CATEGORY

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Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

http://chemeng.hust.edu.vn/jca/

Well-defined rod coil diblock copolymers based on poly(3-hexylthiophene) and poly(methyl methacrylate) via metal-free atom transfer radical polymerization

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ARTICLE INFO

Received: 03/4/2018
Accepted: 08/5/2018

Keywords:
rod-coil diblock copolymers, poly(3-hexylthiophene)-*block*-poly(methyl methacrylate), metal-free atom transfer radical polymerization, pyrene

ABSTRACT

We have successfully demonstrated a facile synthetic route for well-defined three poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) rod-coil diblock copolymers (P3HT-*b*-PMMA), $P3HT_{50}$-*b*-$PMMA_{16}$, $P3HT_{50}$-*b*-$PMMA_{21}$, and $P3HT_{50}$-*b*-$PMMA_{63}$ by metal-free atom transfer radical polymerization using pyrene as an organic photocatalyst. Polymerization of methyl methacrylate is efficiently activated with light leading to excellent control over the molecular weight, polydispersity, and compositions of the resulting diblock copolymers. The structure and properties of the resulting P3HT-*b*-PMMA diblock copolymers were characterized by proton nuclear magnetic resonance, gel permeation chromatography, fourier transform infrared.

Introduction

The self-assembly of rod-coil block copolymers based on π-conjugated rod segment as regioregular poly(3-hexylthiophene) (P3HT) has attracted significant interest owing to its potential in a variety of applications such as chemical and optical sensors, light-emitting diodes (OLED's), field-effect transistors (OFET's), smart windows and organic photovoltaic (OPV) devices [1–7]. The preparation of these block copolymers typically involves either elaborating an end-functionalized polythiophene into an appropriate macroinitiator for the chain extension of a second block via a polymerization process that is mechanistically distinct from that of P3HT or coupling preformed homopolymers with complementary end-functionalities [8, 9]. Atom transfer radical polymerization (ATRP) is one of the most used controlled radical polymerization (CRP) for the synthesis of diblock copolymers with controlled molecular weight low polydispersity, well-defined architecture, and their compositions. The rod-coil diblock copolymers containing regioregular P3HT have already been reported by a number of research groups, such as the synthesis of P3HT-*b*-poly(methyl methacrylate), P3HT-*b*-polystyrene, and P3HT-*b*-poly(isobornyl methacrylate) by traditional ATRP with a transition metal catalyst (i.e., Cu(I), Ru(II), Fe(II)) [10-12]. However, the metal catalysts have been used in traditional ATRP process that lead to a contamination of metal in electronic devices [13, 14].

In recent years, metal-free ATRP using organic photoredox catalysts to generate the radicals between active and deactive species under light irradiation [15]. Hawker *et al*. was the first group to develop 10-phenylphenothiazine as an organic catalyst to perform metal-free ATRP of methyl methacrylate (MMA) and dimethylaminoethyl methacrylate [16]. Miyake and co-workers have reported the perylene/diaryl dihydrophenazines as photoredox catalyst to conduct the ATRP of MMA under visible light [17, 18]. Currently, the applications of metal-free ATRP have been applied to synthesize the polymer-inorganic hybrid materials as well as functional surface modification [19-21]. However, the synthesis of rod-coil diblock copolymers containing regioregular poly(3-hexylthiophene) has not been explored via metal-free ATRP.

Herein, we investigated the utilization of pyrene as a photocatalyst for the synthesis of well-defined poly(3-hexylthiophene)-*block*-poly(methyl methacrylate) via metal-free ATRP. Moreover, the synthesized diblock copolymers were characterized via FT-IR, GPC and ^{1}H NMR for determination of chemical structures, average molecular weight and polydispersity.

Materials and Methods

2.1. Materials

All reactions were performed in oven-dried glassware under prepurified nitrogen. N,N-dimethylformamide (DMF, 99.8%), sodium borohydride ($NaBH_4$, 99%), phosphorus(V) oxychloride ($POCl_3$, 99%), pyrene (98%) triethylamine (99%), and 2-bromo-propionyl bromide (98%) were purchased from Sigma Aldrich. Monomer methyl methacrylate (Aldrich, 98%), was passed through the Al_2O_3 column prior to polymerization. Potassium acetate (KOAc, 99%), sodium carbonate (99%), and magnesium sulphate (98%) were purchased from Acros and used as received. Chloroform ($CHCl_3$, 99.5%), toluene (99.5%) and tetrahydrofuran (THF, 99%) were purchased from Fisher/Acros and dried using molecular sieves under N_2. Dichloromethane (99.8%), n- n-heptane (99%), and methanol (99.8%) were purchased from Fisher/Acros and used as received.

Characterization: FT-IR spectra collected as the average of 256 scans with a resolution of 4 cm^{-1}, were recorded from KBr disk on the FT-IR Bruker Tensor 27. ^{1}H NMR spectra was carried out on a 500 MHz spectrometer – Bruker AMX500 apparatus in $CDCl_3$. ^{1}H NMR chemical shifts are referenced to TMS (δ 0.00 ppm). The following abbreviations are used to describe the NMR signals: s (singlet), d (doublet), t (triplet), q (quartet), and br (broad). Size exclusion chromatography (SEC) measurements were performed on a Polymer PL-GPC 50 gel permeation chromatograph system equipped with an RI detector, with tetrahydrofuran as the eluent at a flow rate of 1.0 mL/min, 35 ^{0}C. Molecular weights and molecular weight distributions were calculated with reference to polystyrene standards.

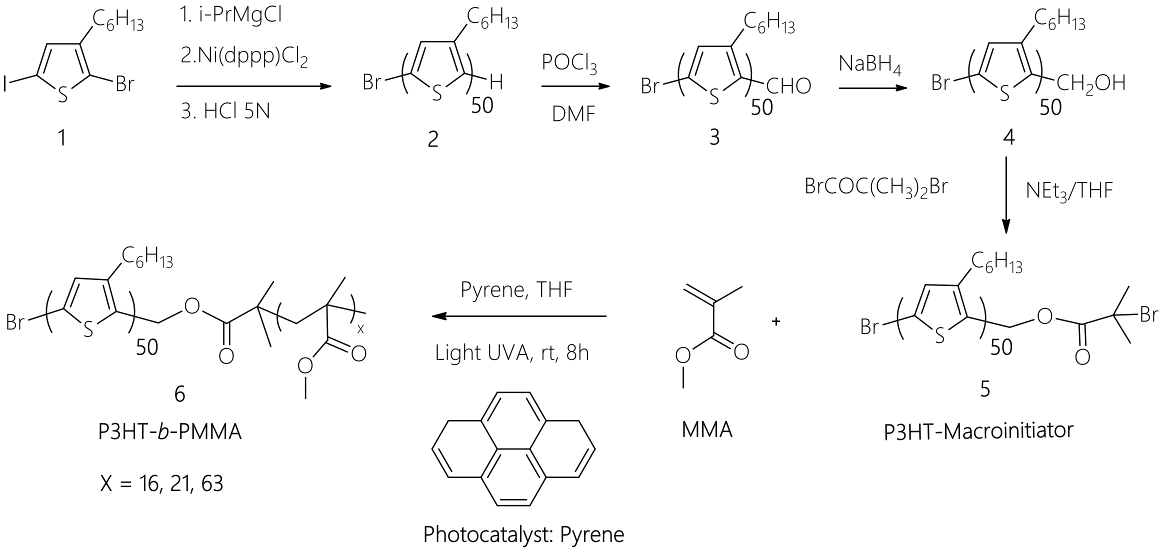
2.2. Metal-free atom transfer radical polymerization of methyl methacrylate from a poly(3-hexylthiophene)-macroinitiator using pyrene catalyst

P3HT-*b*-PMMA was obtained as process shown in Scheme 1. The synthesis of $P3HT_{50}$ - macroinitiator ($M_n{}^1{}_{H\ NMR}$ = 8400 g/mol, PDI_{GPC} = 1.31) was carried out using Grignard metathesis reaction (GRIM) procedure [22]. P3HT-*b*-PMMA copolymers with different coil length were synthesized from $P3HT_{50}$ - macroinitiator (P3HT-MI) via metal-free ATRP. The preparation of $P3HT_{50}$-*b*-$PMMA_{21}$ is exemplified below, and the reaction conditions are summarized in Table 1. The diblock copolymer P3HT-*b*-PMMA was prepared by Metal-free ATRP from P3HT-marcrointator using pyrene catalyst in the solvent THF. The molar ratio was $[MMA]_0$:$[P3HT\text{-}MI]_0$:$[Pyrene]_0$ = 100:1:1. A dry 25 mL Schlenk flask was charged with P3HT-macroinitiator (50 mg, 5.95 × 10^{-2} mmol), to which 2 mL of degassed THF was added by syringe. The macroinitiator solution was stirred until it became homogeneous. Monomer solution was prepared separately: methyl methacrylate (63.7 μL, 5.95 mmol), pyrene (1.21 mg, 5.95 × 10^{-2} mmol) as the catalyst were added in a round-bottom flask, and the flask was degassed by three freeze-pump-thaw cycles. The flask was irradiated by UVA light (365 nm, 9W, 0.05 mW/cm^2 UV light intensity) at room temperature for 8 h under nitrogen. The conversion of MMA to block copolymer was determined gravimetrically. The solution was precipitated into cold methanol, filtered, and dried under vacuum to give 85 mg of polymer P3HT-*b*-PMMA as a purple solid. FT-IR (cm^{-1}): 724, 818, 1090, 1376, 1451, 1509, 1561, 1725, 2853, 2922, 2953. ^{1}H NMR (500 MHz, CDCl3) δ (ppm): 6.98 (s, 1 H), 3.36 (s, 3 H), 2.80 (t, 2 H), 1.71 (m, 2H), 1.41-1.44 (m, 4 H), 1.35 (m, 4 H), 0.8-1.04 (t, 6 H). GPC: M_n = 16124 g/mol, PDI = 1.26. The polymerization condition of the other two block copolymers, $P3HT_{50}$-b-$PMMA_{16}$ and $P3HT_{50}$-b-$PMMA_{63}$ are listed in Table 1.

Results and Discussion

The synthesis of P3HT-*b*-PMMA diblock copolymers was presented in scheme 1. The three well-defined rod-coil diblock copolymers were prepared via the combination of 'quasi-living' GRIM polymerization of the P3HT block and subsequent metal-free ATRP of MMA monomers.

In the first stage, the P3HT-macroinitiator was synthesized via 6 steps, including a controlled 'quasi-living' GRIM polymerization of the 2-bromo-3-hexyl-5-iodothiophene monomer. The obtained P3HT with H/Br end groups had a GPC recorded number average molecular weight (M_n) value of 7400 g/mol, which is close to the theoretical one, and moderate polydispersity index of 1.31. Then, a quantitative conversion of Br-P3HT-H into α-bromo-α-bromoisobutyrate poly(3-hexylthiophene) (5) was achieved by a 3-step procedure. Based on the integral ratio between the methine (ring) protons of P3HT at 6.98 ppm and methyl protons of the α-bromoisobutyrate end group at 1.95 ppm, an M_n value of 8400 g/mol was estimated. Finally, the bromoester terminated P3HT was used as the macroinitiator for the metal-free ATRP of MMA monomer, in presence of pyrene as catalytic system.



Scheme 1: Synthetic route of rod - coil P3HT-*b*-PMMA diblock copolymers

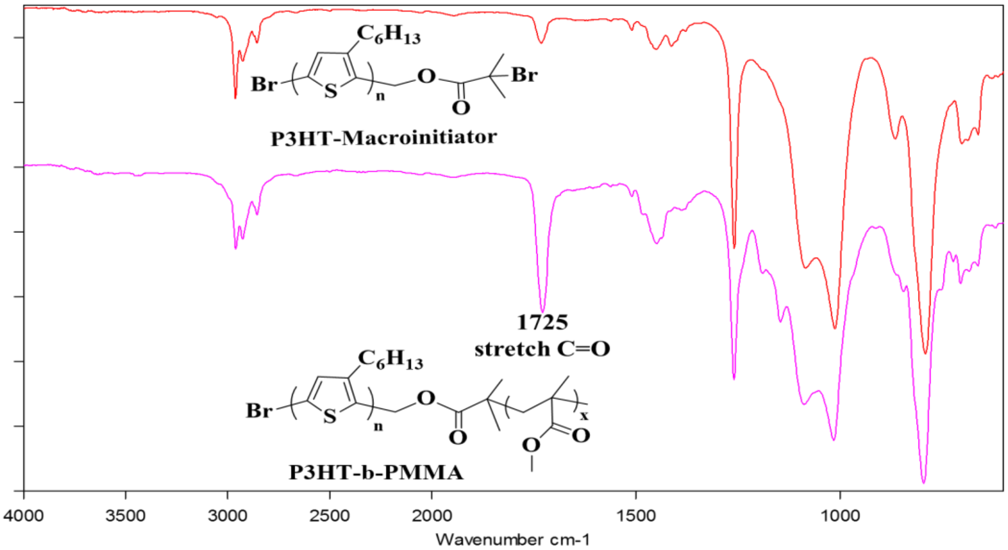


Figure 1: FT-IR spectra of P3HT-macroinitiator and P3HT-*b*-PMMA

Figure 1 shows the FT-IR spectra of the obtained P3HT macroinitiator and the P3HT-*b*-PMMA. A peak at 1725 cm^{-1} appears in the spectrum of the diblock copolymer attributed to the stretching vibration of the carbonyl groups (C=O) of the PMMA block.

The P3HT-*b*-PMMA diblock copolymers were then characterized by ^1H NMR, as shows the in Fig. 2. The proton resonances (ppm) at 0.88–1.04, 1.82–1.91, and 3.60 ppm are assigned to the methyl, methylene, and the oxymethylene of the PMMA segment, respectively.

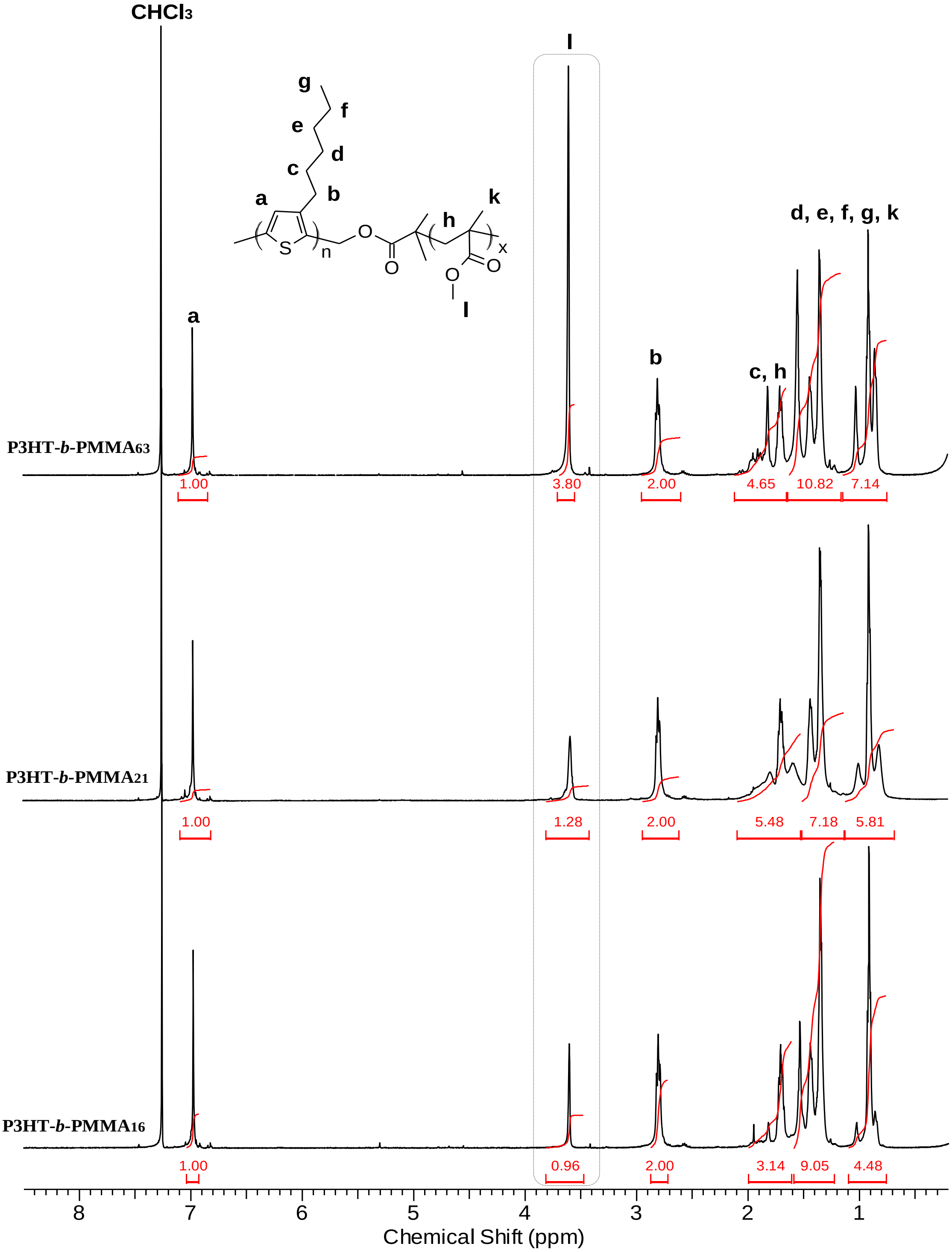


Figure 2: ^1H NMR spectrum of P3HT-*b*-PMMA in $CDCl_3$

The signals between 1.41–1.44 ppm are attributed to the methylene of the hexyl group of thiophene ring.

The polymerization degree of the PMMA block was calculated from the recorded ^1H NMR spectrum by comparing the relative signal intensity of the methylene protons of the MMA residue at δ = 3.60 ppm (peak l, Fig. 2), respectively, with that of the methine (ring) protons of the P3HT at δ = 6.98 ppm (peak a, Fig. 2). The estimated MMA repeating units of three copolymers from M_n are 16, 21, and 63, and thus denoted as P3HT$_{50}$-*b*-PMMA$_{16}$, P3HT$_{50}$-*b*-PMMA$_{21}$, and P3HT$_{50}$-*b*-PMMA$_{63}$, respectively.

^{1}H NMR spectra and GPC were used to confirm the successful synthesis of the copolymers P3HT-*b*-PMMA. The GPC profiles of the block copolymers shift to the high molecular weight regions with enhanced the feed ratio, as shown in Fig. 3. As seen in Table 1, the M_n of these P3HT-*b*-PMMA copolymers are 11452, 16214, and 25163 g/mol with PDI values of 1.64, 1.26, and 1.35, respectively.

Table 1: Polymerization conditions, average molecular weights and polydispersity index of P3HT-b-PMMA copolymers prepared by metal-free ATRP using pyrene catalyst

Polymers	$[M]_0$:[P3HT-MI]$_0$ ^{a}	Conversion^b (%)	M_n^{c} (g/mol)	PDI^c	M_n^{d} (g/mol)
P3HT$_{50}$-Macroinitiator	-	-	7423	1.31	8400
P3HT$_{50}$-*b*-PMMA$_{16}$	50	32	11452	1.64	10000
P3HT$_{50}$-*b*-PMMA$_{21}$	100	41	16214	1.26	10500
P3HT$_{50}$-*b*-PMMA$_{63}$	200	31.5	25163	1.35	14700

[a] The reactions were carried out in THF at room temperature for 8 h irradiation by UVA light 365 nm (0.05 mW/cm^2 UV light intensity).

[b] Conversion as determined gravimetrically: Conv = $[(m - m_I - m_{PC})/m_M]$ x 100%, where m denotes the weight of the product, and m_I, m_{PC} and m_M are the weights of the macroinitiator, photocatalyst pyrene and monomer MMA, respectively.

[c] M_n and PDI determined by GPC using THF eluent at 35 ^{0}C.

[d] M_n = M_{nP3HT} + DP_{exp} × M_{wMMA}, where DP_{exp} is the experimental degree of polymerization, as calculated from the relative intensities of methylene protons of MMA (δ = 3.60 ppm), and the methine (ring) protons of P3HT (δ = 6.98 ppm). MMA experimental number-average molar mass as determined by ^{1}H NMR spectroscopy (see Fig. 2).

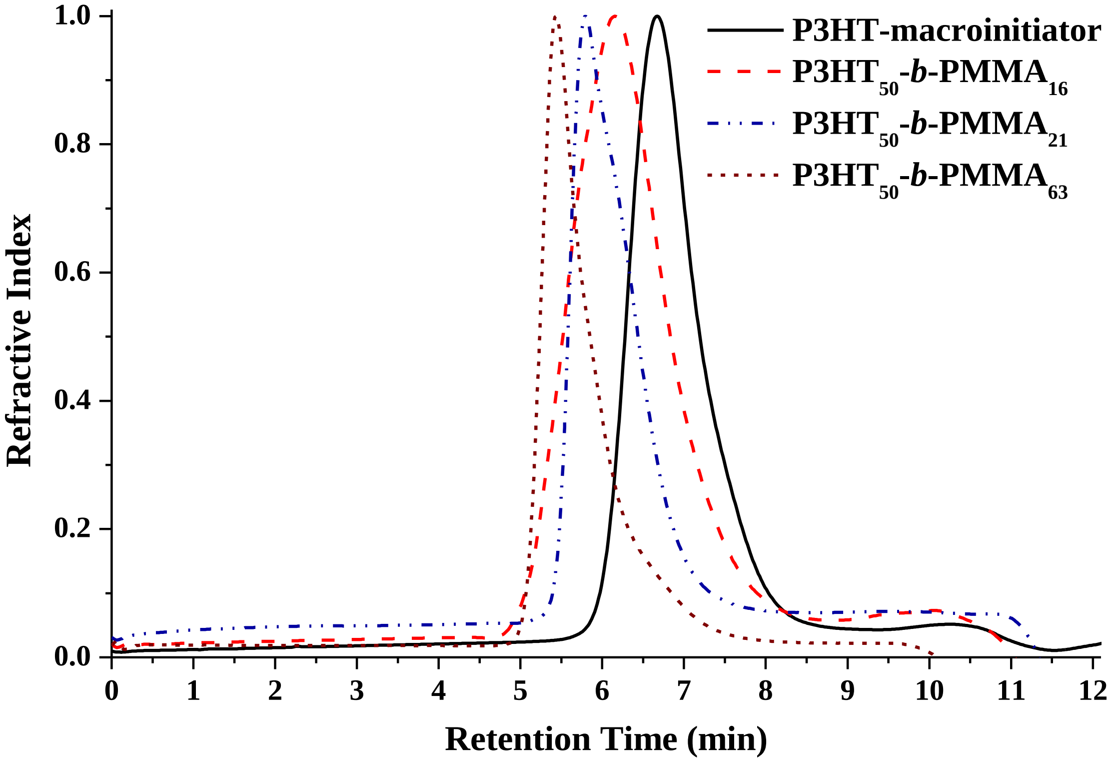


Figure 3: GPC profiles of P3HT-macroinitiator and P3HT-b-PMMAs

Conclusion

In conclusion, we have successfully prepared three conjugated rod-coil diblock copolymers of P3HT-*b*-PMMA by metal-free ATRP using pyrene as the catalyst under UV irradiation. The reactions employed in this study were simple and efficient. The structures of diblock copolymers were clarified through ^{1}H NMR, GPC and FT-IR characterizations. In addition, it could be applicable to synthesize P3HT-containing block copolymer with various categories of coil segments. We expected that this well-defined P3HT-*b*-PMMA could be used as P3HT nanopatterns, which would be applied to organic electronic devices such as OFETs, OPVs.

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number "104.02-2016.56".

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