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A Proof of Concept Zinc-Mediated RDRP of Alanine Acrylamide for Efficient Dye Encapsulation to Clean the Wastewater for Green Environment

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ABSTRACT

A PH-responsive synthetic biohybrid module poly (L-alanine acrylamide)-block-poly(methylmethacrylate (PAAIa-*b*-PMMA) diblock biohybrids, based on hydrophilic PAAIa and hydrophobic PMAA segments, is developed via direct switching from Zinc (Zn) catalyst polymerization. EbiB was used as an initiator to Zn-mediate Reversible deactivation radical polymerization (RDRP) of alanine-derived monomer, Alanine acrylamide (AAIa), yielding a series of (PAAIa-*b*-PMAA)-The copolymer's stimuli response has been assessed against pH. The aim of this investigation was to translate this structure into a synthetic polymer. The block-copolymer is capable of removal of toxic dye from wastewater. The produced polymer has remarkable adsorption capabilities towards a range of synthetic dyes, providing viable options for wastewater treatment that is sustainable. By using this creative approach, this research offer a practical and environmentally friendly way to deal with one of the most enduring environmental problems: dye contamination-induced water pollution. The study also looks at how this RDRP approach may be scaled up for industrial applications, guaranteeing a major decrease in environmental toxicity and encouraging the creation of environmentally friendly wastewater management solutions. This approach not only enhances the effectiveness of dye removal but also contributes to the development of eco-friendly and recyclable materials for wastewater purification for green environment.

Keywords: Amino Acid; Smart Polymer; Biohybrid; Biohybrid; PH-Responsive; Dye Encapsulations

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1. Introduction

The production of organic hazardous dyes usually takes place in underdeveloped nations from a variety of industrial effluents associated with the food, pharmaceutical, textile, paper, rubber, plastics, and leather industries. In the last few decades, responsive polymers—also referred to as “smart materials” have piqued natural scientists’ curiosity. Precision polymers with adjustable molecular weights, dispersities, macromolecular architecture, and end group functionality may now be produced more easily by reversible deactivation radical polymerization (RDRP) processes^[1–4]. Atom transfer radical polymerization (ATRP)^[5], single electron transfer live radical polymerization (SET-LRP), reversible addition fragmentation chain transfer (RAFT) polymerization (7, 8), and organometallic-mediated radical polymerization are a few of the widely used RDRP processes. The widespread industrial use of acrylate monomer RDRP has been hindered by a number of issues, though: (a) RAFT, which results in undesirable odor, color, and toxicity due to the presence of S-chain ends (9); and (b) SET-LRP, which is difficult to remove residual Cu(I) and/or Cu(II) precursors from the final polymers (10). Excessive amounts of moderate reducing agents are utilized in activators regenerated by electron transfer (ARGET) ATRP (11–14), which do not yield molecules capable of beginning an ATRP. Reducing agents can be inorganic, like tin (II) 2-ethylhexanoate or zerovalent copper, or organic, such as glucose, ascorbic acid, hydrazine, phenols, amines, or even an excess of ligands investigated various inorganic species (15, 16), including zerovalent metals, Zn⁰, Mg⁰, and Fe⁰, in quest of novel reducing agents (17). Block copolymers derived from amino acids have garnered significant attention recently. In this regard Acryloyl β -alanine (ABA) was successfully polymerized by ATRP in the presence of CuBr/Bpy water-methanol solutions as a solvent at room temperature, as reported by Chung et al. in 2005 (18). Using the ATRP technique and CuCl/bipy as a catalyst system, a peptide-based monomer bearing the well-known sheet-forming sequence alanine-glycine-alanine-glycine was synthesized in 2005 by Ayres et al.^[18]. In 2016, Rafiee et al. reported the ATRP of a monosubstituted acrylamide containing the amino acid moiety N-acryloyl-L-alanine (AAla) in the presence of two independent initiators at

room temperature: sodium 4-(bromomethyl)benzoate (SBB) and 2-hydroxyethyl-2'-methyl-2'-bromopropionate (HMB) (20). However, the technology must be further refined before it can replace conventional manufacturing methods. But their extensive use to design advanced materials for the above-mentioned applications is limited. This can be explained in terms of the following reasons: Easy, quick, reproducible tailoring of stimuli-responsive polymer networks based on polymers is still in its infancy. Reports on the zinc catalyst-mediated RDRP are quite rare. Among these is the ATRP of methyl methacrylate and styrene at 80 °C mediated by zinc oxide nanowires (21). Furthermore, RAFT of N,N-dimethylacrylamide, benzyl acrylate, benzyl methacrylate, and 2-hydroxypropyl methacrylamide in the presence of ZnTPP at 25 °C was conducted on methacrylate, methyl methacrylate at 25 °C. Zinc (Zn) catalyst is one of the most recently developed RDRP catalyst (25). However, the Zinc catalyst has not been explored as a catalyst for amino acid based RDRP. To the best of my knowledge, there is no report Zn-mediated RDRP of AAla and its Block copolymer. Herein, the research report, for the first time, zinc catalyst -mediated RDRP of monomer, leading to the synthesis of PAAAla at ambient temperature and a well-defined pH-responsive amphiphilic diblock copolymer poly(L-alanine acrylamide)-block-poly(methylmethacrylate (PAAAla-*b*-PMAA). Thus I believe that this Biomaterial will be employed for encapsulation of toxic dye from the waste industrial water to clean the environment.

2. Materials and Methods

The detailed experimental procedure for synthesizing the materials and their characterization techniques are given in the Supporting Information.

2.1. Synthesis of Acryloyl Alanine

Acryloyl-alanine (AAla) was prepared following a modification of a procedure reported earlier^[17].

2.2. General Procedure for the Zn-Mediated ATRP of Acryloyl Alanine

In a typical zinc mediated ATRP of alanine acryla-

mide was done by atom transfer radical polymerization using PMDETA as ligand system as well as EbiB initiator.

2.3. Synthesis of Poly Acryloyl Alanine with Varying M_{ns}

Alanine acrylamide of varying molecular weights was synthesized using the protocol described above, just by varying $[AAla]_0/[EBiB]_0$ ratio, keeping the amount of PMDETA and Zn catalyst constant.

2.4. Synthesis of PAAIa -*b*-PMMA Diblock Copolymer

Generally, PAAIa₄₀-*b*-PMMA₄₀ diblock copolymer was prepared via Zn-mediated ATRP described above using PAAIa-Br macroinitiator.

3. Results and Discussion

Here the work has shown that the varying molecular weight Polyalanine acrylamide (PAAIa) was prepared by very straightforward method (Figure 1). In this work, the polymerization condition was EbiB as an initiator and PMDETA/Zn ligand and catalyst system in the presence of DMSO. Alanine acrylamide (AAla) a monomer derived from alanine, was synthesized by a straightforward reaction and it was characterized using IR (see Supporting Information Figure S6) and NMR spectroscopy (see Supporting Information, Figures S1). The IR stack plot of alanine and AAla was shown that clear synthesis of amino acid monomer. (Figure S6)

The new NMR peak at 5.5–6.2 (amino acid and monomer (Figure S1)) clearly confirms the formation of a comonomer of alanine acrylamide. The IR peak of ala-

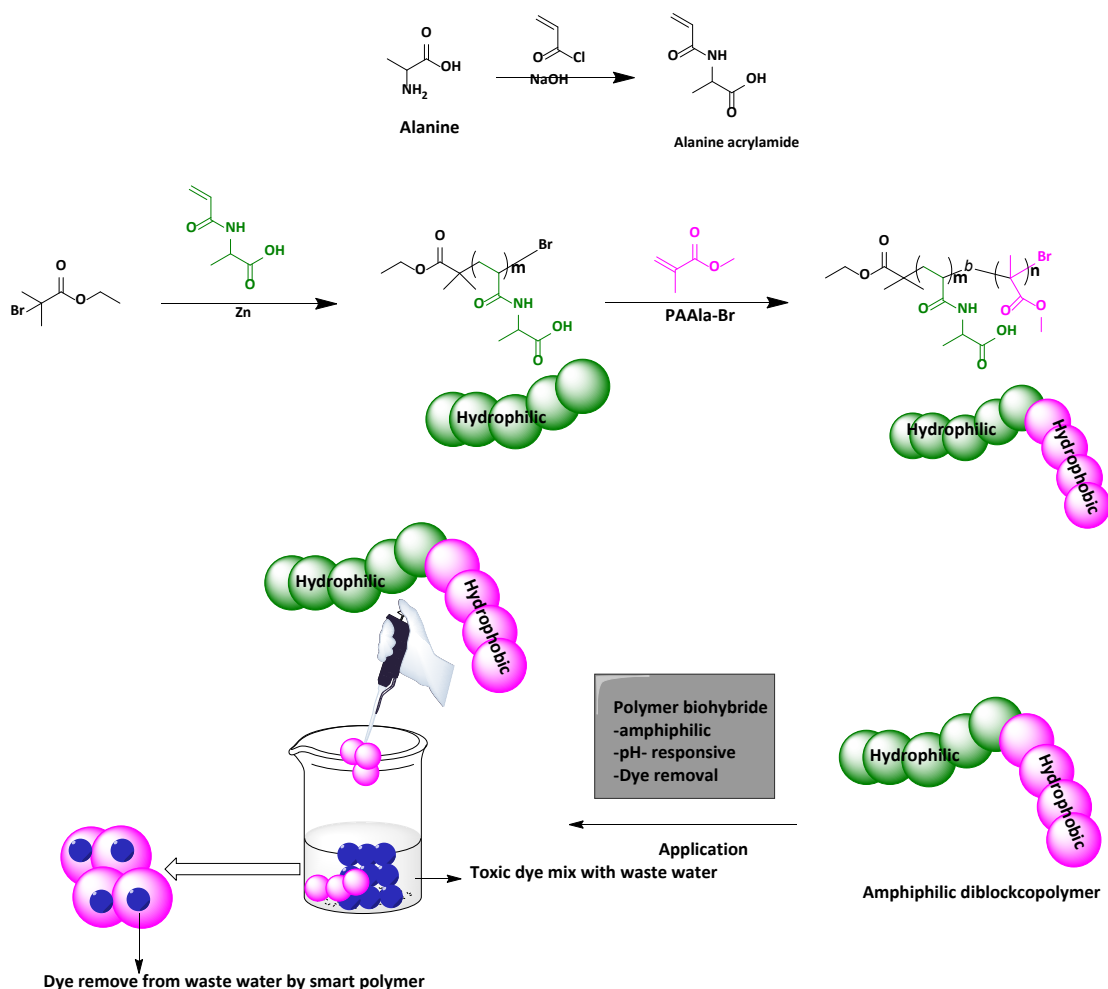


Figure 1. Synthesis of PAAIa-*b*-PMMA Diblock Copolymer via Mechanistic Transformation of Atom Transfer Radical Polymerization.

nine, monomer (**Figure S6**) and its polymer copolymers exhibited characteristic absorption band corresponding to PAAIa segment (at 1725 and 1650 cm^{-1} corresponding to the C=O stretching vibration of the amide functionalities) and alanine (1151 cm^{-1}), attributed to the stretching vibrations C–N functionality, (3100–3300, cm^{-1} assigned to the ester N–H stretching, the broad spectra of 3400 cm^{-1} attributed to the OH vibration. A range of homopolymerization syntheses carried out just varying monomer/initiator. In that case, I have seen DP=16 I got the polymer after 1 h and the % yield was 42 % gravimetrically. When vary the DP= 24, 32 and 40 the polymerization time was 1 h and % yield was 41 %, 57 % and 67 %, respectively (**Table S1**). All the homopolymerization were done in the presence of EbiB as initiator in the presence of Zn/PMDTA as the catalyst/Ligand system. (**Figures S3, S4 and S5**). ^1H NMR spectrum (DMSO-d_6), the characteristic peaks at 1.0–1.2 (EbiB end chain and the CH_3), The disappearance of vinyl peaks at 5.60–5.62, 6.09–6.12 and 6.26–6.32 ppm

confirmed conversion of monomer to poly(AAla) after 1 h reaction time. Peak at 1.5–2.3 (CH_2CH in the backbone, PAAIa), 3.8–4.6 (NCHCOO), and 7.3–8.4 (NH) ppm are clearly seen, which are attributed to the poly(A-Ala-OH) main chain ^[24]. Resonance of acidic and amidic protons at 12.68 and 7.6 ppm, C–Br end chain 4.27 ppm (**Figure S3**). Using PAAIa₄₀-Br as a macroinitiator in the presence of Zn/PMDTA as the catalyst/Ligand system amphiphilic block copolymer PAAIa-*b*-PMMA was synthesized. The NMR of homopolymer and block copolymer showed that in block there are two central blocks were present one comes from PAAIa part and other from the PMMA part. NMR peak and IR spectra. This block copolymer contains two part one is hydrophilic (PAAIa) and other one hydrophobic (PMMA). Typically, ^1H NMR spectrum of the PAAIa-*b*-PMMA block copolymer (BCP) (**Figure 2**) shows the characteristic signals of the PMA first block at 1.8 ppm, ($-\text{CH}_2$ of MA), 2.0–2.5 ppm (CH_2CH in the backbone, PAAIa) and 3.5 ppm ($-\text{CH}_3$ of MA).

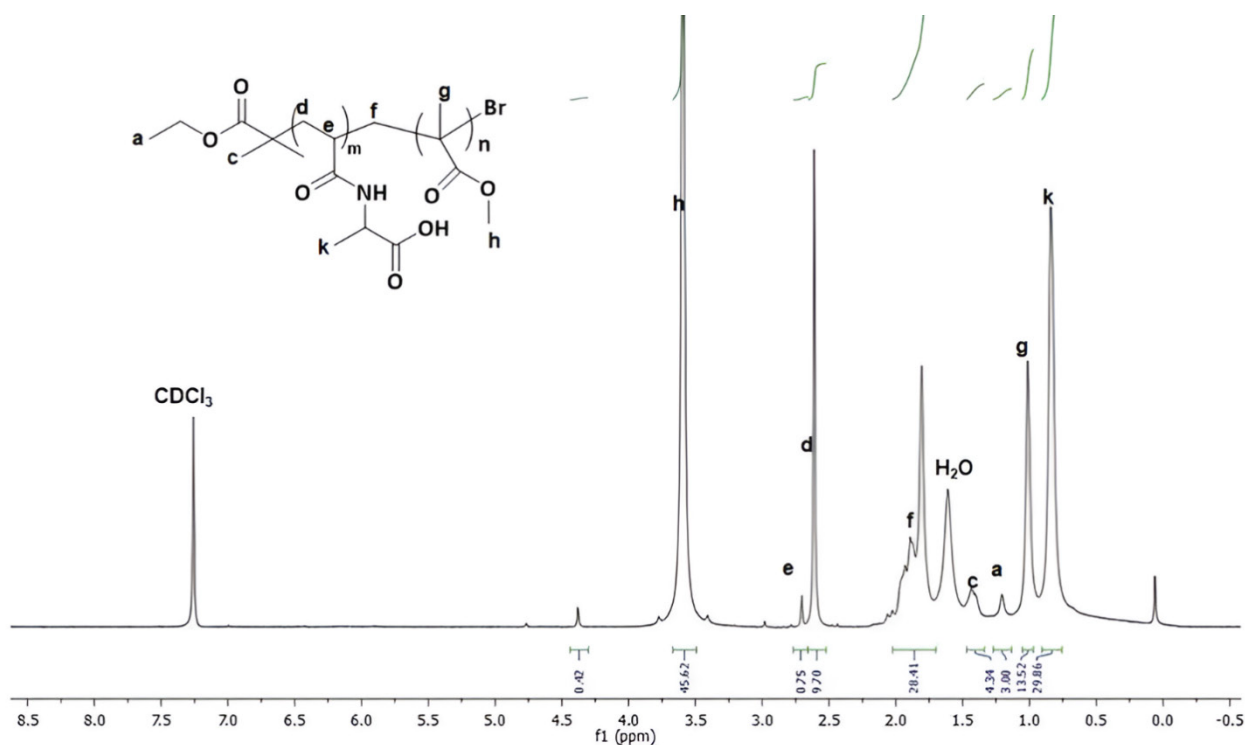


Figure 2. ^1H Spectra (CDCl_3 , 25 $^\circ\text{C}$) of Polyalanineacrylamide-*b*-Polymethylmethacrylate (PAAIa-*b*-PMMA).

3.1. PH-Responsive Property

It is expected that PAAIa will be pH-responsive (**Figure 3**). In the study at $\text{pH} < 1.8$, there is the possibility of the protonation of the COOH group, and due to protonation, there is also a possibility of H-bonding with the water medium and $\text{pH} > 8$, there is a possibility of deprotonation of COOH group and formation of COO^- . In a glass cuvette, the PAAIa solution was taken and the UV and COOH peak was shown at 210 nm (black spectra). In this solution, 0.1 N HCl was added and due to H-bonding with water the UV absorbance decreased with broad spectra (red and blue spectra). In the same solution when 0.25 (N) NaOH was added due to deprotonation and formation of COO^- and Na^+ the redshift has been shown, as well as the increase in the absorbance spectra (green and violet spectra).

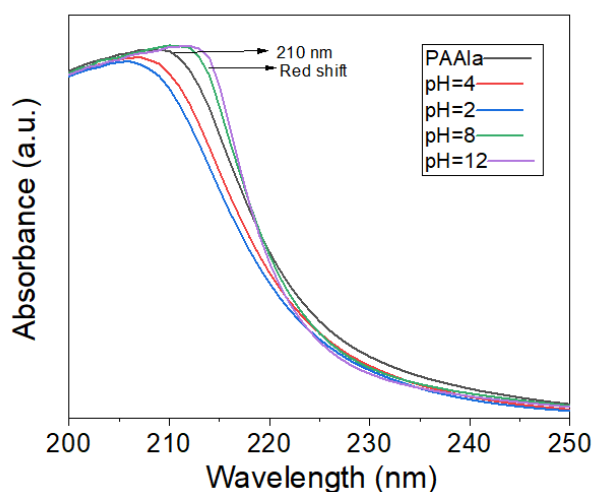


Figure 3. PH-Responsive Study of Polyalanineacrylamide.

3.2. Dye Encapsulation from Wastewater

Usually, a solution of methylene blue was added to the synthesized PAAIa-*b*-PMMA diblock copolymer, and it was left undisturbed for 5 hours. UV-vis spectroscopy was used to track the percentage of dye encapsulation over time (**Figure 4**). The removal of a representative hydrophobic dye (Methylene Blue, MB) from water is evaluated to determine the effectiveness of PAAIa-*b*-PMMA, and the encapsulation capacity was determined using UV-vis spectroscopy. Methylene blue's absorbance at 665 nm steadily dropped with time (**Figure 4b**), resulting in a 40% dye exchange after 5 hours of incubation (**Figure 4a**). After five hours, the UV absorbance spectrum (**Figure 4c** and **4d**)

demonstrates the dye's encapsulation. The peak position, however, stays the same, indicating that the dye encapsulation was successful.

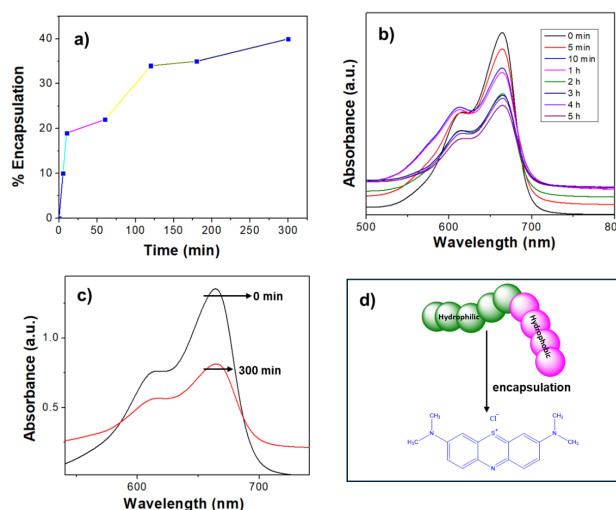


Figure 4. (a) Evaluation of % Encapsulation of MB with Time; After Incubating with PAAIa-*b*-PMMA; (b) Time-Dependent (Initial-0 h, Final-300 Min) UV-Vis Spectra of MB; (c) UV Spectra at 0 Min and After 300 Min; (d) The Model Polymer and the Dye.

4. Conclusions

In summary, this research presents the synthesis of a novel amphiphilic pH-responsive (PAAIa-*b*-PMMA) diblock copolymer via Zinc mediated RDRP. The block copolymer was made by Polyalanine hydrophilic moiety. This transformation was achieved through a mechanistic transformation from living radical polymerization. It is possible to combine the functions of two distinct terms (synthetic polymer and biomolecule) with this new class of innovative biohybrids. The produced zwitterionic copolymer exhibits single stimuli responsive (pH), a reduction in protein adsorption at its zwitterionic state, and the ability to switch between zwitterionic, anionic, and cationic forms. The synthesized polymer is capable of removing the toxic dye from wastewater. The benefits of group-free chemistry, handling, recovery, and reusability in addition to the ease of catalyst synthesis, could make this simple synthesis protocol highly applicable for synthesizing biohybrids in many exciting fields, such as material science and biomedical science. The pH-responsive biohybrid that was synthesized could be helpful in the development of multi-stimulus responsive actuators for use in biomedical

applications.

Supplementary Materials

The following supporting information can be downloaded at: <https://ojs.bilpub.com/public/NEFM-297-Supplementary-Material.docx>

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Informed Consent Statement

Not applicable.

Data Availability Statement

All the data were created during the current study. It is available in the supporting information and it will be available from the corresponding author on reasonable request.

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Conflicts of Interest

The author declares no conflict of interest.

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