

Organocatalyzed polymerization of diblock copolymer based on poly(3-hexylthiophene) and poly(furfurylmethacrylate)

Hai Le Tran^{1,2,3,4} , Chau Duc Tran^{2,4} , Cam Hong Thi Nguyen¹ , Thao Phuong Le Nguyen¹ ,
Le-Thu Thi Nguyen^{2,4} , Thiet-Quoc Nguyen⁵ , Mai Ha Hoang⁶ , Tam Huu Nguyen^{1,4}  and
Ha Tran Nguyen^{1,2,4*} 

¹National Key Laboratory of Polymer and Composite Materials, Ho Chi Minh City University of Technology – HCMUT, Ho Chi Minh City, Vietnam

²Ho Chi Minh City University of Technology – HCMUT, Ho Chi Minh City, Vietnam

³University of Science, VNU-HCM, Ho Chi Minh City, Vietnam

⁴Vietnam National University Ho Chi Minh City – VNU-HCM, Ho Chi Minh City, Vietnam

⁵Institute of Applied Materials Science, Vietnam Academy of Science and Technology, Ho Chi Minh City, Vietnam

⁶Institute of Chemistry, Vietnam Academy of Science and Technology, Ha Noi, Vietnam

*nguyentrinha@hcmut.edu.vn

Abstract

A novel conjugated rod–coil diblock copolymer poly(3-hexylthiophene)-*block*-poly(furfuryl methacrylate) (P3HT-*b*-PFMA) has been successfully synthesized for the first time using photoinduced organocatalyzed atom transfer radical polymerization (O-ATRP). This process utilized an organic photoredox catalyst of N-aryl phenoxazine, namely 10-(Perylene-3-yl-10H-Phenoxazine, under 365 nm UV irradiation. The diblock copolymer P3HT-*b*-PFMA was produced efficiently in a controlled manner, resulting in designed average molecular weights and a narrow polydispersity index. Notably, the furfurylmethacrylate (FMA) monomer derived from biomass-based furfuryl compounds was applied for this controlled polymerization, leading to the formation of conjugated diblock copolymers. The synthesized P3HT-*b*-PFMA was characterized through ¹H-NMR, FT-IR, and GPC methods. Furthermore, the optical and hydrophilic-hydrophobic properties of P3HT-*b*-PFMA were also evaluated through UV-Vis spectroscopy and contact angle measurements.

Keywords: *diblock copolymer, poly(3-hexylthiophene), organic photocatalyst, biomass-based monomer, atom transfer radical polymerization.*

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1. Introduction

Over the past decades, the conjugated polymer has become a promising organic material for optoelectronic applications^[1-5]. This is because they have numerous excellent properties, including high conductive properties in the oxidization state, good solubility in typical solvents, low toxicity, and strong chemical stability in normal environmental conditions. Among conjugated polymers, poly(3-hexylthiophene) (P3HT) has been intensively researched for widespread electronic applications, including organic solar cells, organic field effect transistors, the electrode in lithium batteries, and protective coating^[6-10]. Additionally, there have been many reports showing that rod-coil block copolymers based on poly(3-hexylthiophene) are potentially utilized in organic electronics^[11-14]. Such block copolymers based on P3HT have contributed advanced properties by improving

mechanical strength and forming self-organized structures in various morphologies on the nanometer scale, such as lamellar, cylindrical and spherical structures^[15-17]. Moreover, the incorporation of functionalized coil block segments in the P3HT-based block copolymers can pave the way for the development of optical sensor organic materials^[18,19].

The controlled/living radical polymerization methods have been used as primary techniques for synthesizing rod-coil diblock copolymers^[12]. Among these methods, atom transfer radical polymerization (ATRP) has been extensively utilized for the synthesis of rod-coil diblock copolymers. ATRP has been proven successful in creating various advanced polymers with well-defined structures and controlled architecture^[20-23]. In traditional ATRP, metal catalysts are employed in the polymerization

process, which archived a control over the molecular weight, the narrow polydispersity index, and controlled end-groups of the resulting polymers. However, such polymers produced through traditional ATRP with transition metal catalysts may retain traces of metal, which causes tremendous damage in subsequent uses of the polymeric products^[24]. This poses challenges for applications in biomedicine and optoelectronic fields. To address this issue, organic photocatalyst (O-ATRP/metal-free ATRP) has been explored and developed for controlled radical polymerization, gradually replacing traditional ATRP with transition metal catalysts^[25-29].

On the other hand, biomass-derived furfuryl methacrylate (FMA), prepared from cellulosic-biomass-derived furfural, emerges as a potential substitute for the current petroleum-based methacrylate monomers, such as methyl methacrylate (MMA) and *iso*-butyl methacrylate^[30]. The FMA monomer owns a reactive functional furfuryl group, making it a valuable material for practical applications such as coatings, sealing, and adhesives^[31,32]. However, when FMA monomer undergoes conventional radical polymerization and classical anionic polymerization, it results in insoluble poly(furfuryl methacrylate) (PFMA). This outcome is attributed to excessive chain transfer related to the reactive furfuryl group present in both the polymer and the monomer. To overcome this challenge, atom-transfer radical polymerization (ATRP) of FMA has been employed to produce gel-free polymers with controlled average molecular weight^[33]. Pérez et al.^[34] reported diblock copolymers consisting of poly(trimethylene carbonate) and poly(furfuryl methacrylate) PFMA end blocks. These copolymers were synthesized through sequential organocatalytic ring-opening polymerization (ROP) and photoinitiated metal-free atom-transfer radical polymerizations (O-ATRP) of furfuryl methacrylate. These copolymers exhibited thermoreversible properties. Additionally, Raffa et al. synthesized a series of copolymers of styrene and furfuryl methacrylate, applied for self-healing materials due to the thermally reversible Diels–Alder (DA) reaction^[35]. However, there is a lack of reports on the synthesis and investigation of diblock copolymers based on a coil segment of poly(furfuryl methacrylate) with P3HT as a rod segment.

To address this, we reported the synthesis of rod-coil diblock copolymer utilizing regioregular poly(3-hexylthiophene) (P3HT) as the rod segment and poly(furfuryl methacrylate) (PFMA) polymerized from furfuryl methacrylate as the coil segment. The polymerization of the FMA monomer was conducted through photoinitiated organocatalyzed atom transfer radical polymerization under UV irradiation, employing 10-(Perylene-3-yl)-10H-Phenoxazine (PPOZ) as a photocatalyst. The resulting diblock copolymer, termed poly(3-hexylthiophene)-*block*-poly(furfuryl methacrylate) (P3HT-*b*-PFMA), was characterized using ¹H NMR, FTIR spectroscopies, and GPC analysis. Furthermore, we explored the optical properties of the diblock copolymer through UV-Vis spectroscopy.

2. Materials and Methods

2.1 Materials

3-Hexylthiophene, (Diacetoxyiodo)benzene, 3-Bromo perylene, 10H-phenoxazine, furfuryl alcohol,

1,3-Bis(diphenylphosphino)propane nickel(II) chloride, iodine, chloro 1-methylethyl magnesium solution (2 mol/L in THF), methacryloyl chloride, potassium carbonate (K₂CO₃, 99.5%) and N-bromosuccinimide were purchased from Fisher and Acros Organics. These chemicals were preserved in a glove box at ambient temperature. Anhydrous tetrahydrofuran (THF, 99.8%), 2-2-Bromo-2-methylpropionyl bromide (Br-iBuBr), triethylamine (NEt₃, 99%), sodium borohydride (NaBH₄, 99%), copper(I) bromide (CuBr, 98%), Palladium(II) acetate (Pd(OAc)₂, 98%), tri-*tert*-butylphosphine (P(*t*-Bu)₃, 97%), sodium *tert*-butoxide (NaOtBu, 97%), and phosphoryl chloride (POCl₃, 99%) were obtained from Sigma-Aldrich. Methanol (99.8%), chloroform (CHCl₃, 99.5%), toluene (99.5%), n-hexane (99%), ethyl acetate (99%), and diethyl ether (99%) were acquired from Fisher and Acros Organics. All the solvents were used as received.

2.2 Measurements

TLC analysis was collected on glass surface coated by a fluorescent indicator F-254. FT-IR analysis was carried out on a Tensor 27 Bruker instrument, involving 264 scans with a resolution set at 4 cm⁻¹. For ¹H NMR spectra, a Bruker Avance 500 MHz instrument was utilized, employing a solvent of deuterated chloroform (CDCl₃) and an internal reference of Tetramethylsilane. GPC analysis was executed by using gel permeation chromatography (Varian Polymer PL-GPC 50) with an RI detector. The GPC experiments employed anhydrous THF as the eluent, with a flow rate of 1.0 mL.min⁻¹. Polystyrene (PS) standards were used to evaluate the average molecular weight and the molecular weight distribution of the resulting polymers. The optical properties of the polymers were assessed through UV-Vis spectroscopy using Agilent UV-Vis 8453 diode array, covering a wavelength range from 190 nm to 1100 nm.

2.3 Synthesis of furfuryl methacrylate monomer (FMA)

The synthesis procedure involved dissolving furfuryl alcohol (5 mL, 1 eq) in 20 mL of THF, followed by an addition of triethylamine (10 mL, 1.25 eq) to the solution. The mixture was then cooled to 5 °C, and methacryloyl chloride (8.4 mL, 1.5 eq) was dropwise added over 1 h. The reaction proceeded for 16 h at room temperature. Subsequently, the mixture was diluted with 30 mL of dichloromethane and subjected to multiple washes by deionized water (50 mL). Then, the organic phase was dried using anhydrous K₂CO₃ and subsequently filtrated to collect the anhydrous organic mixture. The solvent was then removed under reduced pressure to obtain the crude product. Purification of the crude product was achieved through silica gel column chromatography using ethyl acetate: n-hexane (1:50) as the eluent, resulting in the isolation of a light-yellow oil with a yield of 95%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 1.95 (s, 3H), 5.14 (s, 2H), 5.57 (s, 1H), 6.13 (s, 1H), 6.36 (d, 1H), 6.42 (d, 1H), 7.42 (s, 1H). Elemental Analysis for C₉H₁₀O₃: Calculated C, 65.05; H, 6.07; O, 28.88. Found: C 66.20; H, 5.96; O, 27.84.

2.4 Synthesis of photocatalyst 10-(perylene-yl)-10H-phenoxazine (PPOZ)

PPOZ was synthesized with a modified synthetic procedure from our previous article^[36]. A magnetic stir bar was introduced

into a 25 mL round-bottom flask, which was then evacuated and filled with nitrogen. Subsequently, 8 mL of toluene was added to the reaction flask. The 10H-phenoxazine (160 mg, 0.81 mmol), Pd(OAc)₂ (3.61 mg, 0.016 mmol), NaOtBu (116 mg, 1.20 mmol), and P(t-Bu)₃ (6.50 mg, 0.032 mmol) were sequentially added to the solution. Following this, 3-Bromo perylene (297 mg, 0.90 mmol) was introduced to the reaction. The reaction proceeded at 110 °C for 4 h. Then, the temperature of the flask was reduced to ambient temperature. Afterwards, the mixture was diluted with CHCl₃ (50 mL), washed with deionized water, and dried over K₂CO₃. The organic layer was then filtered, and the solvent evaporated using a rotary evaporator to obtain the crude product. Purification of the crude product was achieved through column chromatography using a mixture of ethyl acetate: n-hexane (5:95), resulting in the isolation of a white solid powder. The product was further dried at 70 °C under vacuum for 24 h, yielding 85%. ¹H NMR (500 MHz, CDCl₃): δ (ppm): 5.88 (d, 2H), 6.53 (t, 1H), 6.64 (t, 2H), 6.73 (d, 2H), 7.48 (t, 1H), 7.54 (t, 3H), 7.75 (t, 2H), 7.91 (d, 1H), 8.25 (t, 3H), 8.35 (d, 1H). Elemental Analysis for C₃₂H₁₉NO: Calculated C, 88.66; H, 4.42; N, 3.23; O, 3.69. Found: C, 87.92; H, 4.63; N, 3.36; O, 4.09.

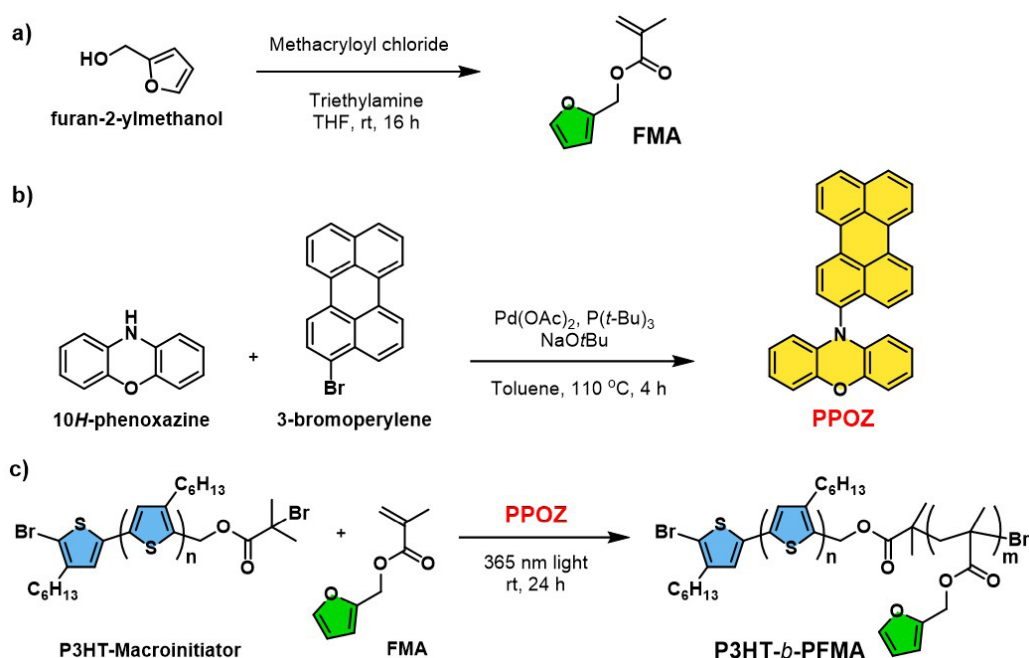
2.5 Synthesis of rod-coil diblock copolymer poly(3-hexylthiophene)-block-poly(furfuryl methacrylate) (P3HT-*b*-PFMA)

P3HT-*b*-PFMA was synthesized through metal-free atom transfer radical polymerization (ATRP) utilizing the P3HT-macroinitiator and PPOZ as a photoredox catalyst according to our previous report^[37]. In a 25 mL flask, 100 mg of P3HT-macroinitiator (M_n¹H NMR = 9000 g/mol, 0.011 mmol) was combined with 5 mL of THF solvent using a syringe, and the solution was stirred

until homogeneous. Then, a solution of FMA (36.5 mg, 0.22 mmol) and PPOZ (2.38 mg, 0.005 mmol) was added. The mixture underwent three freeze-pump-thaw cycles for degassing, followed by continuous stirring until homogeneity was achieved. Subsequently, the solution was inserted in a UV-box (365 nm) for 24 h at room temperature. Finally, the resulting polymer solution was extracted with CHCl₃, precipitated into cold methanol, and dried under vacuum, yielding 125 mg of the desired product with a conversion rate of 68%. FT-IR (cm⁻¹): 795, 1014, 1453, 1509, 1561, 1728, 2853, 2922, 2953. ¹H NMR (500 MHz, CDCl₃), δ (ppm): 6.96 (s, 1H), 3.60 (s, 3H), 2.80 (t, 2H), 1.69 (sex, 2H), 1.49 (q, 6H), 0.89 (t, 3H). GPC: M_n = 12400 g/mol, Đ = 1.42. M_n estimated by ¹H NMR = 12650 g/mol.

3. Results and Discussion

Scheme 1 presents the preparation of the monomer FMA and the synthesis of diblock copolymer poly(3-hexylthiophene)-*block*-poly(furfuryl methacrylate) (P3HT-*b*-PFMA) through O-ATRP using a photocatalyst PPOZ. The P3HT macroinitiator was synthesized using the GRIM method, providing end groups for the macroinitiator^[37]. The FMA monomer was obtained from an esterification reaction between furfuryl alcohol and methacryloyl chloride in the presence of triethylamine, yielding 95%. On the other hand, the photocatalyst PPOZ was synthesized from 10H-phenoxazine with 3-Bromo perylene through a C-N cross-coupling reaction, resulting in an 85% yield. The PPOZ exhibited maxima absorption at 254 nm, 350 nm, and 440 nm. The obtained results of ¹H NMR and gel permeation chromatography (GPC) determined the M_n of the P3HT macroinitiator was approximately 9000 g/mol^[38]. Subsequently, the P3HT macroinitiator

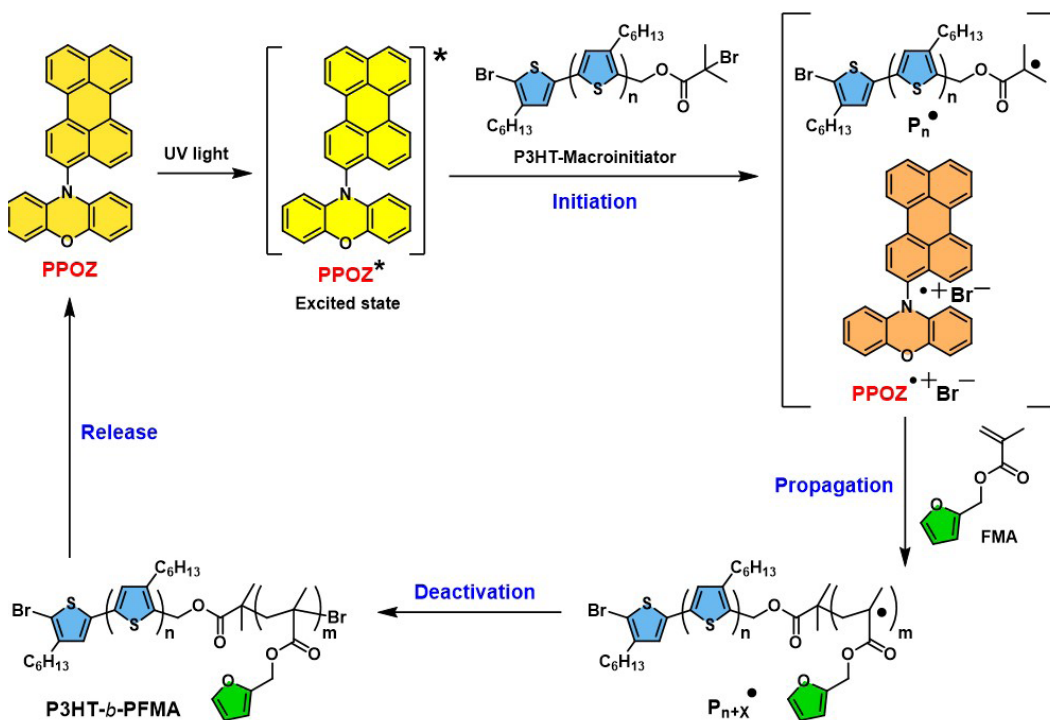


Scheme 1. Synthesis route of FMA, PPOZ, and diblock copolymer P3HT-*b*-PFMA.

was utilized to polymerize of FMA monomer in the presence of the PPOZ with various contents under UV irradiation to produce the diblock copolymers. To achieve a controlled metal-free ATRP, the molar ratio of monomers/ macroinitiator/PPOZ was established as follows: $([FMA]/[P3HT\text{-macroinitiator}]/[PPOZ]) = 100/1/0.01\text{-}0.5$. The polymerization was conducted at room temperature for 24 h using anhydrous tetrahydrofuran. The resulting diblock copolymers P3HT-*b*-PFMA were precipitated in cold methanol, followed by filtration under vacuum. Subsequently, the diblock copolymers P3HT-*b*-PFMA were dried at 70 °C for 24 hours.

Based on the principles of conventional ATRP established by the Pearson et al.^[39], and Matyjaszewski group^[40], the proposed mechanism for the O-ATRP using the PPOZ as the photocatalyst can be illustrated in Scheme 2. Upon UV irradiation, PPOZ is excited to a state capable of reducing the P3HT-macroinitiator through an oxidation

process, generating an activated radical for polymerization propagation. Additionally, the oxidation of the PPOZ^{•+}Br⁻ complex creates a deactivation, leading to the regeneration of P3HT-macroinitiator and the neutral state of PPOZ. This activation and deactivation process maintains control over the radical polymerization. When conducting the O-ATRP for furfuryl methacrylate with a low content of photocatalyst ($[FMA]:[P3HT\text{-macroinitiator}]:[PPOZ] = 30:1:0.01$) in THF solvent, the polymerization conversion was low, which accounted for 10% (Entry 1, Table 1). Increasing the catalyst content to 0.05 equivalents while maintaining other reaction parameters, the polymerization conversion significantly increased to 68% (Entry 2, Table 1). Conversely, at a catalyst content of 0.1 equivalent, the polymerization conversion decreased to 54% (Entry 3, Table 1). The result could be due to the high loading of PPOZ, which generates many radicals, leading to the quenching of polymerization propagation and resulting in polymers with lower molecular



Scheme 2. Proposed mechanism of O-ATRP of FMA using an organic photocatalyst PPOZ.

Table 1. Macromolecular characteristics of P3HT-*b*-PFMA polymerized by organic photocatalyst ATRP process using P3HT-Macroinitiator ($M_{n,NMR} = 9000$ g/mol, $\bar{D} = 1.10$) and PPOZ.

Entry	$[FMA]/[P3HT\text{-Macroinitiator}]/[PPOZ]$	Conv. (%) ^a	$M_{n,GPC}$ (g/mol) ^b	\bar{D} ^b
1	30/1/0.01	10	10500	1.27
2	30/1/0.05	68	12400	1.42
3	30/1/0.1	54	11700	1.47

^aConversion was calculated by gravimetric method, as follow: $Conv = (m - m_1 - m_{PPOZ})/m_M$ wherein, m is the weight of product, m_1 is the weights of the macroinitiator, m_{PPOZ} and m_M are the weights of the PPOZ catalyst and monomer, respectively; ^bNumber-average molecular weight (M_n) and polydispersity index (\bar{D}) as determined by GPC in THF at 35 °C.

weight compared to the theoretical number-average molar mass of the polymer.

The obtained diblock copolymers from the O-ATRP were analyzed via ^1H NMR after 24 h. In Figure 1, the peak at 6.97 ppm corresponds to the methine proton of thiophene moieties, while the other peaks at 0.91, 1.35, 1.71, and 2.8 ppm are attributed to the alkyl chain of 3-hexylthiophene. Additionally, the peak at 4.91 ppm is assigned to the methylene of furfuryl methacrylate units, and the peaks at 6.35 ppm and 7.43 ppm correspond to the protons of furfuryl ring moieties, revealing signals corresponding to the PFMA block (peaks c, d, e, and f). Consistent with the results of ^1H NMR characterization, the GPC traces of the diblock copolymer P3HT-*b*-PFMA were found to shift toward higher molecular weights over reaction time (Figure 2). This confirms the successful synthesis of diblock copolymer P3HT-*b*-PFMA. The determination of the polymerization degree of the PFMA block was conducted on ^1H NMR spectroscopy, calculated based on the relative intensities of the methine group of P3HT (peak

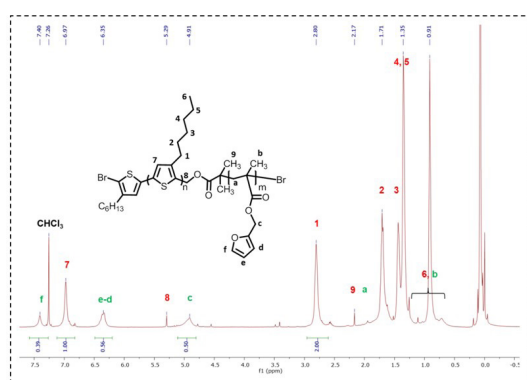


Figure 1. ^1H NMR spectra of P3HT-*b*-PFMA after 24h of irradiation time (entry 2, Table 1).

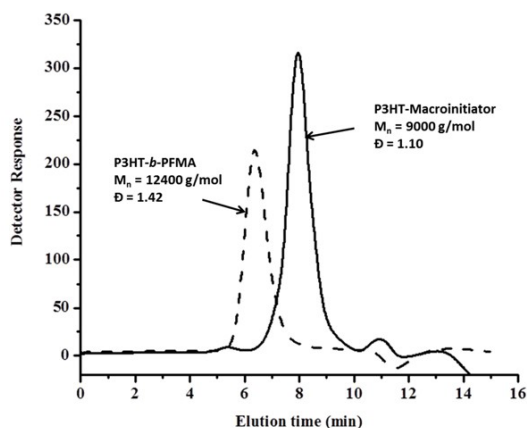


Figure 2. GPC traces of P3HT-*b*-PFMA before and after 24h of irradiation time (entry 2, Table 1).

7, $\delta = 6.97$ ppm) and that of furfuryl (peak f, 7.43 ppm). The estimated molecular weight (M_n) of the coil polymer block PFMA was calculated to be approximately 3650 g/mol, corresponding to 22 repeating units of furfuryl methacrylate. Consequently, the M_n of diblock copolymers P3HT-*b*-PFMA was estimated to be around 12650 g/mol. The estimated M_n for the P3HT-*b*-PFMA diblock copolymers aligns reasonably well with the experimental molecular weights evaluated by GPC, although GPC molecular weights are not absolute values.

To investigate the influence of UV light on the organic photocatalyst polymerization, controlled polymerization experiments were conducted by switching on/off the UV light. The experiments used a ratio of [FMA]:[P3HT-Macroinitiator]:[PPOZ] = 30:1:0.05 under a nitrogen condition. The polymerization flask experienced replicated cycles of UV illumination exposure for 2 h, followed by periods of darkness for 1 h at each interval to isolate the copolymer product and calculate the polymerization conversion. The copolymers acquired at each time point were analyzed using GPC for a determination of the average molecular weight. The results indicated that monomers were not consumed when the UV light turned off (Figure 3A). Additionally, the molecular weight increased when exposed to UV light during the reaction. Furthermore, a linear plot of conversion versus polymerization time confirmed that the FMA polymerization followed first-order kinetics throughout the reaction (Figure 3B). In Figure 3C, the GPC traces of copolymers clearly illustrate a gradual increase in molecular weight with reaction time.

The solubility of the diblock copolymer P3HT-*b*-PFMA was investigated in various solvents using UV-Vis spectroscopy. The UV-Vis absorption spectrum of P3HT-*b*-PFMA in various solvents and as a thin film is presented in Figure 4. The results indicate that the diblock copolymers P3HT-*b*-PFMA exhibited good solubility in chloroform (CHCl_3), dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), and toluene. However, in ethyl acetate, the diblock copolymers P3HT-*b*-PFMA was not completely soluble and precipitated, leading to P3HT chain aggregation. Additionally, the solid thin film of P3HT-*b*-PFMA showed a red-shift with a maximum absorption at 520 nm and a shoulder absorption at 610 nm. The absorption spectrum of the thin film P3HT-*b*-PFMA is similar to that of the homopolymer *rr*-P3HT, which has an optical band gap of 1.9 eV.

The incorporation of a coil polymer into the rod segment could change the hydrophilicity of P3HT-based materials. Therefore, the surface wettability of diblock copolymers P3HT-*b*-PFMA was examined through contact angle measurements. Figure 5 shows the water contact angle when water was deposited on the surfaces of homopolymer P3HT and diblock copolymers P3HT-*b*-PFMA. The homopolymer P3HT exhibited a contact angle value of 98.8° throughout the experiment, indicative of hydrophobic properties. In contrast, water contact angles on diblock copolymers P3HT-*b*-PFMA exhibited a value of 71.8° , indicating a more hydrophilic nature. This result proves that the incorporation of the PFMA segment into the hydrophobic P3HT changes the hydrophilicity of P3HT from hydrophobic to amphiphilic properties.

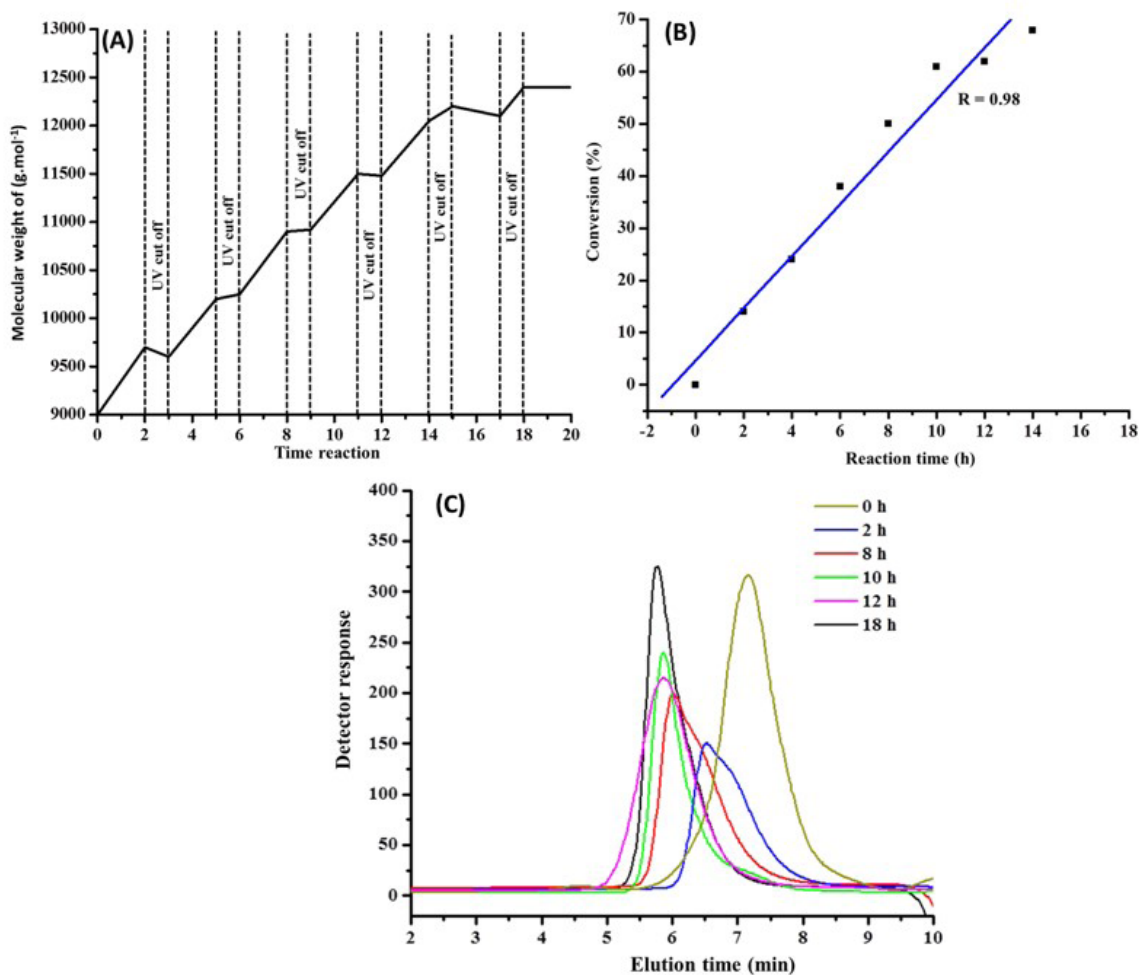


Figure 3. (A) Plot of molecular weight of copolymer P3HT-*b*-PFMA vs time demonstrating the control over polymerization propagation through irradiation ([FMA]:[P3HT-Macroinitiator]:[PPOZ] = 30:1:0.05; (B) First-order kinetic plot of monomer conversion vs time; (C) GPC traces of P3HT-*b*-PFMA diblock copolymers vs reaction time.

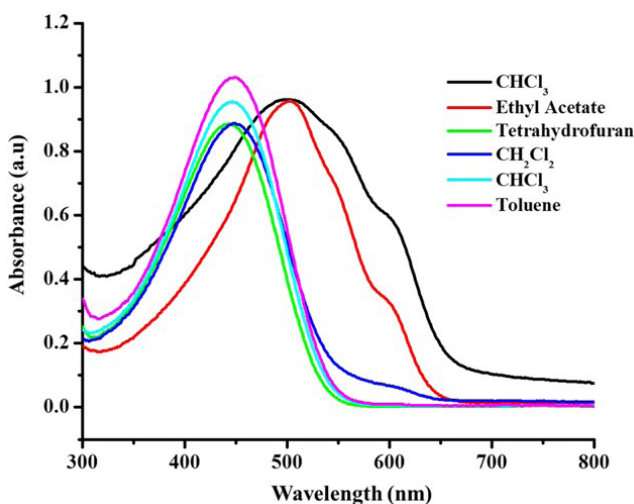


Figure 4. The UV-Vis absorption spectra of P3HT-*b*-PFMA in different solvents and in thin film.

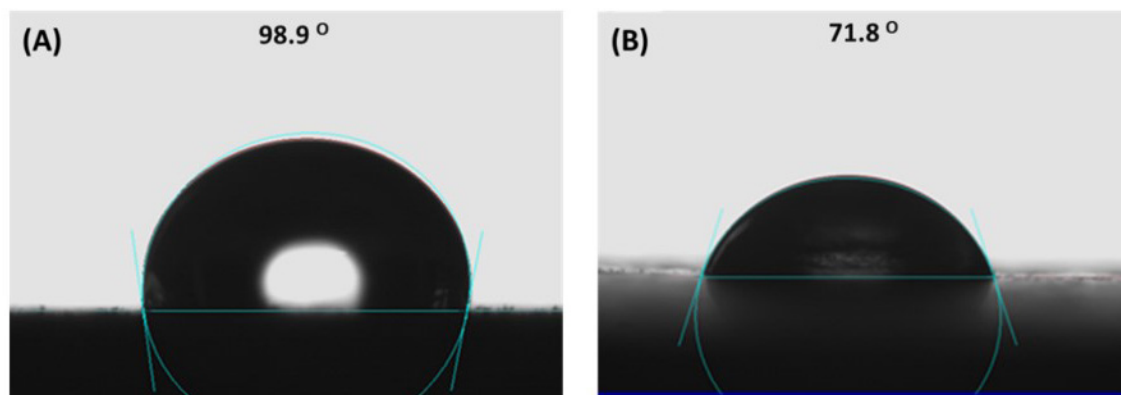


Figure 5. Water contact angles on P3HT thin film (A) and P3HT-*b*-PFMA thin film (B).

4. Conclusion

In the present work, we have successfully synthesized a new rod-coil diblock copolymer, P3HT-*b*-PFMA, through O-ATRP using the organic photocatalyst polymerization of furfuryl methacrylate monomers. The P3HT-*b*-PFMA was characterized by using ^1H NMR, GPC, FT-IR, and UV-vis methods to evaluate their chemical structure and optical properties. Additionally, the hydrophilicity of diblock copolymer P3HT-*b*-PFMA was assessed through contact angle measurements. The obtained P3HT-*b*-PFMA exhibited amphiphilic properties, making them soluble in various organic solvents. This result holds potential significance for electronic circuit printing using novel organic semiconductors.

5. Author's Contribution

- **Conceptualization** – Hai Le Tran; Ha Tran Nguyen.
- **Data curation** – Hai Le Tran; Thiet Quoc Nguyen; Mai Ha Hoang.
- **Formal analysis** – Hai Le Tran.
- **Funding acquisition** – Hai Le Tran.
- **Investigation** – Hai Le Tran; Chau Duc Tran.
- **Methodology** – Cam Hong Thi Nguyen; Thao Phuong Le Nguyen; Le-Thu Thi Nguyen; Thiet-Quoc Nguyen; Mai Ha Hoang; Tam Huu Nguyen; Ha Tran Nguyen.
- **Project administration** – Ha Tran Nguyen.
- **Resources** – Hai Le Tran; Ha Tran Nguyen.
- **Software** – Thiet-Quoc Nguyen; Mai Ha Hoang.
- **Supervision** – Ha Tran Nguyen.
- **Validation** – Ha Tran Nguyen.
- **Visualization** – Hai Le Tran.
- **Writing – original draft** – Hai Le Tran; Ha Tran Nguyen.
- **Writing – review & editing** – Ha Tran Nguyen.

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