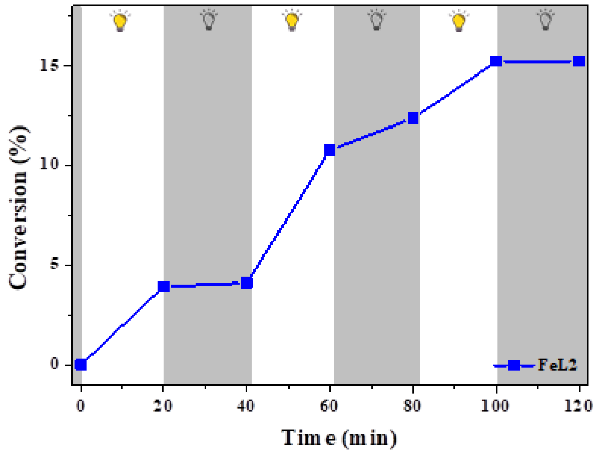
Entry	PC	Molar ratio MA/Ph-Br/PC/EDB	(%)	Time (min)	Mn (g.mol^{-1})	Đ
1	-	200/0/0/1	-	-*	-	-
2	-	200/1/0/0	80	120	96000	2.5
3	-	200/1/0/1	53	5	365000	2.2
4	FeL1	200/0/0/1	-	-*	-	-
5	FeL1	200/1/0,02/1	68	90	173000	1.7
6	FeL1	200/1/0,04/1	63	120	75000	2.2
7	FeL1	200/1/0,06/1	59	120	107000	2.0
8	FeL1	200/1/0,08/1	56	120	115000	1.7
9	FeL2	200/0/0/1	-	-*	-	-
10	FeL2	200/1/0,02/1	70	50	418000	1.6
11	FeL2	200/1/0,04/1	35	120	66000	2.0
12	**FeL2**	**200/1/0,06/1**	**44**	**120**	**48000**	**1.4**
13	FeL2	200/1/0,08/1	33	120	34000	1.4

-* 3 days

The Fe(III) complexes mediated the photopolymerization of methyl acrylate in the presence of the additives EDB and Ph-Br under 365 nm irradiation. Notably, the FeL2 complex, when used at a 200/1/0.06/1 ratio, demonstrated excellent control over the photo-ATRP process. Additionally, the Fe(III) complexes were effective in preparing hydrogels with high conversion rates, further demonstrating their versatility in polymerization applications.

To investigate the "on-off" photopolymerization behavior of MA, the FeL2/Ph-Br/EDB system was utilized in a light-responsive process, switching between on and off states under 365 nm LED irradiation, as shown in Figure 1.

Figure 1. On-off photopolymerization profile of MA with FeL2/Ph-Br/EDB (200/1/0,02/1) upon irradiation with LED 365 nm.



Polymerized hydrogels preparation

As indicated in Table 2, and 3 HEMA-based hydrogels were synthesized using a three-component system consisting of the photocatalyst (PC), Ph-Br, and EDB, under different conditions and 365 nm LED irradiation at room temperature.

Table 2. Polymerized hydrogels of HEMA with water and initiated by **FeL1**/PhBr/EDB upon irradiation with LED 365 nm.

Entry	PC	% H_2O	Conversion (%)
1	-	-	70
2	FeL1	-	70
3	FeL1	5	73
4	FeL1	15	80
5	FeL1	25	84
6	FeL1	35	87
7	FeL1	45	88

Figure 2. Polymerized hydrogels of HEMA function conversion (%) vs % H_2O initiated by **FeL1**/PhBr/EDB upon irradiation with LED 365 nm.

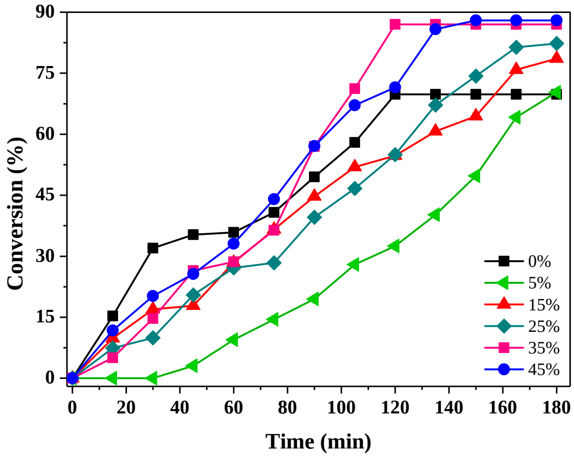


Table 3. Polymerized hydrogels of HEMA function conversion (%) vs % H_2O initiated by **FeL2**/PhBr/EDB upon irradiation with LED 365 nm.

Entry	PC	% H_2O	Conversion (%)
1	-	-	70
2	FeL2	-	86
3	FeL2	5	60

The Fe(III) complexes mediated the preparation of hydrogels with high conversion rates using HEMA as the monomer and EDB and Ph-Br as additives under 365 nm irradiation. The FeL1 complex showed the best performance in hydrogel formation, particularly in the system containing 45% water, achieving a conversion of 88%.

Copolymerization reactions

As shown in Figure 3 and 4, PHEMA-b-PBA copolymers were prepared using a three-component system comprising the photocatalyst (PC), Ph-Br, and EDB, under various conditions with 365 nm LED irradiation at room temperature and copolymers were subsequently diluted in tetrahydrofuran (THF, 1 mL) and analyzed by gel permeation chromatography (GPC) to determine the number-average molecular weight (Mn).

Figure 3. GPC traces of PHEMA-b-PBA with FeL1.

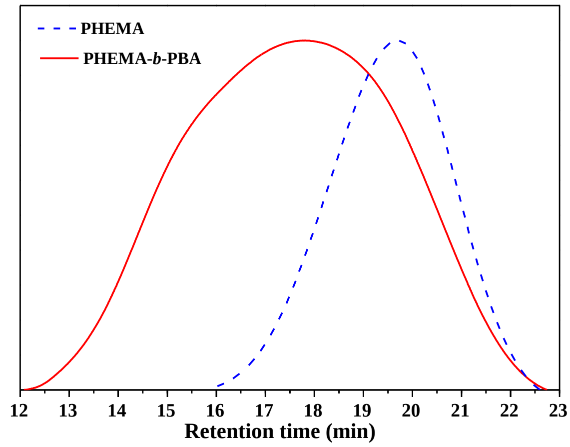
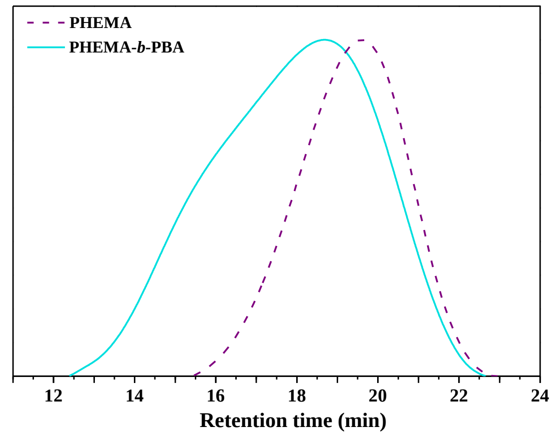


Figure 4. GPC traces of PHEMA-b-PBA with FeL2.



The resulting copolymers were characterized by ^1H NMR, according to Figure 5 and 6.

Figure 5. ^1H NMR of PHEMA-b-PBA with FeL1.

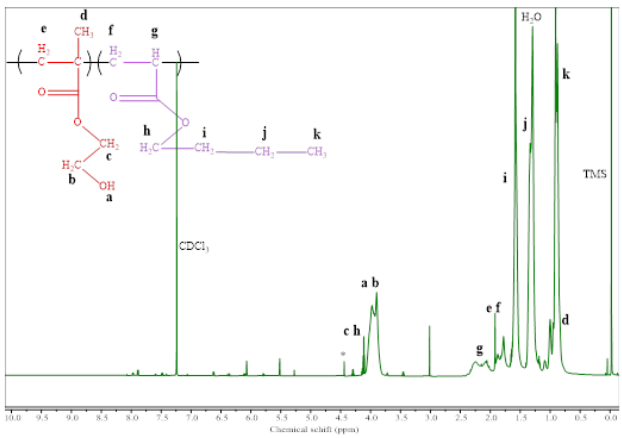
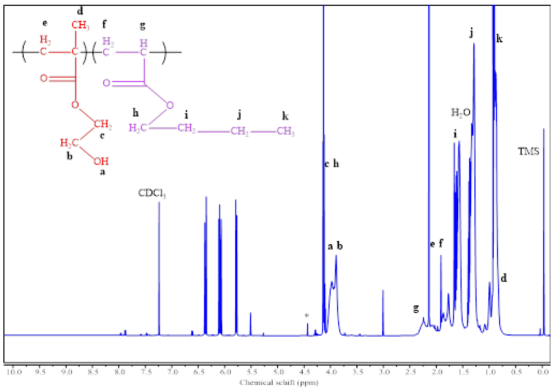


Figure 6. ^{1}H NMR of PHEMA-b-PBA with FeL2.



Conclusions

In conclusion, the results demonstrate that ligands and their corresponding complexes were successfully characterized using complementary techniques, including FTIR, UV–Vis spectroscopy, and cyclic voltammetry. Additionally, ^{1}H NMR spectroscopy was employed for the ligands, while MALDI-TOF mass spectrometry provided further confirmation for the complexes.

These complexes were able to mediate the photopolymerization of methyl acrylate in the presence of the additives EDB and Ph-Br under 365 nm irradiation, with the FeL2 complex at a 200/1/0.06/1 ratio demonstrating good control over the photo-ATRP process.

The Fe(III) complexes were able to prepare hydrogels with high conversion rates using HEMA as the monomer and EDB and Ph-Br as additives under 365 nm irradiation. The FeL1 complex exhibited the best performance in hydrogel formation, standing out in the system containing 45% water, where a conversion of 88% was achieved.

Fe(III) complexes enabled the copolymerization of HEMA and BA monomers using EDB and Ph-Br as additives under 365 nm LED irradiation. The resulting copolymers were further characterized by ^{1}H NMR spectroscopy.

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