

Supporting Information

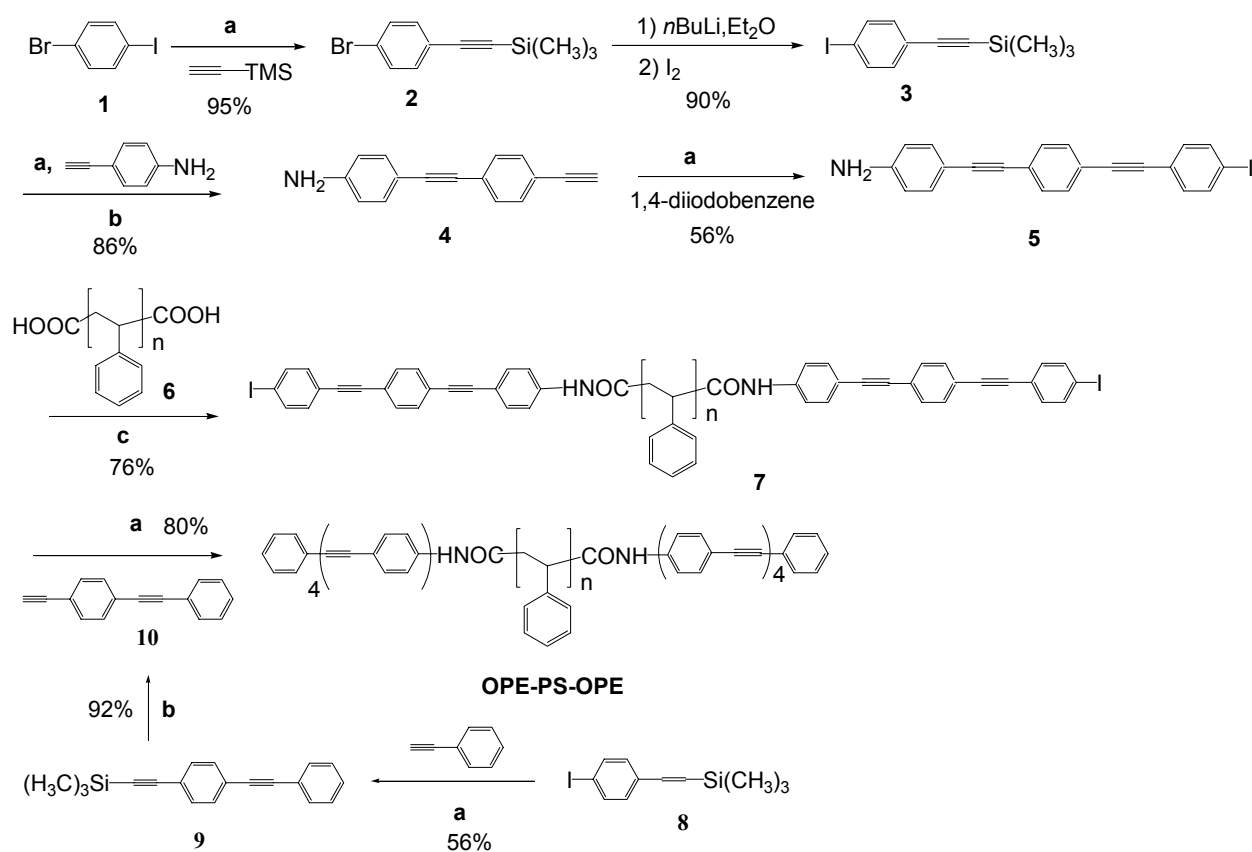
Multiple Self-Assembled Nanostructures from an Oligo(*p*-phenyleneethynylene) Containing Rod-Coil-Rod Triblock Copolymer

Kun Li and Qing Wang

Department of Materials Science and Engineering

The Pennsylvania State University

University Park, PA 16802



Reagents: **a.** $\text{PdCl}_2(\text{PPh}_3)_2$ (3 mol%), CuI (1 mol%), $\text{Et}_3\text{N}/\text{THF}$ (1:1).
b. K_2CO_3 , CH_3OH , CH_2Cl_2
c. i) SOCl_2 , reflux 5 hours; ii) Trimer **1**, $\text{THF}/\text{Pyridine}$ (2:1)

Scheme 1. Synthesis of the triblock copolymer **OPE-PS-OPE**.

Experimental Section:

1-Bromo-4-(trimethylsilylethynyl)benzene (**2**), 1-iodo-4-[(trimethylsilyl)ethynyl]-benzene (**3**), and 4-[(4-ethynylphenyl)ethynyl]-benzenamine (**4**) were prepared according to literature procedures.^{1,2} Dicarboxyl terminal polystyrene was brought from the Polymer Source Inc. ($M_n=4500$, $M_w=5000$, $PI=1.12$, functionality >1.95). Tetrahydrofuran (THF) was distilled from Na⁺/benzophenone ketyl. All the other chemicals were purchased from the Aldrich Chemical Co. and used as received unless otherwise stated.

Synthesis of trimethyl{[4-(phenylethynyl)phenyl]ethynyl}silane (9**):** 1-Iodo-4-[(trimethylsilyl)ethynyl]-benzene (**8**, 2.655 g, 8.84 mmol), phenylacetylene (0.988 mL, 9 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.077 g, 0.109 mmol), and copper(I) iodide (0.037 g, 0.194 mmol) were dissolved in dry THF (10 mL) and triethylamine (10 mL). The mixture was stirred at room temperature overnight and the solvent was then evaporated in vacuum. The residue was purified through a silica gel column eluting with 1: 10 dichloromethane/hexane. Yield: 1.35 g (56%). FTIR (KBr, cm^{-1}): ν 2200 (w, $C\equiv C$), 2153 (s, $C\equiv C-Si$). 1H NMR (300 MHz, $CDCl_3$, ppm): δ 7.48 (m, 2H, Ph), 7.43 (s, 4H, Ph), 7.32 (m, 3H, Ph), 0.24 (s, 9H, CH_3). ^{13}C -NMR (300 MHz, $CDCl_3$, ppm): δ 131.94, 131.67, 131.43, 128.53, 128.44, 123.39, 123.05, 122.94, 104.69, 96.29, 91.33, 89.07, 0.027. MS: m/z calcd. for $C_{19}H_{15}Si$ (found) M^+ : 274.11 (274.11).

1-Ethynyl-4-(phenylethynyl)benzene (10**):** Trimethyl{[4-(phenylethynyl)phenyl]ethynyl}silane (**9**, 1.0 g, 3.65 mmol) and K_2CO_3 (0.504 g, 3.65 mmol) were added in dichloromethane (5 mL) and methanol (10 mL). The mixture was stirred at room temperature overnight and the solvent was then evaporated in vacuum. The residue was

purified through a silica gel column eluting with 1: 10 dichloromethane/hexane. Yield: 0.68 g (92%). FTIR (KBr, cm^{-1}): ν 3282 (s, -C-H), 2210 (w, $\text{C}\equiv\text{C}$), 2108 (w, $\text{C}\equiv\text{CH}$). ^1H -NMR (300 MHz, CDCl_3 , ppm): δ 7.53 (m, 2H, Ph), 7.46 (s, 4H, Ph), 7.34 (m, 3H, Ph), 3.15 (s, 1H). ^{13}C -NMR (300 MHz, CDCl_3 , ppm): δ 132.12, 131.70, 131.53, 128.59, 128.46, 123.83, 122.98, 91.43, 88.89, 83.34, 78.95. MS: m/z calcd. for $\text{C}_{16}\text{H}_{10}$ (found) M^+ : 202.07 (202.07).

4-({4-[(4-Iodophenyl)ethynyl]phenyl}ethynyl)aniline (5): 4-[(4-Ethynylphenyl)ethynyl]-benzenamine (**4**, 1.3 g, 6.0 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.126 g, 0.149 mmol), and copper(I) iodide (0.091 g, 0.48 mmol) were dissolved in dry THF (10 mL) and triethylamine (10 mL). A solution of 1,4-diodobenzene (6.0 g, 18.2 mmol) in 10 mL dry THF was added dropwise over a period of 5 hours via a additional funnel. The mixture was stirred at the room temperature for 12 hours and the solvent was then evaporated. The residue was purified through a silica gel column eluting with 2: 1 dichloromethane/hexane. Recrystallization from toluene/ethanol gave a yellow needle solid. Yield: 1.44 g (56%). ^1H -NMR ($\text{CDCl}_2\text{-CDCl}_2$, 300 MHz, ppm) δ 3.90 (s, 2H), 6.66 (d, 2H), 7.26 (d, 2H), 7.34 (d, 2H), 7.49 (s, 4H), 7.70 (d, 2H). ^{13}C -NMR ($\text{CDCl}_2\text{-CDCl}_2$, 300 MHz, ppm): δ 116.5, 133.3, 133.4, 135.0, 139.3. UV-Vis (toluene): $\lambda_{\text{max}} = 345\text{nm}$. MS: m/z calcd. for $\text{C}_{22}\text{H}_{14}\text{IN}$ (found) M^+ : 419.26 (419.20).

Compound 7: Dicarboxyl terminal polystyrene (**6**, 1.0 g, 0.22 mmol) was dissolved in 15 mL thionyl chloride. After refluxing at 110 °C for 6 hours, the reaction mixture was cooled down to room temperature and the excess thionyl chloride was removed under vacuum. The compound **5** (0.339 g, 0.81 mmol) in 2 mL dry THF was added via syringe. After the solution cooling to 0 °C, pyridine (4 mL) was added. The

reaction mixture was stirred for 1.5 hour at 0 °C and 3 hours at room temperature. The solvent was removed under vacuum. The residue was isolated and purified through a silica gel column eluting with 3:1 dichloromethane/hexane to give light yellow powders. Yield: 0.77 g (76%). FTIR (KBr, cm^{-1}): ν 3058, 2906, 1945, 1869, 1695, 1653, 1603, 1521, 1493, 1452, 1378, 1305, 712. Raman (cm^{-1}): ν 2209, 1592, 1121. GPC (THF, polystyrene standards): PDI= 1.14, M_n = 5532. UV-Vis (toluene): λ_{max} = 335 nm.

OPE-PS-OPE: Compound **7** (0.5 g, 0.095 mmol), 1-ethynyl-4-(phenylethynyl)-benzene (**10**, 0.076 g, 0.38 mmol), bis(triphenylphosphine) palladium(II) dichloride (0.01 g, 0.014 mmol), and copper(I) iodide (0.005 g, 0.026 mmol) were dissolved in dry THF (3 mL) and triethylamine (3 mL). The reaction mixture was stirred at room temperature for 24 hours and the solvent was removed under vacuum. The residue was isolated and purified through a silica gel column eluting with hexane with increasing dichloromethane content (from the hexane: dichloromethane 1:0 to hexane: dichloromethane 1:3). The procedure of chromatography was monitored by UV-vis spectrophotometer and the eluent with an absorption maximum at 355 nm was collected. The product was further precipitated twice from THF into MeOH and dried under vacuum to give light yellow powders. Yield: 0.40 g (81%). FTIR (KBr, cm^{-1}): ν 3061, 2913, 1943, 1870, 1693, 1653, 1601, 1522, 1494, 1452, 1424, 1376, 1307, 710. Raman (cm^{-1}): ν 2205, 1593, 1120. GPC (THF, polystyrene standards): PDI= 1.15; M_n = 6107. UV-Vis (toluene): λ_{max} = 355 nm.

Characterization. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer. Molecular weights and distribution of polymers were determined by gel permeation chromatography (GPC) with a Waters Associates liquid chromatography

equipped with a Water 510 HPLC pump, Waters 410 differential refractometer, and Waters 486 tunable absorbance detector. UV-Vis spectra were collected by a Varian Cary 100 UV-Vis spectrophotometer with DRA-CA-30I sphere accessory for thin film reflectance measurements. The emission spectra were collected by a Varian Cary Eclipse spectrophotometer. Raman spectra were performed on a Bio-Rad Fourier transform Raman II spectrometer equipped with a Nd:YAG laser and a liquid nitrogen-cooled germanium detector. The laser produced a continuous source of radiation at 1064 nm, and the power at the sample was approximately 400 mW. Raman spectra were collected at a resolution of 4 cm⁻¹. Transmission electron microscopy (TEM) was performed on a Phillips EM410 microscope operated at an acceleration voltage of 80 kV.

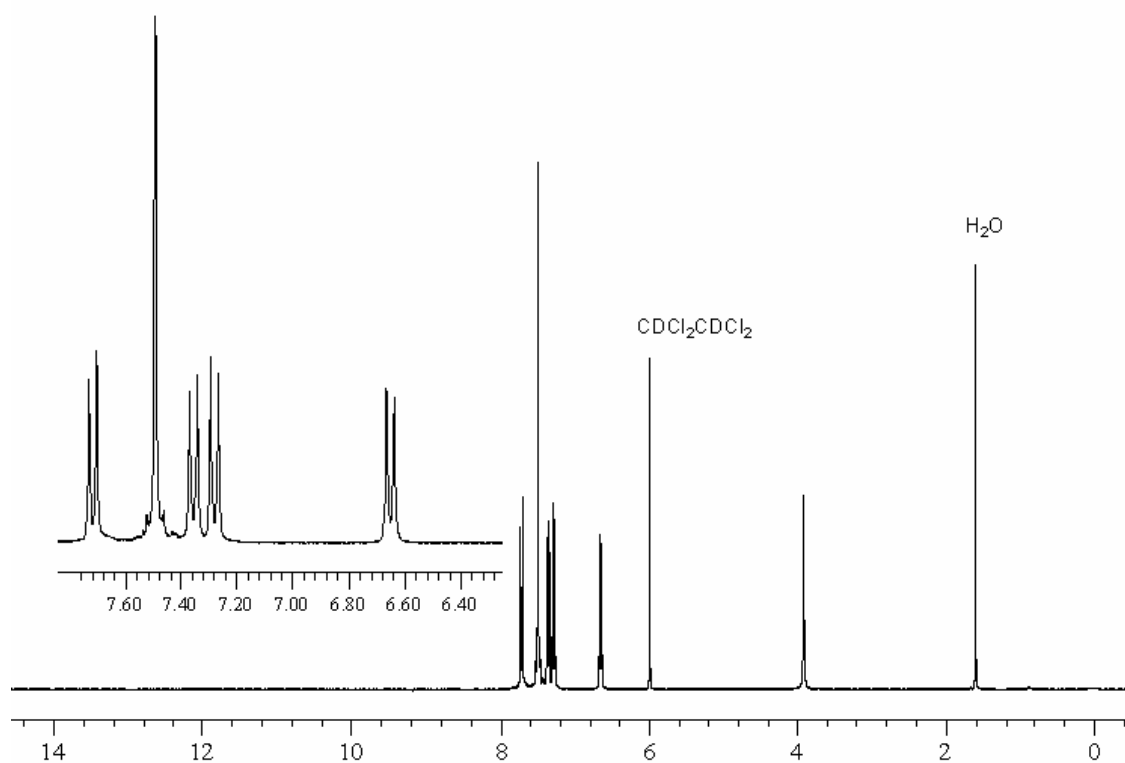
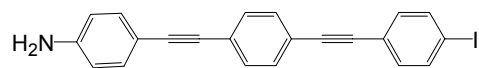
[1] Steinmetz, M.G.; Yu, C. J.; Li, L. *J. Am. Chem. Soc.* **1994**, *116*, 932.

[2] Lavastre, O.; Cabioch, S.; Dixneuf, P. H. *Tetrahedron.* **1997**, *53*, 7595.

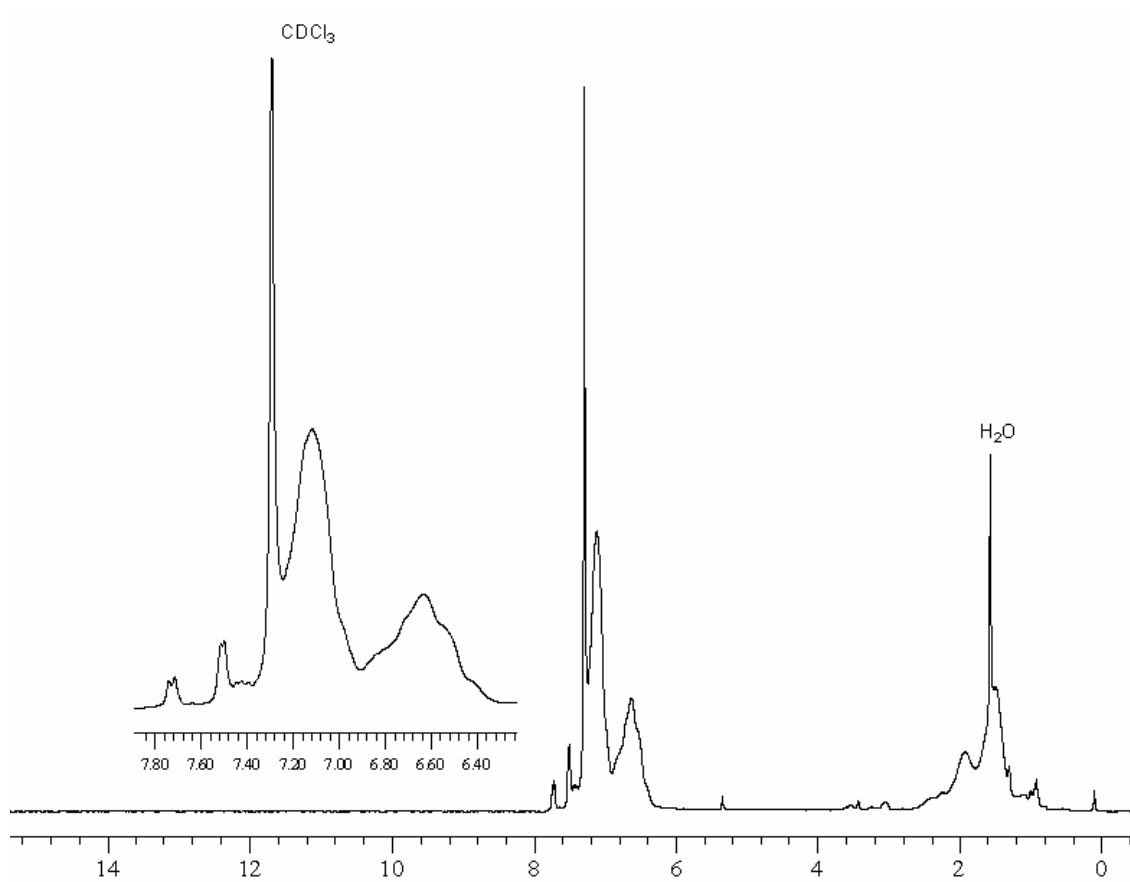
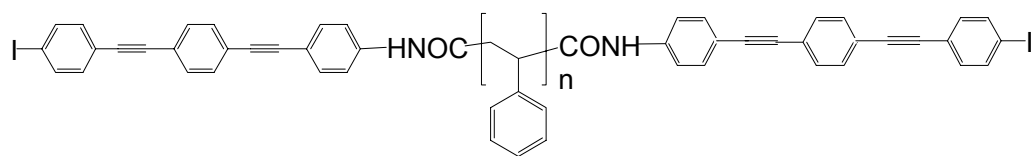
Results and Discussions:

Synthesis and Structural Characterization. The synthetic approach to the triblock structure **OPE-PS-OPE** is depicted in Scheme 1. Starting from 1-bromo-4-iodobenzene, a phenyleneethynylene trimer, **5**, with amino and iodo end groups was prepared in four steps. The presence of the terminal amine functionality allows the coupling of **5** to a monodispersed α,ω -dicarboxyl-terminated polystyrene (**6**) to yield polymer **7**. Condensation of polymer **7** with 2 equiv of 1-ethynyl-4-(phenylethynyl)benzene using Pd(PPh₃)₂Cl₂ and CuI as the catalysts afforded **OPE-PS-OPE**. The structures of the polymers were confirmed by spectroscopic studies and elemental analysis. After the coupling reaction of **5** and **6**, the ¹H NMR spectrum of **7**

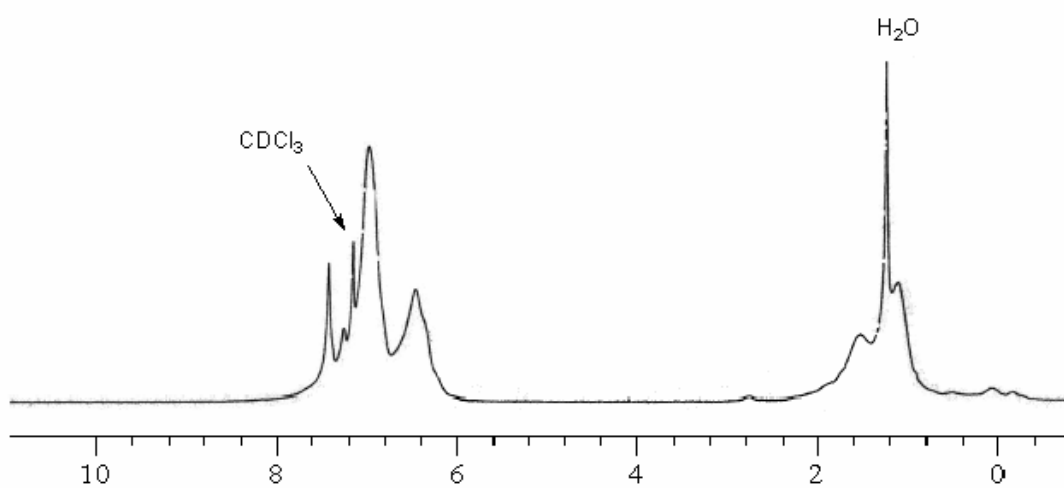
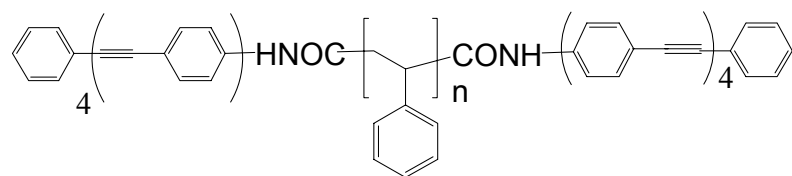
shows no signal for residual amine groups at 3.92 ppm and affords a doublet at 7.75 ppm and a singlet at 7.54 ppm, which are characteristic signals of benzylic protons from OPE. The ethine carbons from OPE are found at δ 90 - 94 in the ^{13}C NMR spectrum of polymer **7**. In the ^1H NMR spectrum of **OPE-PS-OPE**, the increased intensity of a singlet at δ 7.49 and the absence of a doublet at δ 7.69 corresponding to aromatic protons adjacent to the iodo group indicate the presence of pentamer OPE in the triblock copolymer. The Raman peaks of **OPE-PS-OPE** are located around 1118, 1591 and 2210 cm^{-1} , and are ascribed to triple bond stretching of OPE pentamer. The optical properties of the synthesized structures were investigated by UV-vis and fluorescence spectroscopy. The π - π^* transition of the conjugated backbones, observed in compound **5** at 345 nm, was blue-shifted to 335 nm for polymer **7** because of the electron withdrawing effect of amido bonds. The absorption maximum of **OPE-PS-OPE** appears at 363 nm due to the increase in conjugation length. Fluorescence measurements give rise to an emission maximum at 391 nm and a photoluminescence quantum yield of 0.78 for **OPE-PS-OPE** in dilute toluene solution of 10^{-3} mg/mL.



$^1\text{H-NMR}$ spectrum of compound **5**



$^1\text{H-NMR}$ spectrum of compound 7.



¹H-NMR spectrum of the triblock copolymer **OPE-PS-OPE**.

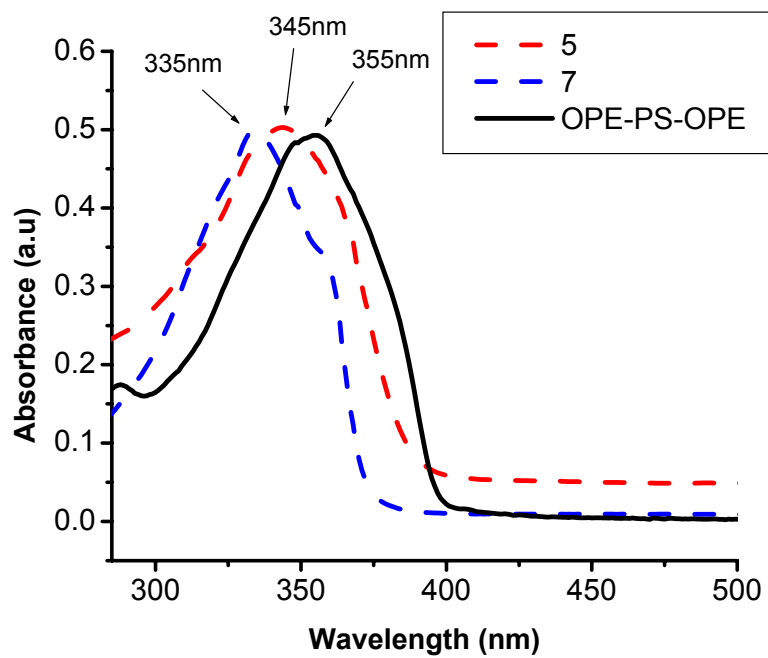


Figure 1. UV/vis absorption spectra of compound **5**, polymer **7**, and **OPE-PS-OPE** in dilute toluene solution (10^{-3} mg/mL).

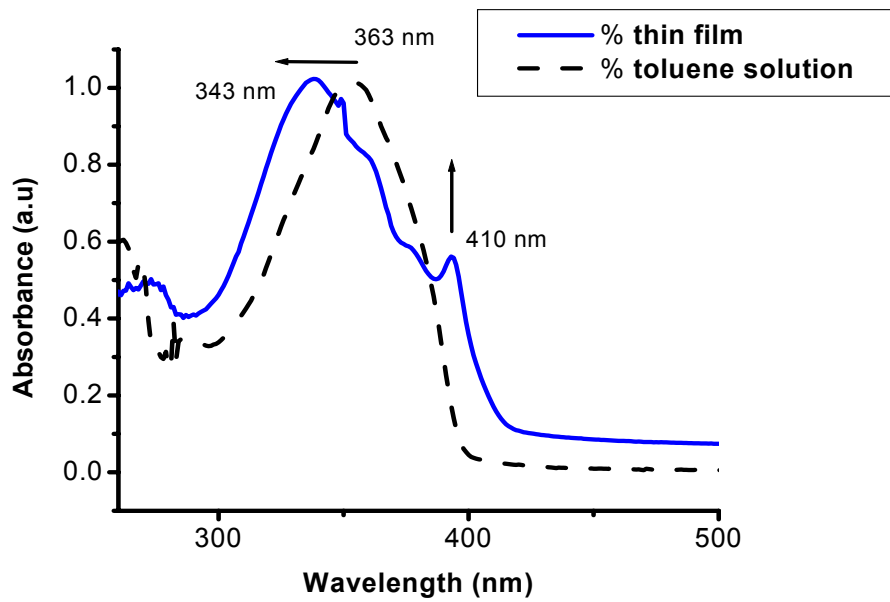


Figure 2. UV/vis absorption spectra of **OPE-PS-OPE** toluene solution and thin film.