

Review

Polythiophene-block-poly(phenyl isocyanide) Copolymers: One-pot Synthesis, Properties and Applications*

Li Zhou, Zhi-qiang Jiang, Lei Xu, Na Liu** and Zong-quan Wu**

Department of Polymer Science and Engineering, School of Chemistry and Chemical Engineering, and Anhui Key Laboratory of Advanced Catalytic Materials and Reaction Engineering, Hefei University of Technology, Hefei 230009, China

Abstract Conjugated block copolymers have gained increasing interests in recent years. Development of a novel method for facile synthesis of conjugated block copolymers with desired structures and functions is greatly desired. In this mini review, we summarized the recent advances in one-pot synthesis of conjugated block copolymers containing π -conjugated polythiophene and helical polyisocyanide segments by using a nickel(II) complex as single catalyst. The sequential living polymerization of the two monomers proceeded in a controlled manner, affording expected block copolymers in high yields with controlled molecular weights (M_n s) and narrow molecular weight distributions (M_w/M_n s). By using this method, a family of block copolymers with expected structure and tunable compositions can be facilely prepared. Introducing functional groups onto the pendant, these block copolymers can exhibit interesting self-assembly property, tunable light emission and multi-responsiveness.

Keywords Conjugated polymer; Helical polymer; Polyisocyanide; Block copolymer; Living polymerization

INTRODUCTION

Helix is the central structural motif in biological macromolecules such as right handed α -helix in protein and right handed double helices in DNA^[1, 2], and also the ubiquitous object in nature from microscopic to macroscopic points of view. Since the discovery of the helical structure in biopolymers, chemists were stimulated to design and synthesize artificial helical polymers^[3–6]. The aims of these researches are not only to mimic the helical structures and functions of the nature occurring helices but also to bring out new materials with novel properties and functions. Since the pioneer work by Okamoto and Nolte in 1970s^[7, 8], a variety of artificial helical polymers with different composition and structures were developed^[9–11]. However, it is still in the primary stage; the number and type of helical polymers are rather limited as compared to a large amount of synthetic polymers^[12–15]. Among the reported helical polymers, polyisocyanide is one of the most studied helical polymers owing to stable rigid rod-like helical conformation^[16, 17] and wide applications in self-assembly^[18], chiral recognition^[19], enantiomer separation^[20] and liquid crystallization^[21]. Taking advantage of the rigid rod helical conformation, polyisocyanide has been fabricated into various block copolymers to control the self-assembly morphology.

Recently, conjugated polymers have gained great attention from the synthetic chemists to polymer scientists

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** Corresponding authors: Na Liu (刘娜), E-mail: liuna@hfut.edu.cn

Zong-quan Wu (吴宗铨), E-mail: zqwu@hfut.edu.cn

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because of their great potentials in optoelectronics^[22–26], including organic photovoltaics (OPVs)^[27, 28], light emitting devices^[29], and organic field-effect transistors (OFET)^[30, 31]. The performance of these devices relies greatly on the morphology of the active material in nanoscale to maximize charge separation, recombination, and transfer. Although self-assembly is an alluringly inexpensive route to pattern on the 10–100 nm length scale of relevance to organic optoelectronics, only recently successful demonstrations of self-assembly in semiconducting polymers have emerged. Therefore, it is important to incorporate a polymer with desirable self-assembly properties with those that exhibit useful electronic properties into block copolymers to afford controlled and highly ordered morphologies^[32–35]. Among the reported conjugated polymers, polythiophene and its derivatives are of the most studied ones due to their excellent electronic properties and synthetic accessibility as well as the numerous methods available for their modification^[36, 37]. Since polyisocyanide is a kind of rigid rod helical polymer and has desired self-assembly property, incorporating helical polyisocyanide into polythiophene can generate a series of novel block copolymers with new properties and functions^[38–40]. However, a typical method for preparation of polythiophene block copolymers involves either elaborating an end-functionalized polythiophene into an appropriate macroinitiator for the chain extension of a second block or coupling preformed homopolymers with complementary end-functionalities^[41, 42]. Such methodologies, however, can be complex and inefficient, frequently resulting in materials that contain inseparable homopolymer impurities. Thus, development of a novel and convenient method for incorporation of polyisocyanide into polythiophene is of great significance.

Recently, Wu and coworkers developed a novel method for one-pot synthesis of polythiophene-*b*-polyisocyanide copolymers *via* the sequential living polymerization of the two corresponding monomers using a nickel(II) as the single catalyst^[43–47]. Although the two monomers were polymerized under distinct mechanisms, the one-pot block copolymerization was revealed to proceed in living/controlled manner, affording block copolymers in high yields with controlled molecular weights (M_n s), narrow molecular weight distributions (M_w/M_n s) and tunable compositions. Taking advantage of this method, a variety of polythiophene-*b*-polyisocyanide block copolymer with different structures and properties was facilely prepared. In this mini review, we will describe the recent advances of the one-pot synthesis of conjugated polythiophene-*b*-polyisocyanide copolymers and the related properties.

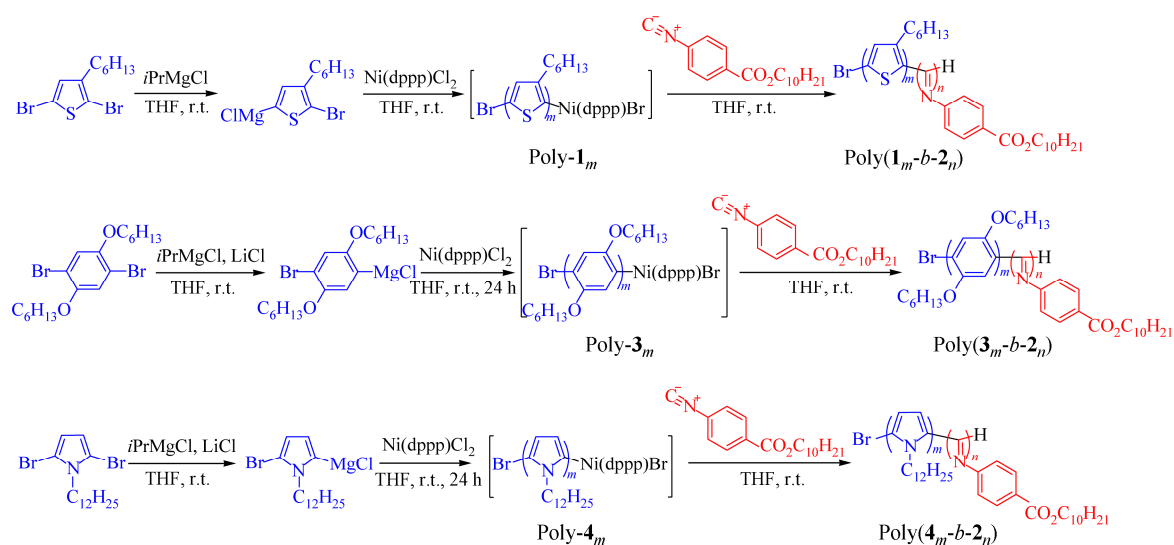
METHODOLOGY OF ONE-POT SYNTHESIS

*One-pot Synthesis of Polythiophene-*b*-polyisocyanide Copolymers*

Polyisocyanides are usually prepared *via* the polymerization of the C≡N group of isocyanide monomers. The most used catalysts for isocyanide polymerization are transition metal complexes such as Ni(II)^[48], Pt(II)-Pd(II)^[49], Rh(III) complexes^[50], and recently developed Pd(II) complex^[17]. Ni(II) complexes are one of the widely used catalysts for the polymerization of alkyl and aryl isocyanide monomers. In addition to small molecules such as nickel(II) salt and organonickel(II) complexes, macromolecule bearing nickel(II) complex on the chain end can also be used as a macroinitiator to promote the polymerization of isocyanide to give block copolymers containing helical polyisocyanide segment. Regioregular poly(3-hexylthiophene) (P3HT) is usually prepared through the polymerization of 2,5-dibromo-3-hexylthiophene *via* Ni(II)-catalyzed Kumada catalyst-transfer polymerization developed by McCullough *et al.* and Yokozawa *et al.*, which is also known as Grignard metathesis (GRIM) polymerization^[51, 52]. The polymerization was proved to proceed in a quasi-living manner, leading to the formation of regioregular P3HT with controlled M_n and narrow M_w/M_n . After the polymerization, a reactive Ni(II) species resides at the P3HT terminus in the resting state of the catalytic cycle. Taking advantage of the living chain end of the produced Ni(II)-terminated P3HT, Wu and coworkers reported the synthesis of well-defined P3HT-*b*-poly(phenyl isocyanide) (P3HT-*b*-PPI) copolymers *via* two sequential, mechanistically distinct polymerizations using a nickel complex as single catalyst^[54].

The one-pot block copolymerization is displayed in Scheme 1. First, 2-bromo-3-hexyl-5-chloromagnesiiothiophene was generated from the reaction of 2,5-dibromo-3-hexylthiophene (**1**) and *i*PrMgCl, which was then polymerized in THF using Ni(dppp)Cl₂ as catalyst. When the polymerization was accomplished as indicated by

size exclusion chromatography (SEC) analysis of the aliquots taken out from the reaction solution, the polymerization solution of the generated Ni(II)-terminated P3HT was treated with phenyl isocyanide (**2**) in THF at room temperature. The SEC analysis revealed the block copolymerization occurred. As displayed in Fig. 1(a), the SEC trace of the generated block copolymer shifted to shorter retention time as compared to the P3HT precursor. The M_n of the resulting P3HT-*b*-PPI block copolymer poly(**1_m-b-2_n**) was increased as compared to the P3HT precursor as confirmed by SEC, while the M_w/M_n remained narrow. To investigate the living nature of the one-pot block copolymerization, a series of block copolymerization of monomer **2** using a common Ni(II)-terminated P3HT as a macroinitiator was performed in different initial feed ratios of monomer to macroinitiator. All the generated P3HT-*b*-PPI block copolymers showed symmetric and single model elution peak on recorded SEC. More importantly, the M_n of the block copolymers was linearly correlated to the initial feed ratio of monomer to macroinitiator (Fig. 1b), and all the block copolymers showed narrow molecular weight distribution. This study confirmed that the one-pot block copolymerization proceeded in a living/controlled chain growth manner although the two monomers were polymerized under distinct mechanisms. Taking advantage of this synthetic approach, a variety of well-defined P3HT-*b*-PPI block copolymers with controlled M_n , narrow M_w/M_n , and tunable compositions can be facilely prepared just by varying the initial feed ratio of the two monomers to the nickel(II) catalyst. Such P3HT-*b*-PPI block copolymer can self-assemble into higher order supramolecular structure. As displayed in Fig. 1(c), the thin film of the P3HT-*b*-PPI block copolymer exhibited nanofibrillar morphology as investigated by atomic force microscopy (AFM) observations. The nanofibrils were unidirectionally aligned and exhibited long-range order with the persistent lengths up to 1 μm . Because of the immiscibility of the two blocks, P3HT-*b*-PPI copolymer was capable of undergoing phase separation as revealed by DSC studies (Fig. 1d). These results further confirmed the success of the one-pot block copolymerization of the two monomers using a single Ni(II) catalyst.



Scheme 1 One-pot synthesis of P3HT-*b*-PPI, poly(phenylene)-*b*-PPI, and poly(pyrrole)-*b*-PPI block copolymers *via* mechanistically distinct, two sequential living polymerizations using a nickel complex as single catalyst

One-pot Synthesis of Poly(pyrrole)-*b*-PPI and Poly(phenylene)-*b*-PPI Copolymers

Inspired by the one-pot synthesis of P3HT-*b*-PPI block copolymer, block copolymers containing polythiophene and poly(alkyl isocyanide) segments can be facilely prepared following the similar procedure^[54]. Moreover, other conjugated block copolymers containing helical polyisocyanide can be prepared by the similar method, because the Ni(II)-catalyzed catalyst transfer condensing living polymerizations can be utilized in the preparation other conjugated polymers such as poly(pyrrole), poly(phenylene) and so on^[55]. The polymerization generates conjugated polymers also containing reactive Ni(II) complex on the chain end, thus, the one-pot

synthetic method for P3HT-*b*-PPI can be extended to the synthesis of hybrid block copolymer of poly(pyrrole)-*b*-PPI and poly(phenylene)-*b*-PPI by using the *in situ* generated Ni(II)-terminated conjugated polymers as a macroinitiator (Scheme 1)^[54]. Although the two monomers were polymerized under distinct mechanisms, the one-pot block copolymerization was revealed to proceed in living/controlled manner because the molecular weights of the block copolymers were linearly correlated to the initial feed ratio of monomer **2** to the common macroinitiator. Thus a series of desired hybrid block copolymers can be facily prepared in high yields with controlled M_n s and narrow M_w/M_n s.

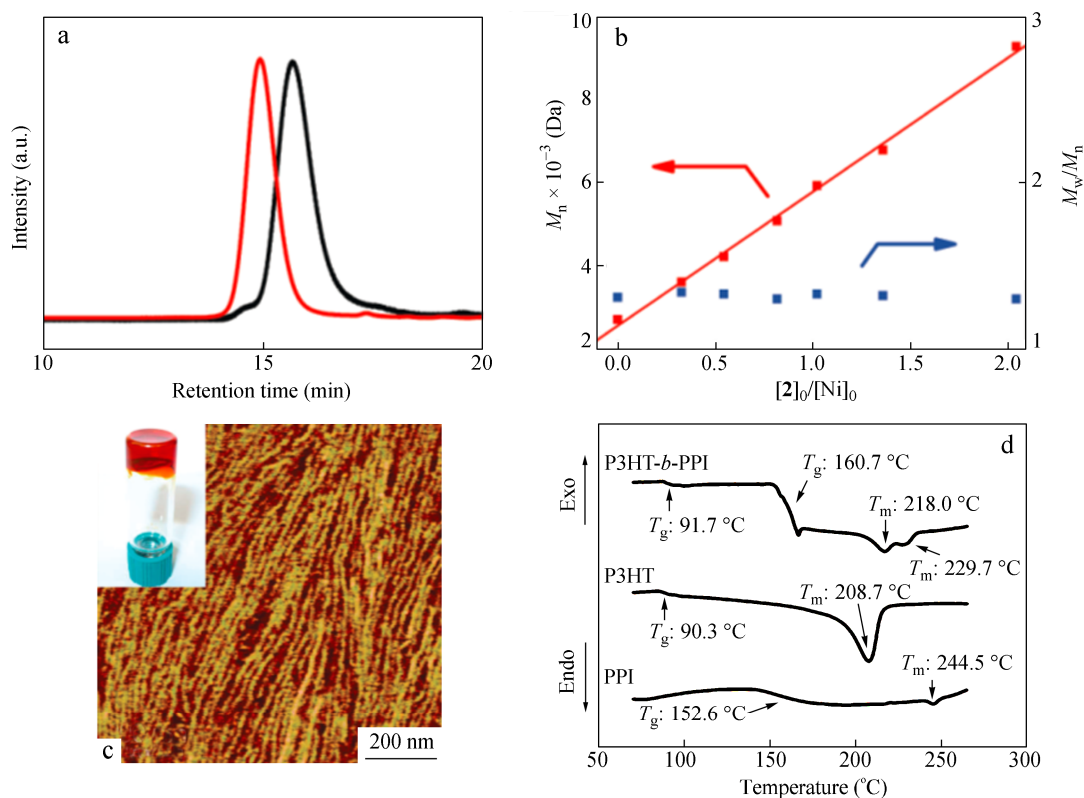


Fig. 1 (a) Representative size exclusion chromatograms of homopolymer poly-**1_m** (black) and its corresponding block copolymer poly(**1_m-b-2_n**) (red); (b) Plot of M_n and M_w/M_n values of poly(**1_m-b-2_n**) measured as a function of the feed ratio of **2** to poly-**1_m** ($M_n = 2.70$ kDa; $M_w/M_n = 1.31$); (c) AFM phase image of poly(**1_m-b-2_n**) drop-casted from CHCl_3 onto a Si wafer (Inset: photograph showing gelation behavior in CHCl_3); (d) DSC thermograms of the block copolymer and the corresponding homopolymers (Reproduced with permission from Ref. [53]; Copyright (2010) American Chemical Society) (The online version is colorful.)

Compared to the traditional approaches for synthesis of block copolymers, the methodology described here possesses many advantages: (1) the conjugated block copolymers were facily prepared in one-pot by using Ni(II) complex as a single catalyst *via* two sequential living polymerizations; (2) although the two monomers were polymerized under distinct mechanisms, the one-pot block copolymerization proceeded in a living/controlled manner, and a series of block copolymers with controlled structures and tunable compositions could be readily obtained; (3) considering the modifications on monomers, more complicated semi-conducting materials with novel functions and properties can be facily prepared by using this method.

PROPERTIES AND APPLICATIONS

By using the one-pot synthetic method, Qi and coworkers synthesized a series of rod-rod P3HT-*b*-PPI (poly(**1_m-b-5_n**)) block copolymers by inducing amide groups onto the pendant of PPI segment. The amide group of the

adjacent repeating units could form intramolecular hydrogen bonding, which induced the PPI segment (poly-**5_m**) to adopt a rigid rod helical conformation^[14]. Compared to the vastly investigated rod-coil block copolymers, reports on the synthesis and self-assembly of rod-rod block copolymer are relatively rare. The one-pot synthesized rod-rod block copolymer poly(**1_m-b-5_n**) exhibited interesting self-assembly and optoelectronic properties. The hybrid block copolymers could self-assemble into spherical supramolecular structures with P3HT in core and PPI in shell in THF solution and exhibit amorphous state in CHCl₃. AFM observation revealed that the block copolymers could self-assemble into nanofibrils on the substrate (Fig. 2)^[56]. Interestingly, this block copolymer can be used as semiconducting materials in electronic devices. Transistors based on this rod-rod block copolymer were fabricated on the surface of Si/SiO₂ *via* spin casting from CHCl₃ solution. Field-effect mobility was measured in bottom-gate and top-contact thin film transistor devices. The saturation field-effect mobility of the device was estimated to be $7.1 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, and the on/off current ratio was 1.8×10^2 . These results are comparable with those of the other P3HT containing block copolymers, such as P3HT-*b*-poly(γ -benzyl-L-glutamate) ($7.0 \times 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$).

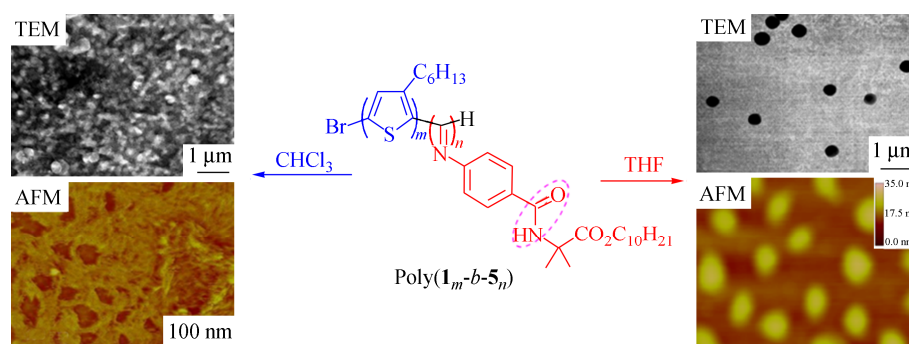
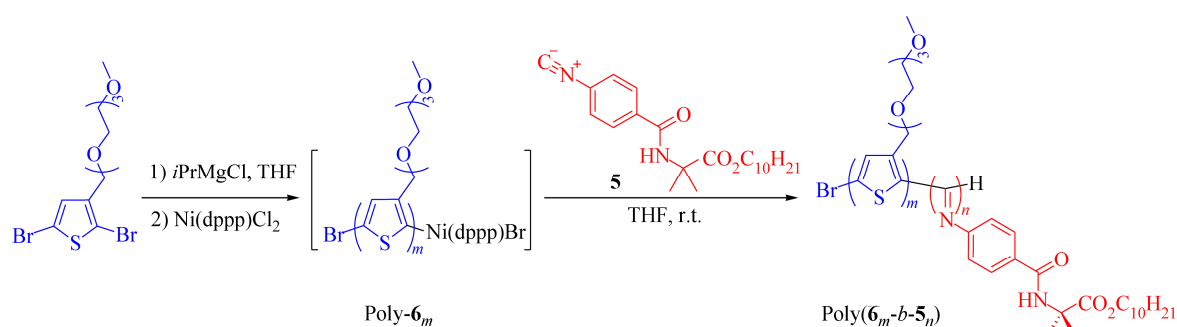


Fig. 2 Structure of the one-pot synthesized block copolymer poly(**1_m-b-5_n**) and its TEM and AFM images (Reproduced with permission from Ref. [56]; Copyright (2013) Wiley-VCH) (The online version is colorful.)

Inspired by the self-assembly properties of these rod-rod block copolymers, Liu *et al.* reported on the one-pot synthesis of amphiphilic rod-rod block copolymer (poly(**6_m-b-5_n**)) by introducing hydrophilic 3-triethylene glycol chain onto polythiophene instead of *n*-hexyl (Scheme 2). This block copolymer was also synthesized in one-pot using a nickel(II) as a single catalyst. The structure of this block copolymer was characterized by ¹H-NMR, FTIR, and UV-Vis spectroscopy^[57].



Scheme 2 One-pot synthesis of poly(**6_m-b-5_n**) block copolymer

Due to the amphiphilic character, poly(**6_m-b-5_n**) showed good solubility in most common organic solvents with different polarity. Because of the immiscibility of two blocks, this block copolymer can self-assemble in selective solvents. In non-selective THF, a good solvent for both segments, the block copolymer was molecularly dissolved. Dynamic light scattering (DLS) analysis suggested the hydrodynamic size was *ca.* 10 nm. However,

in methanol, a selective solvent for hydrophilic poly- $\mathbf{6}_m$ segment, the hydrodynamic diameter was increased to *ca.* 25 nm due to the self-assembly of the amphiphilic block copolymer. Upon adding THF to the methanol solution, the size of the aggregates was increased (Fig. 3a). In addition to the changes of the hydrodynamic diameter, the emission property of the block copolymer is also dependent on the solvent used. In THF, it showed orange emission under the irradiation of UV light at 365 nm, similar to P3HT homopolymer. In methanol solution, the block copolymer exhibited a blue emission under the same experimental conditions. Thus, a variety of different light emissions could be facily obtained in different composition of THF and methanol (Fig. 3c). Very interestingly, the block copolymer showed a white-light emission in THF/methanol (3/2, *V/V*) solution. The white-light emission of an organic material is of great interest, because they have great potentials in white-light devices and liquid crystal displays. The fluorescent spectra of the block copolymer in various solvents further confirmed the tunable emission property. The fluorescent spectrum of the block copolymer in THF showed emission peaks at 410, 430, 460, and 560 nm. The long wavelength emission (560 nm) is similar to that of P3(TEG)T in THF, and the short wavelength emissions are similar to that of P3(TEG)T in methanol. When the solvent was changed from THF to methanol, the long wavelength emission was completely quenched while the short wavelength emissions were considerably increased. Hence, the block copolymer exhibited orange light emission in THF and blue light emission in methanol. In the THF/methanol (3/2, *V/V*) solution, the emission intensities at the short wavelength region (410, 430, and 460 nm) were decreased compared to that in methanol, whereas the emission at the long wavelength region (560 nm) appeared, giving whole emissions from 400 nm to 700 nm in visible light region. Thus, it showed a white-light emission, and the quantum yield was estimated to be 0.21 (Fig. 3b).

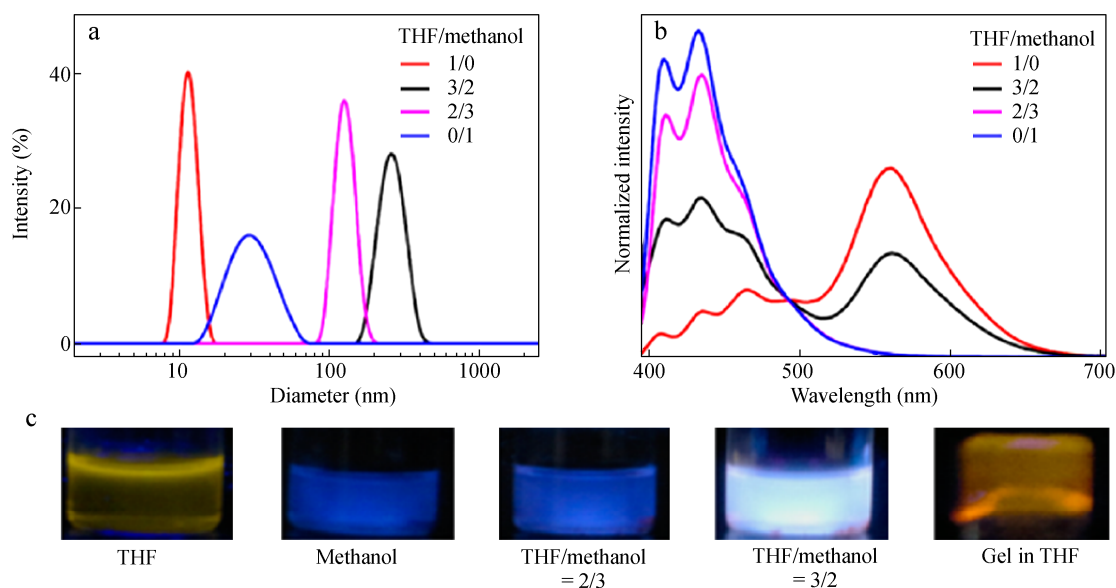


Fig. 3 (a) Size distributions, (b) fluorescent spectra, and (c) distinct emission colors of P3(TEG)T-*b*-PPI block copolymer poly($\mathbf{6}_m$ -*b*- $\mathbf{5}_n$) in different solvents (*c* = 0.1 mg/mL in solution and 1.0 mg/mL in gel, excited at 365 nm) (Reproduced with permission from Ref. [57]; Copyright (2013) American Chemical Society) (The online version is colorful.)

The morphology of the self-assembled supramolecular structures was further investigated by TEM and AFM observations. It was found that in mixture of THF and methanol with 2/3 volume ratio, the block copolymer self-assembled into core-shell supramolecular structure (Figs. 4a and 4b), while in the THF/methanol mixture with 3/2 volume ratio, the block copolymer self-assembled into donut-like morphology as revealed by TEM and AFM (Figs. 4c and 4d). Thus, the different emission properties of the block copolymer in solvent were ascribed to the different self-assembled supramolecular structures. The solvent-induced light emission color changes were

completely reversible, suggesting that the tunable emission properties were indeed ascribed to the morphological transitions of the assemblies, not the changes on chemical structures of the block copolymers (Fig. 4e).

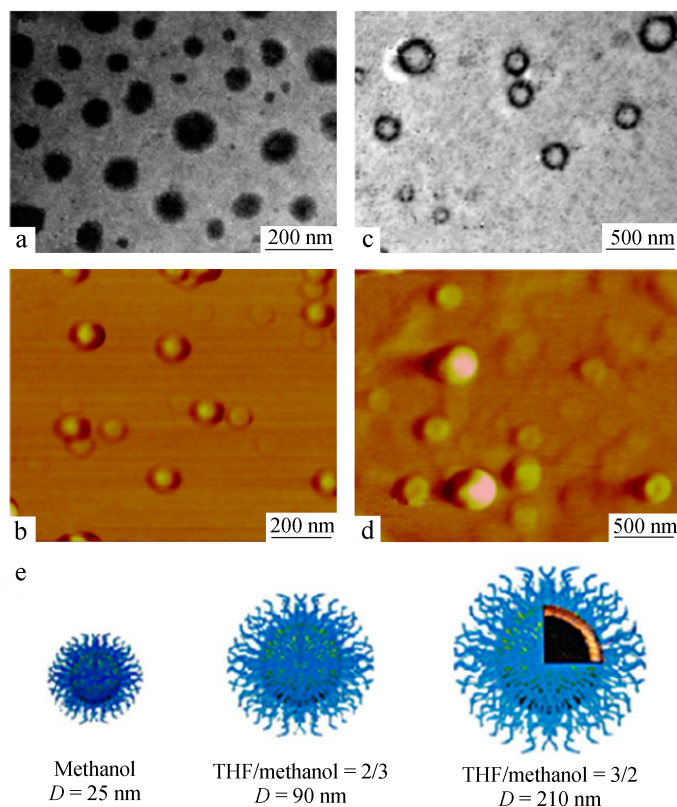


Fig. 4 TEM images of the assemblies formed from P3(TEG)T-*b*-PPI block copolymer in THF/methanol mixture with (a) 2/3 and (c) 3/2 volume ratios and AFM phase images of the supramolecular structures in the THF/methanol mixture solution with (b) 2/3 and (d) 3/2 volume ratios; (e) Illustration of the assembly structures of block copolymer in different solvents (Reproduced with permission from Ref. [58]; Copyright (2013) American Chemical Society) (The online version is colorful.)

Via the similar synthetic approach, Su *et al.* synthesized another amphiphilic P3HT-*b*-PPI block copolymer (poly(**1_m-b-7_n**)) containing hydrophobic P3HT and hydrophilic poly(phenyl isocyanide) block bearing hydrophilic tri(ethylene glycol) monomethyl ether chains (Fig. 5a)^[58]. The block copolymers had good solubility in most organic solvents and, importantly, were highly-soluble in water. The concentration in water could be as high as 10.0 g·L⁻¹. Very interestingly, the amphiphilic block copolymers showed multiple stimuli-responsive behaviors, such as temperature, pH, and solvents. In addition, such block copolymers could be further utilized in live cell imaging^[58].

In water solution, this block copolymer showed interesting thermo-responsiveness. As shown in Fig. 5(b), the clear transparent solution turned to turbid upon heating. The lowest critical solution temperature (LCST) was around 57 °C. The LCST value depended on the block ratio and the concentration of the solution. Increasing the hydrophilic poly(phenyl isocyanide) content of the block copolymer or decreasing the concentration could increase the LCST. Moreover, P3HT-*b*-PPI block copolymers also exhibited pH-responsiveness. As shown in Fig. 6(a), the orange color solution of poly(**1₃₀-b-7₆₀**) in CHCl₃ gradually turned to gray upon adding trifluoroacetic acid (TFA). The absorption spectra of the block copolymer in CHCl₃ also support this acid-induced color change (Fig. 6b). It exhibited a strong absorption at 450 nm in CHCl₃; however, the intensity gradually decreased upon the addition of TFA, accompanied by new absorption peaks at 580 and 610 nm, whose intensity increased until the TFA was saturated. The acid-induced color change and the absorption change were

reversible. Neutralizing the acidic solution of the block copolymer using triethylamine (TEA), the color and absorption spectra could be recovered.

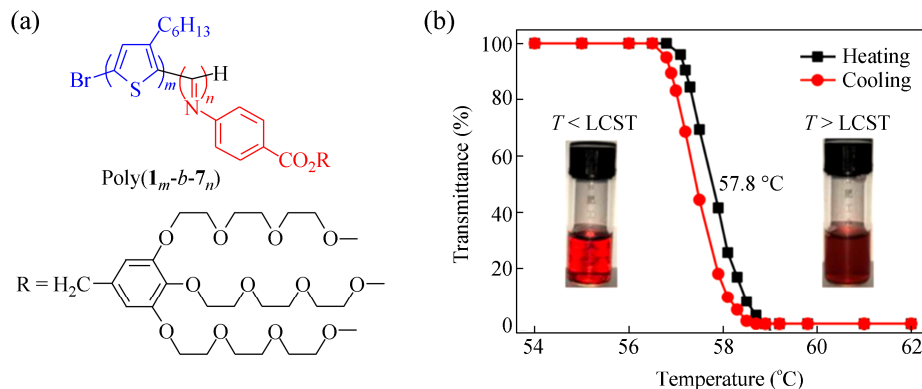


Fig. 5 (a) Chemical structure of the one-pot synthesized poly(1_m - b - 7_n) block copolymer; (b) Photographs and transmittance versus temperature traces for poly(1_{30} - b - 7_{60}) in water ($c = 0.5 \text{ g}\cdot\text{L}^{-1}$) (Reproduced with permission from Ref. [58]; Copyright (2015) The Royal Society of Chemistry) (The online version is colorful.)

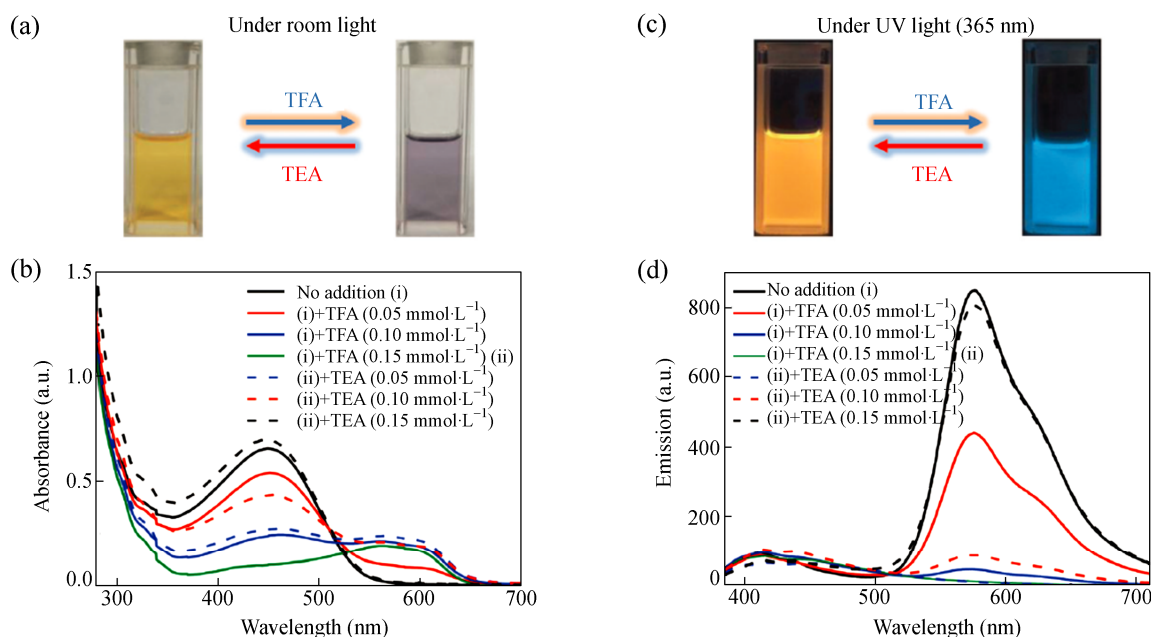


Fig. 6 Photographs of the P3HT- b -PPI block copolymer poly(1_{30} - b - 7_{60}) in CHCl_3 ($c = 0.05 \text{ g}\cdot\text{L}^{-1}$) upon alternate additions of TFA and TEA under (a) room light and (c) UV light at 365 nm; (b) Absorption and (d) emission spectra of poly(1_{30} - b - 7_{60}) in CHCl_3 upon alternate additions of TFA and TEA at 25°C ($c = 0.05 \text{ g}\cdot\text{L}^{-1}$) (Reproduced with permission from Ref. [58]; Copyright (2015) The Royal Society of Chemistry) (The online version is colorful.)

The emissions of the poly(1_{30} - b - 7_{60}) block copolymer also exhibited pH-responsive properties. Upon the addition of TFA, the orange emission gradually turned blue (Fig. 6c). By neutralizing the TFA in the CHCl_3 solution with addition of TEA, the emission of poly(1_{30} - b - 7_{60}) could be gradually recovered, indicating that the emission of the block copolymer is pH-responsive. The emission spectra of poly(1_{30} - b - 7_{60}) in CHCl_3 upon the additions of TFA and TEA also support the excellent pH-responsive behavior (Fig. 6d).

The examples described above demonstrate that through introduction of functional groups into thiophene and isocyanide monomers, a variety of novel block copolymers could be readily prepared. Some of these block

copolymers showed interesting properties including self-assembly, multi-stimuli responsiveness and tunable light emissions. These works confirm that the one-pot synthetic method is a useful approach in the synthesis of functional materials.

CONCLUSIONS AND PROSPECTS

The researches on conjugated block copolymer have grown rapidly in recent years, especially in the optoelectronic field. Development of novel and convenient strategy for controlled synthesis of conjugated block copolymer with desired structures and functions is of great necessity. This mini review summarized the Ni(II)-catalyzed, one-pot synthesis of conjugated block copolymers containing conjugated polymer and helical polyisocyanide segments *via* two sequential living polymerizations. Although the two monomers were polymerized under different mechanisms, the one-pot block copolymerization was revealed to proceed in a living/controlled manner. Taking advantage of this method, a variety of block copolymers with desired pendants and expected structures were readily prepared. Some of these block copolymers showed interesting properties, including self-assembly, tunable white-light emission, and multi-stimuli responsiveness.

It can be anticipated that, taking advantage of the one-pot synthetic method, new semi-conducting materials with novel properties and functions can be facilely prepared just through modifications on the structural monomers, *e.g.*, donor-acceptor diblock copolymers for optoelectronic devices, chemical sensor, and new generation materials for liquid crystal and so forth. The current work on the synthesis of polythiophene-*b*-polyisocyanide block copolymer has not touched chirality. However, the polyisocyanide can form a stable helical conformation in solution and in solid state. As we know, helix is inherent chiral, thus controlling the helix sense of the polyisocyanide segments would bring out novel chiral materials with great potentials in chiral sensor, enantiomer separation, and important circular polarized photoluminescence. These are the directions of the future works in this research area.

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