One-Step Synthesis of a Thienylenepyridazinylenethienylene-Based Coil-Rod-Coil Copolymer with Enhanced Emission and Improved Fluorescence Stability

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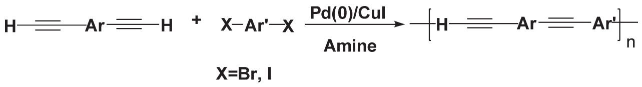
ABSTRACT: A new coil-rod-coil copolymer is synthesized via Sonogashira coupling using one-step methodology. The copolymer PEG-OEPETPT-PEG constitutes of poly(ethylene glycol) (PEG) as the coil block, and oligo[*p*-(ethynylenephenyleneethynylene)-*alt*-(thienylenepyridazinylenethienylene)] (OEPETPT) as the rod segment. The conjugated polymer PEPETPT with the same conjugated building blocks is also synthesized for comparison. The structures of both polymers are confirmed by NMR, combined with other characterizations. PEG-OEPETPT-PEG has a 12 nm blue-shift in the emission maximum compared with that of PEPETPT, and a higher quantum yield of fluorescence in THF. PEG-OEPETPTE-PEG tolerates up to 20% water content in H_2O/THF mixed solvent without significantly changing the emission wavelength and intensity, while the fluorescence of PEPETPT is dramatically quenched by a very small quantity of water. Further photophysical studies about these two polymers indicate that the introduction of PEG coils onto the conjugated block retards the water-induced-aggregation and therefore improves the fluorescence stability of PEG-OEPETPT-PEG. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1636–1644

KEYWORDS: aggregation; block copolymers; conjugated polymers; fluorescence; oligomers

INTRODUCTION Conjugated polymers have received continued research interest for the past 30 years due to their wide application in many fields.[1–4] Developing new soluble conjugated polymers with certain specific building blocks will bring new properties as well as broaden the applications. Heterocyclic aromatic structures always displayed unique features in photochemistry and photophysics, coordination chemistry, self-assembly, and so forth.[5–7] Pyridazine, a six-member aromatic ring with two nitrogen atoms neighboring to each other, has been widely studied as the ligand in preparing the many metal complexes as well as the supramolecular metal coordinating units.[6,8–13] In addition, pyridazine is often used as a structural component of compounds for bio-related studies, such as antinociceptive drugs,[14] antibacterial agents,[15] anti-inflammatory compounds,[16] and antihypertensive medicines.[17] Besides the metal cation coordinating tendency, pyridazine also exhibits electron-withdrawing features; thus, it has also been incorporated with a certain electron-donating structure to build up the intramolecular charge transfer (ICT) molecules.[18] The ICT character for the molecules, such as strongly stokes-shift additional fluorescence bands and facility for further charge separation, makes them especially useful in creating new sensing systems, used as photovoltaic materials or in other applications.[19–23] Combining pyridazine with thiophene, a typical electron-donating aromatic unit, provides the charge transfer structure.[24,25] In addition, this structure also provides the S⋯N interaction,[26–28] which may lead to certain unique coordinating and assembling properties. The thiophene-pyridazine-thiophene (TPT) structure has been synthesized as small molecules and the properties have been studied.[24] To our best knowledge, only one literature reported such a structure in conjugated polymer systems.[25] However, the solubility always poses challenges, which resulted in difficulty in the study of solution properties of these polymers, or building-up the supramolecular structure. In addition, it was very difficult to control and tune the solid state morphology, which actually is a key factor influencing the final performance of certain applications.

Sonogashira coupling has been demonstrated to be a powerful synthetic tool toward poly(aryleneethynylene)s.[29–31] Bisalkyne and dihaloarene monomers can be used to obtain a linear polymer (Scheme 1). By selecting different monomers

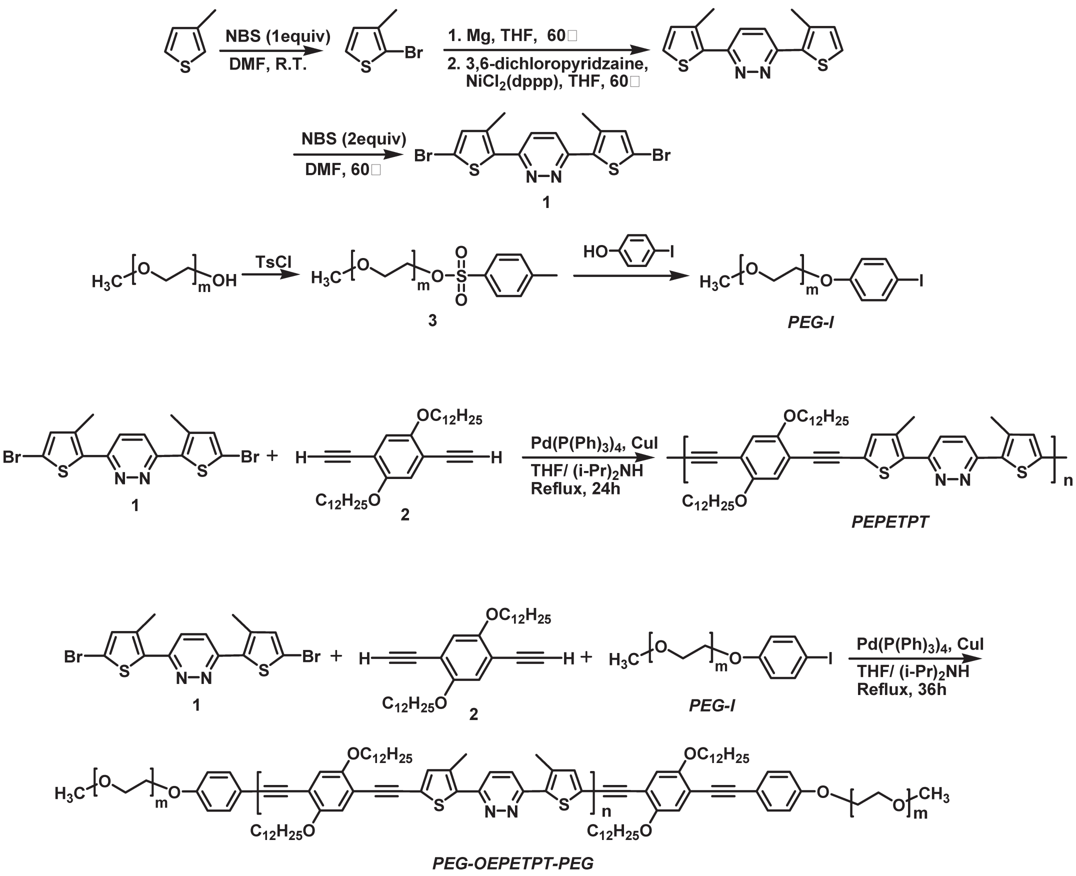
Additional Supporting Information may be found in the online version of this article.



SCHEME 1 General synthetic strategy for poly(aryleneethynylene)s using Sonogashira coupling protocol.

as the building blocks, a variety of poly(aryleneethynylene)s with different backbones and pendant groups can be synthesized. Generally, the molar ratio between the two monomers should be 1:1 to achieve high molecular weight, according to the polycondensation theory. Sonogashira coupling was also employed in this study for the synthesis of the conjugated polymers. To solve the solubility problem, ethynylene phenylene ethynylene (EPE) building block, which has long alkoxyl groups, copolymerize the TPT building block through Sonogashira coupling to obtain a new conjugated polymer (PEPETPT) (Scheme 2). To further improve the solubility, flexible poly(ethylene glycol) (PEG) chains were introduced to both ends of the conjugated segment to form a coil-rod-coil triblock polymer (PEG-OEPETPT-PEG). After the modification of the commercial PEG, the coil-rod-coil polymer was synthesized through the same Sonogashira coupling polymerization, in one-step, by adding the modified PEG (PEG-I) and the conjugated polymer building blocks in the reaction system (Scheme 2). Compared with other methods for synthesizing such triblock copolymers,[32–39] several advantages are obvious for this one-step approach. First, the reaction sequence is greatly shortened. Second, this approach circumvents the post-polymerization reaction. This is desirable since reactions that take place on the polymer chain usually are not as simple compared to small molecular systems and sometimes the reactions cannot be completed. Third, the length of the PEG chains can be fixed by selecting the commercial compound according to the requirements. In addition, the length of the conjugated rod can be adjusted by the feeding ratio, due to the polycondensation nature of polymerization under Sonogashira coupling protocol, which will be discussed in detail later.

This coil-rod-coil polymer is expected to have certain unique properties in various applications, since it combines many interesting characteristics, as mentioned above, in one molecule. As an initial study of its properties, the investigation of photophysics was carried out for the polymer in dilute solution. The results showed that the PEG-OEPETPT-PEG polymer has enhanced emission and improved fluorescence stability over the PEPETPT polymer. The relationship between the fluorescence of polymers in dilute solution and the composition of mixed solvent was also investigated. Different aggregation behaviors have been observed from the emission of the two polymers, which can be attributed to the difference in the polymer structure.



SCHEME 2 Synthetic strategies for the small molecules and polymers in this study.

EXPERIMENTAL

Materials

3-Methylthiophene, 3,6-dichloropyridazine, 1,3-bis(diphenylphosphinol)propane nickel(II) chloride ($NiCl_2$(dppp)), 4-iodophenol, tetrakis(triphenylphosphine) palladium (($(PPh_3)_4Pd$), cuprous iodide (CuI), and PEG monomethyl ether ($M_n = 1900$, PDI = 1.05) were purchased from Alfa Aesar Chemical and used as received. Other commercially available reagents were from Sinopharm Chemical Reagent and were used without further purification unless otherwise noted. Tetrahydrofuran was dried by distillation from sodium metal and kept under argon. Diisopropylamine was distilled over potassium hydroxide before use. 3,6-Bis(2-(5-bromo-3-methylthienyl))pyridazine (**1**)[25] and 1,4-diethynyl-2,5-didodecyloxybenzene (**2**)[40] were synthesized according to the published procedures.

Measurements

^{1}H NMR spectra were recorded on an Inova 400 MHz NMR spectrometer with tetramethylsilane as the internal standard. The FTIR spectra of the monomers and polymers were obtained on Nicolet 6700 FTIR spectrophotometer (thermo) with KBr pellets. Elemental microanalyses were carried out on a Carlo-Erba Elemental Analyzer EA 1110. Gel permeation chromatography (GPC) measurements were performed on a Waters 1515 system with THF as the mobile phase and polystyrene as the standard. The UV–vis absorption spectra were collected on a Hitachi U-3900/3900H spectrophotometer, and photoluminescence (PL) emission spectra were measured on a Horiba FluoroMax-4 spectrofluorometer using excitation at 440 nm with 1 nm slits. The concentration of the polymers was held at 1 μM with respect to the repeating unit of the conjugated polymer backbone. The fluorescence quantum yields in solution of the polymers were determined relative to quinine sulfate in 0.5 M H_2SO_4 solutions with a quantum yield of 0.546, excited at 365 nm.

Synthesis

3,6-Bis(2-(5-bromo-3-methylthienyl))pyridazine (1)

Compound **1** was synthesized according to literature methods.[25,40] Satisfactory NMR characterization of all stable intermediates was observed. The final product was obtained as a light-yellow solid (yield 75%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.66 (s, 2H), 6.95 (s, 2H), 2.52 (s, 6H). FTIR (KBr, cm^{-1}): 2951, 2928, 2852, 1554, 1433, 1384, 1141, 1054, 993, 823, 748, 729. Anal. Calcd for $C_{14}H_{10}Br_2N_2S_2$ (%): C, 39.07; H, 2.33; N, 6.51; found: C, 39.29; H, 2.49; N, 6.51.

1,4-Diethynyl-2,5-didodecyloxybenzene (2)

Compound **2** was synthesized according to published procedures.[41] The product was a light-yellow crystalline solid (yield 80%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 6.95 (s, 2H), 3.95 (t, 4H), 3.33 (s, 2H), 1.78 (m, 4H), 1.50–1.20 (m, 36H), 0.88 (t, 6H). FTIR (KBr, cm^{-1}): 3285, 2920, 2848, 1500, 1465, 1384, 1273, 1218, 1199, 1029, 864, 781, 670, 645. Anal. Calcd for $C_{34}H_{54}O_2$ (%): C, 82.59; H, 10.93; found: C, 82.85; H, 10.98.

PEG methyl tosylate (3)

Compound **3** was synthesized under argon atmosphere. PEG monomethyl ether (13.2 g, 6.90 mmol) was dissolved in 15 mL of dry pyridine under argon. A solution of toluene-*p*-sulfonyl chloride (1.40 g, 7.30 mmol) in 15 mL of pyridine was then added dropwisely to the mixture. After being stirred for 24 h at room temperature under argon, the resulting solution was poured into water and extracted with methylene chloride. The organic layer was washed with water, dried over anhydrous magnesium sulfate. After filtration, the solvent in the filtrate was removed in a rotary evaporator to obtain the crude product, which was further purified by silica gel column chromatography (ethyl acetate as eluent) to afford a white solid (8.60 g, yield 60%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 2.31 (s, 3H), 3.37 (s, 3H), 3.54–4.02 (m, 176 H), 7.35 (d, Ar—H), 7.80 (d, 2H). FTIR (KBr, cm^{-1}): 2869, 1963, 1721, 1638, 1459, 1351, 1299, 1250, 1198, 1102, 944, 846, 689. Anal. Calcd for $C_{96}H_{186}O_{47}S$ (%): C, 54.29; H, 8.77; found: C, 53.32; H, 9.14.

PEG methyl-p-iodophenyl ether (PEG-I)

Potassium carbonate (2.40 g, 17.4 mmol) and 4-iodophenol (1.50 g, 6.80 mmol) was slowly added into a solution of **3** (4.00 g, 3.45 mmol) in ethanol (100 mL) at room temperature. The reaction system was refluxed for 24 h and cooled to room temperature. The resulting mixture was poured into a large amount of water and extracted with methylene chloride. Then the organic layer was washed with water, and dried over anhydrous magnesium sulfate. After filtration, the solvent in the filtrate was removed in a rotary evaporator. The obtained crude product was further purified by column chromatography (silica gel, ethyl acetate eluent) to afford a white solid (2.00 g, yield 50%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 3.37 (s, 3H), 3.54–4.02 (m, 176H), 6.70 (d, Ar—H), 7.56 (d, 2H). FTIR (KBr, cm^{-1}): 2861, 1962, 1638, 1578, 1485, 1467, 1345, 1278, 1243, 1101, 999, 962, 850, 583, 529. Anal. Calcd for $C_{95}H_{183}O_{45}I$ (%): C, 52.53; H, 8.43; found: C, 49.09; H, 8.24.

Poly[p-(ethynylenephenyleneethynylene)-alt-(thienylenepyridazinylenethienylene)] (PEPETPT)

3,6-Bis(2-(5-bromo-3-methylthienyl))pyridazine (**1**) (0.430 g, 1.00 mmol), 1,4-diethynyl-2,5-didodecyloxybenzene (**2**) (0.494 g, 1.00 mmol), $(PPh_3)_4Pd$ (0.0580 g, 0.050 mmol), and CuI (0.0200 g, 0.10 mmol) were placed in a pre-dried Schlenk flask and deoxygenated by several cycles of vacuum-argon cycling. 4 mL of dry diisopropylamine and then 20 mL of dry THF were quickly added into the flask under an argon atmosphere. The mixture was refluxed for 24 h under argon. After cooling to room temperature, the reaction mixture was precipitated in 400 mL of methanol. The precipitate was centrifuged and redissolved in a minimal amount of THF. Then the resulting polymer solution was precipitated in 400 mL of methanol, centrifuged, and dried in vacuum for 24 h to afford a brown solid (0.61 g, yield 80%). GPC (in THF, with polystyrene as the stand) $\overline{M_n} = 2.20 \times 10^4$ g/mol; PDI = 2.05. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.6–7.8 (2H), 7.1–7.2 (2H), 6.85–7.05 (2H), 3.9–4.15(4H), 2.48–2.7(6H), 1.78–2.0(4H), 1.1–1.48(36H), 0.7–0.95(6H). FTIR (KBr, cm^{-1}): 2920, 2849, 2360, 2190, 1655, 1639, 1551, 1495, 1446, 1410, 1379, 1273, 1210, 1094, 1025, 828, 718, 624, 562,

471. Anal. Calcd for $C_{48}H_{62}O_2N_2S_2$ (%): C, 75.59; H, 8.14; N, 3.67; found: C, 72.93; H, 7.91; N, 3.36.

Poly(ethylene glycol)-b-oligo[p-(ethynylenephenyleneethynylene)-alt-(thienylenepyridazinylenethienylene)]-b-poly (ethylene glycol) (PEG-OEPETPT-PEG)

A pre-dried Schlenk flask was charged with monomer **1** (0.2139 g, 0.50 mmol), monomer **2** (0.3037 g, 0.61 mmol), **PEG-I** (0.5165 g, 0.24 mmol), $(PPh_3)_4Pd$ (0.0481 g, 0.040 mmol), and CuI (0.0066 g, 0.035 mmol). The flask was deoxygenated by several cycles of vacuum-argon cycling. 4 mL of dry diisopropylamine and 20 mL of dry THF were quickly added into the flask under the protection of argon. The final mixture was refluxed for 36 h under argon. After cooling to room temperature, the reaction mixture was precipitated in 400 mL of methanol. The precipitate was centrifuged and redissolved in a small amount of THF. The polymer was precipitated again into a large volume of methanol, centrifuged and dried in vacuum for 24 h to afford a yellow solid (0.561 g, yield 60%). GPC (in THF, with polystyrene as the stand) $\overline{M_n} = 7.1 \times 10^3$ g/mol; PDI = 1.5. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.6–7.8 (2H), 7.1–7.2 (2H), 6.85–7.05 (2H), 3.9–4.15 (4H), 3.37–4.02 (179H), 2.48–2.7 (6H), 1.78–2.0 (4H), 1.1–1.48 (36H), 0.7–0.95(6H). FTIR (KBr, cm^{-1}): 2923, 2852, 2363, 2196, 1721, 1601, 1555, 1499, 1464, 1410, 1386, 1276, 1210, 1115, 1026, 860, 836, 723, 564, 469. Anal. Calcd for $(C_2H_4O)_{44}(C_{48}H_{62}O_2N_2S_2)_4(C_{48}H_{66}O_4)(C_2H_4O)_{44}$ (%): C, 65.46; H, 8.73; N, 1.47; found: C, 68.97; H, 8.80; N, 1.91.

RESULTS AND DISCUSSION

Synthesis and Characterizations

The monomers and polymers were synthesized according to the strategies in Scheme 2. Basically, compound **1** and compound **2** were synthesized according to the published literatures.[25,40,41] Compound **3** was prepared by reacting the commercial PEG monomethyl ether with toluene-*p*-sulfonyl chloride, followed by a procedure similar to literature description.[42] Then, PEG-*p*-iodophenyl ether (PEG-I) was obtained by nucleophilic displacement of tosylate group with 4-iodophenol. The structures of all these compounds were confirmed by routine characterizations, as shown in the Experimental section.

PEPETPT was synthesized by a conventional Pd-catalyzed Sonogashira coupling polymerization, using $(PPh_3)_4Pd$ and CuI as catalysts. The polymerization was performed in THF/diisopropylamine mixed solvent under argon atmosphere. The number average molecular weight of the resulting polymer was found to be 2.20×10^4, with a polydispersity index (PDI) of 2.05. This molecular weight is a typical value for conjugated polymers, and the PDI is very close to the ideal molecular distribution in the polycondensation system. All other characterizations, including ^{1}H NMR (spectrum shown in Fig. 1), elemental analysis and FTIR further demonstrated the successful synthesis of PEPETPT.

As mentioned previously, introducing the PEG blocks to both ends of the PEPETPT conjugated polymer may bring certain unique properties, by combining the properties of the conjugated block, such as the charge transfer characteristic and the strong fluorescence emission, with typical properties of PEG, such as biocompatibility and good solubility in most solvents.

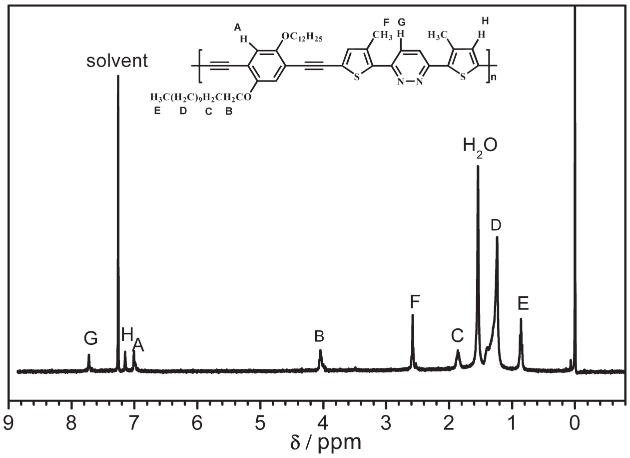


FIGURE 1 ^{1}H NMR spectrum of PEPETPT in $CDCl_3$.

Before employing the strategy described in Scheme 2, several other methods were explored when preparing such coil-rod-coil polymers based on the literature reports.[32,43–45] End group modification strategy (Supporting Information Scheme S1) was attempted. By using a slight excess of monomer **2**, the OEPETPT with terminal ≡C—H at both ends should be synthesized. After purification, this polymer was supposed to react with PEG-I under the Sonogashira coupling protocol to yield the desired PEG-OEPETPT-PEG. However, the synthesis was unsuccessful. An alternative method (Supporting Information Scheme S2) was to modify the terminal ≡C—H with 4-iodophenol right after the polymerization, directly in the polymerization reaction mixture. After the purification, the conjugated polymer with phenol end group was expected to react with PEG-O-Ts (compound **3**) through the nucleophilic displacement of tosylate group to obtain the coil-rod-coil, but this strategy did not work either. The merit for these two strategies was that both rod and coil blocks can be well characterized before being assembled together. The possible reasons for these unsuccessful attempts could be the terminal ≡C—H and phenol group did not survive through the purification process, or the poor solubility of the conjugated polymer and the π-π induced aggregation in the solution made end group modification extremely difficult.

Thus, the one-step strategy in Scheme 2 was used in this study. The merit of this strategy had been advanced in the introduction. The coil-rod-coil polymer was successfully prepared under the Palladium catalyzed Sonogashira coupling protocol, by adding two bifunctional monomers (compound **1** and compound **2**) and one monofunctional monomer (compound **PEG-I**) in a predetermined ratio. According to the mechanism of condensation polymerization, the degree of polymerization of the conjugated block can be tuned by adjusting the ratio between the monomers or ratio between the two types of functional groups. Reducing the length of conjugated block to a certain degree would not have great influence on the photophysics, since the delocalized exciton migration actually has limited distance.[1] However, the solubility can be improved, and the self-assembling or aggregation behavior in the solution will be affected. The molar ratio of about 4:5:2 for monomer **1**, monomer **2** and PEG-I was used in this study, which was based on the comprehensive consideration of the principle of polycondesation,[46] the principle of polymer reactivity,[46] and the mechanism for palladium catalysis.[47,48] Monomer **1** and monomer **2** are the typical bifunctional small molecular monomers for the Sonogashira coupling, as in the synthesis of PEPETPT. PEG-I is a monofunctional macromolecular monomer. Simply considering the Sonogashira coupling mechanism, the dibromopyrene (monomer 1) and the iodoarene (PEG-I) should compete for the coupling reaction with the bisalkyne. It is well known that the reaction rate is affected by the chemical structure of haloarene, such as the iodides react faster than the bromides and the reactants with electron-withdrawing groups react faster than those with electron-donating groups.[47] In this study, the bromide has electron-withdrawing group and the iodide has electron-donating group, which makes the above two influencing factors cancel out each other. However, from the viewpoint of conventional polymer chemistry, it is also well known that the reaction rate of functional groups in a macromolecule is much lower than that of the corresponding low-molecular-weight analogs, such as small molecules or oligomers.[46] Thus it can be envisioned that PEG-I will be much less reactive than the monomer **1** and the conjugated oligomers with the bromide end group. Several factors could account for this slow rate. First, the iodide end group will be embedded in the PEG coil most of the time, which makes it less available for the reaction. Second, the Pd catalytic process requires the reactants to fit into one of the Pd empty orbital in a specific direction.[47,48] Consequently, having a macromolecular tail will make the monomer more difficult to diffuse to where the catalyst is and enter the catalytic circle. In addition, the bulky coiled tail might also retard the monomer of another type to approach the neighboring orbital in attempt to couple with each other.

Thus, we can assume the PEG-I participates in the cross-coupling reaction after the small molecular monomer analogs has been consumed. The initial molar ratio between the monomer dihaloarene and bisalkyne was about 4:5. That is, the bifunctional monomer ratio (r) is about 0.8. In the case of having no PEG-I in the system, the degree of polymerization ($\overline{X_n}$) will be 9, calculated by $\overline{X_n} = (1 + r)/(1 - r)$ according to the principle of condensation polymerization.[46] Thus, the average constituent of the conjugated oligomer should be 4 monomeric units from dihaloarene and 5 monomeric units from bisalkyne, with terminal alkynes at both ends, which will react with the PEG-I if extending the reaction time.

Experimental determination of the conjugated block length would be very useful but challenging. One of the useful methods is the end group analysis in ^{1}H NMR spectrum. Figure 2 showed the spectrum of PEG-OEPETPT-PEG. Most proton peaks from the conjugated block in the coil-rod-coil (Fig. 2) were very similar to those for PEPETPT (Fig. 1), which had been marked out in each figure. As expected, two additional peaks, 3.64 ppm for methylene protons ($C\underline{H}_2$) and 3.37 ppm for the methyl protons ($C\underline{H}_3$) in the end group apparently from the PEG chain, appeared in Figure 2. Theoretically, the ratio of area among different peaks is the same as the ratio of number among the corresponding protons. In Figure 2, the integration area of peak central around 2.55 ppm (marked as F, from the methyl group on the thiophene ring) is about four times that of the peak around 3.37 ppm (marked as P, from the methyl end group). That means, each polymer chain with two methyl end groups, has eight methyl groups on the thiopene, for average. In addition, the ratios of other integration areas are also in proportion with the corresponding number of protons in the coil-rod-coil. The more detailed integration and calculation are shown in Supporting Information as Figure S1 and related discussion. Ultimately, the NMR peak area analysis is consistent with the proposed degree of polymerization according to the feeding ratio.

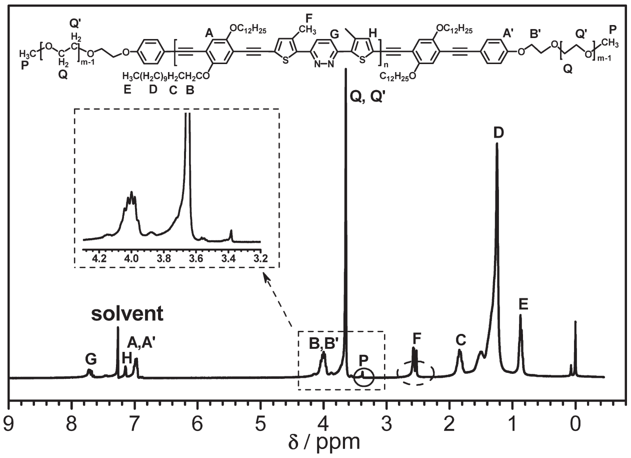


FIGURE 2 ^{1}H NMR spectrum of PEG-OEPETPT-PEG in $CDCl_3$.

The GPC measurements have shown that PEG-OEPETPT-PEG had a number average molecular weight of 7.10 × 10^3 with a PDI of 1.5. Considering the PEG chain has a number average molecular weight of 1900 with a PDI of 1.05, the molecular weight of the middle rod segment can be obtained by subtracting the molecular weight of two PEG segments from that of the total polymer. The results are consistent with the situation discussed above. That is, the degree of polymerization of the conjugated block is about 9 (calculation shown in Supporting Information). It is evident that the conjugated block in the coil-rod-coil triblock polymer had been greatly shortened, comparing with the PEPETPT. The PDI was also reduced, which was consistent with the situation in the condensation polymerization with nonstoichiometry between the two types of the monomers. In addition, the elemental analysis results shown in the experimental section are also consistent with the conjugated block having a degree of polymerization of 9.

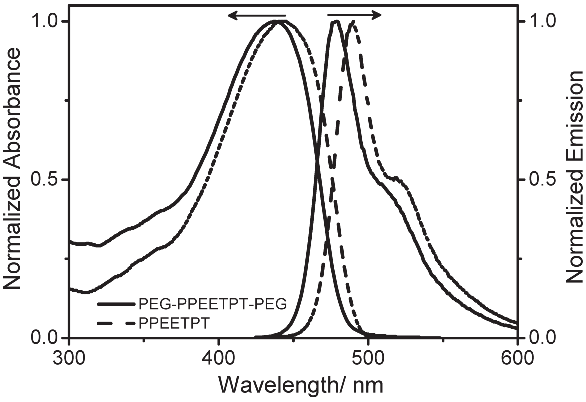


FIGURE 3 Normalized UV–vis absorption and emission spectra of polymers in dilute THF solution at room temperature (excited at 440 nm).

The solubility of polymers was examined. Both of PEG-OEPETPT-PEG and PEPETPT were soluble in many common organic solvents, such as THF, DMF, DMSO, chloroform, and 1,4-dioxane, while PEG-OEPETPT-PEG turned out to be more soluble compared with PEPETPT. THF was found to be the best solvent for both polymers, among all the solvents explored. PEG-OEPETPT-PEG can be easily redissolved in THF with a concentration more than 5 mg/mL, while only <0.5 mg/mL can be achieved for PEPETPT. In addition, PEG-OEPETPT-PEG was slightly soluble in water, methanol, and ethanol, while PEPETPT could not dissolve in these three solvents. The improved solubility in most solvents for PEG-OEPETPT-PEG can be mainly attributed to the introduction of PEG coil block as well as the reduction of length of the conjugated segment.

Photophysical Properties

The normalized UV–vis absorption and PL spectra of PEPETPT and PEG-OEPETPT-PEG in dilute THF solution are shown in Figure 3. The corresponding photophysical data is shown in Table 1. The two polymers displayed very similar spectral profiles, which is very typical for conjugated polymers. The absorption maximum was around 442 nm for PEPETPT and 439 nm for PEG-OEPETPT-PEG. The emission peak was around 490 nm for PEPETPT and 478 nm for PEG-OEPETPT-PEG. Both polymers have an emission shoulder, which was about 35 nm away from the peak at a longer wavelength. The absorption and emission should come from the π-π^* electronic transition along the conjugated polymer backbone and the coexistence of the emission peak and shoulder can be attributed to the existence of the vibrational structure of the polymers.[49,50]

TABLE 1 Photophysical Data for PEPETPT and PEG-OEPETPT-PEG[a]

Polymers	$\lambda_{max,abs}$ (nm)	$\lambda_{max,em}$ (nm)	Φ_F (%)
PEPETPT	442	490	26
PEG-OEPETPT-PEG	439	478	36

[a] Determined in dilute THF solution.

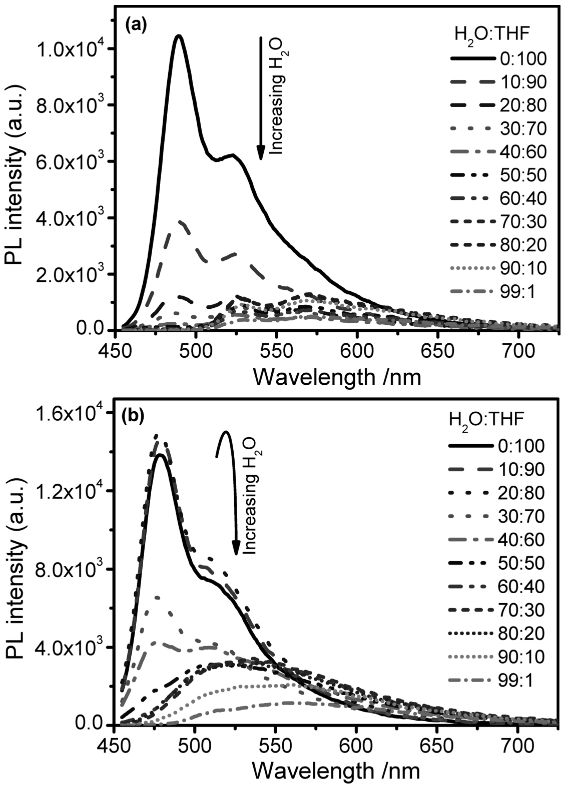


FIGURE 4 The emission spectra of (a) PEPETPT and (b) PEG-OEPETPT-PEG, respectively, in H_2O/THF mixed solvent with different volume percentage of H_2O. The polymer concentrations were fixed at 1 μM with respect to the repeating unit of the conjugated backbone. The excitation was at 440 nm.

In both absorption and emission spectra, slight blue-shifting was found for PEG-OEPETPT-PEG compared to PEPETPT, which is consistent with the fact that PEG-OEPETPT-PEG has a shorter conjugated segment. In addition, the *tri*-block copolymer was found to have a higher quantum yield of fluorescence than PEPETPT. The self-quenching from the π-π interaction among the conjugated blocks was greatly weakened due to the protection of two PEG chains at the two ends, and as a result an increase in emission was observed. Thus, introduction of the PEG coil segments not only increased the solubility, but also improved the photoluminance properties.

Fluorescent Emission and Aggregation Studies

Many applications of conjugated polymers require the presence of water, such as detection of pollutants directly from the river or lake, bioimaging, biolabling, and biosensing. However, most conjugated polymers are hydrophobic and become aggregated, and more or less, quench the fluorescence, when introducing water into the system. THF was selected as the organic solvent to dissolve the polymers based on the fact that it was miscible with H_2O, and

PEPETPT and PEG-OEPETPT-PEG exhibited strong fluorescence in THF, as described previously. The emission spectra of these polymers in H_2O/THF mixed solvent with various compositions were recorded (Fig. 4). Generally, both polymers exhibited a red-shifting in the wavelength of emission peak and a decrease of emission intensity by increasing water content in the mixed solvent. This phenomenon can be attributed to the interactions or aggregation among the conjugated segments, which resulted in the enlargement in the π system as well as the intermolecular fluorescent self-quenching. However, the aggregation and self-quenching behaviors of these polymers differed greatly from each other.

As shown in Figure 4(a), the emission of PEPETPT decreased dramatically by increasing the percentage of H_2O in the mixed solvent. The intensity at the emission maximum was quenched by 63% with the presence of 10% of H_2O, compared with that in pure THF. The profile of spectrum remained almost unchanged, at this point, with a peak around 490 nm and a shoulder around 524 nm. When the percentage of H_2O reached 20%, the emission intensity at 524 nm became almost as strong as the intensity at 490 nm. Increasing the water content to 30%, the emission around 524 nm became stronger than that around 490 nm, and accompanied with another emission peak emerged around 570 nm. Increasing the water percentage to 60% and further, the emission around 490 nm completely disappeared and the emission around 570 nm became the dominating emission peak with the coexistence of the emission shoulder around 524 nm. The residual fluorescence was very low with 99% H_2O in the solvent. The emission behavior of PEPETPT in the mixed solvent is very typical for the common hydrophobic conjugated polymers. Addition of water induced the aggregation among the conjugated polymer backbones, and therefore the broadening and red-shifting of emission spectra accompanied with self-quenching of the fluorescence.

PEG-OEPETPT-PEG showed a superior fluorescence stability toward water, due to the presence of two PEG tails at both ends of the conjugated block, which somewhat prevented the interactions or aggregation among the OEPETPT segments. Initially, the polymer displays a strong emission with the peak centered around 478 nm and a shoulder around 512 nm in THF dilute solution [Fig. 4(b)]. The polymer solution could tolerate a certain quantity of H_2O in the system (up to 20% of H_2O in the mixed solvent), without significant changes in the emission wavelength and intensity, as well as the profile of the spectrum. Interestingly, the introduction of 10–20% water into the solvent resulted in a slightly increased emission intensity at the peak by 7%, with respect to the initial intensity in pure THF. This could possibly be explained by the hydrophilic PEGs, which have a better solubility in H_2O than THF. However, when the amount of H_2O increased to 30%, the intensity decreased to 46% of the initial value. At this stage, loose aggregation might form but the nonaggregated should be still the dominating emission species. The spectra became broad and no fine vibronic structure was found with 50% water in the mixed solvent with the emission maximum around 517 nm. Slightly red-shifting in the emission maximum (530 nm) with similar emission intensity and broad spectra were also founded, when 60–80% of water was present in the solvent. These emission phenomena indicated that certain different emission species, such as the nonaggregated form, associated forms with various degrees of aggregation, must coexisted in the solution with 50–80% of water in the mixed solvent. Increasing the water content to 90–99% led to an even larger red-shift, with an emission maximum around 560 nm and the intensity decreased, suggesting the tightly aggregated form existed as the dominating emission species in the solution and the self-quenching effect was very strong. However, the residual fluorescence was stronger compared to that of PEPETPT, when having 99% H_2O in the solvent.

To evaluate further the fluorescence stability of the two polymers toward water, small amounts of water were titrated into 10 mL of polymer THF solutions. The emission spectra, the relationship between the change in intensity and the water volume are shown in Supporting Information Figure S2. Generally, PEG-OEPETPT-PEG displayed a smooth decline in emission intensity, with increasing the amount of H_2O added directly to the polymer solution, whereas PEPETPT showed a remarkable drop in the intensity.

Absorption and Excitation Studies

To investigate the origin of the fluorescence, the absorption and excitation studies of polymers in certain typical mixed solvent systems were also conducted. As shown in Supporting Information Figure S3, all the spectra for PEPETPT systems had water in the solvent, displaying an absorption profile with two peaks (or one peak and one shoulder, around 474 and 510 nm), which is significantly different from PEPETPT in pure THF, with only one absorption peak around 442 nm. However, no significant change in the absorption spectra (peaked around 439 nm) were found by adding water into the system in the case of PEG-OEPETPT-PEG, with the exception of a small shoulder emerging around 481 nm in certain systems. The UV–vis absorption spectra further confirmed that introduction of PEG to the ends of the conjugated block reduced the influence of water on the photophysics of polymer solution.

Excitation spectra were recorded to examine if different emission peaks or shoulders come from the same electronic transition for different emission species. The systems, with solvent ratios between water and THF as 10:90, 30:70, 70:30, and 90:10, were selected for both polymers. For each system, the emission wavelength was set at the emission peak or shoulder wavelength in the steady-state fluorescence spectra, as shown in Supporting Information Figures S4 and S5, and excitation wavelength was scanned from 350 nm to a wavelength that was 20 nm shorter than the emission wavelength. Table 2 showed the excitation peaks or shoulders existed in the polymer system with different solvent composition.

For PEPETPT, only the 10:90 system displayed a single excitation peak around 437 nm for all emission, indicating that

TABLE 2 The Wavelength (nm) of Excitation Peaks/Shoulders in Different Polymer Systems

Solvent composition (H_2O:THF)	PEPETPT	PEG-OEPETPT-PEG
10:90	437	438
30:70	437, 475, 507	438
70:30	437, 475, 507	438
90:10	437, 475, 507	438, 480

only one electronic transition occurred in this system. However, for all other systems, there were three excitation peaks/shoulders, which is consistent with the information obtained previously that more than one emission species existed in the solution. It is to be noted that sometimes some "electronic communication" among different emission species might exist. Thus, the excitation of a smaller π system may result in the emission of a larger system, due to the energy transfer.[51] However, the situation is much simpler for the case of PEG-OEPETPT-PEG. For 10:90, 30:70, and 70:30 systems, only one excitation peak around 438 nm was found for all the emission peaks and shoulders in the corresponding fluorescence spectra. Only for 90:10, a shoulder around 480 nm emerged besides the the excitation peak around 438 nm. Therefore, larger π systems (tightly aggregated conjugated segments) only appeared by adding no $<$90% water into the mixed solvent for PEG-OEPETPT-PEG. These findings were consistent with previous fluorescence and absorption studies that the introducing PEG coils onto the conjugated block retarded the water-induced-aggregation and therefore enhanced the fluorescence stability.

CONCLUSIONS

A new coil-rod-coil copolymer (PEG-OEPETPT-PEG) with excellent solubility has been successfully synthesized in one-step by Sonogashira coupling polymerization, using two bifunctional small molecular monomers (bisalkyne and dihaloarene) and one monofunctional macromolecular monomer (PEG-I). For comparison, the conjugated polymer PEPETPT without any coil block was also synthesized. The control over the average degree of conjugated block was realized by adjusting the molar ratio between the two bifunctional small molecular monomers. This was based on the consideration that the macromolecular monomer usually has much smaller reactivity, relative to small molecular monomers. Experimental results from the structural analysis further confirmed theoretical consideration. The photophysical study of polymers in pure THF showed that PEG-OEPETPT-PEG has stronger emission and slightly blue-shifted absorption and emission spectra, compared to PEPETPT. PEG-OEPETPT-PEG was demonstrated to have improved fluorescence stability over the PEPETPT towards water. It could tolerate much more water due to the introduction of PEG coils onto the conjugated block, which retarded the aggregation induced by water. Both polymers experienced red-shifts of about 80 nm in emission wavelength, when the solvent was gradually changed from THF to H_2O, while the coil-rod-coil has enhanced fluorescence stability toward its surroundings. This work demonstrated a facile approach for synthesizing such coil-rod-coil copolymer, which may applicable for other conjugated polymer system. In addition, the unique combination the TPT-based conjugated segment with the PEG coils may result in some other interesting properties and useful applications. The related research is currently underway in our laboratory.

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