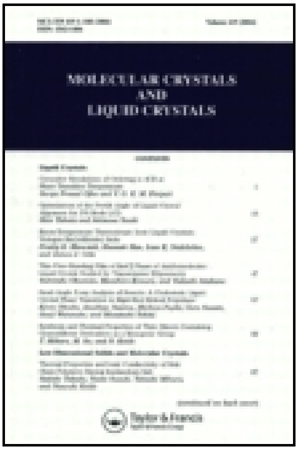

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Synthesis of Maleimide-Functionalized Water-Soluble Poly(arylene ethynylene)s

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Synthesis of Maleimide-Functionalized Water-Soluble Poly(arylene ethynylene)s

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We have synthesized water-soluble poly(arylene ethynylene)s having maleimide groups capable of reacting with thiol-containing biomolecules. The number-average molecular weights of the polymers range from 11,000 to 14,000. The polymerization was carried out by palladium-catalyzed Sonogashira-Hagihara cross-coupling reaction with good yield. The polymers showed blue emission colors in their methanol solutions, while green color was observed in aqueous solutions with decreased emission intensity.

Keywords: fluorescence; maleimide; water-soluble conjugated polymers

INTRODUCTION

Recently water-soluble conjugated polymers have been attracted a great deal of attention because of their unique optoelectronic properties, which may serve as a basis for a new generation of optoelectronic devices and biochemical detection [1–4]. Their peculiar properties stem from the combination of optoelectronic properties of conventional conjugated polymers and water solubility induced by ionic nature of polyelectrolytes [5,6]. Their optoelectronic properties can be easily tuned through the structural alteration of the conjugated structure of the polymer backbones, and the ionic functionality endows them with exceptional features such as electrostatic interaction with oppositely charged species, a high sensitivity toward fluorescence

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quenchers, and the fabrication of exotic supramolecular structures in aqueous solutions [7,8].

The ability of energy transport property of conjugated poly(arylene ethynylene)s has provided in their utilization as chemosensors [9]. To expand the scope and sensory applications of poly(arylene ethynylene), conjugation with biomolecules has been received great interest. The most commonly utilized methodology for the conjugation of biomolecules to organic polymers is closely related to addition and substitution reactions with amine or thiol group in the biomolecules [10]. The thiol functionality can be easily found in cysteine, and, in general, cysteine conjugation reactions employ maleimide as a thiol-acceptor.

We have designed and synthesized water-soluble conjugated poly(arylene ethynylene)s containing maleimide group in the polymer end groups or in the backbones. The optical properties and aggregation behaviors in their aqueous solution was investigated.

EXPERIMENTAL

Reagents and Characterization

All the chemicals were purchase from Aldrich and used without further purification. ^{1}H NMR spectra were collected on a Bruker DRX-300 spectrometer (Korea Basic Science Institute). The molecular weight was determined by gel permeation chromatography (GPC) with dimethyl acetamide (DMAc) as an eluent. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 35 spectrometer. Photoluminescence spectra were obtained on a Perkin Elmer LS 45 equipped with a xenon lamp excitation source. Monomers **1**, **3**, and **4** are synthesized according to the previously published methods [11–13].

Synthesis of P1

201.62 mg (0.297 mmol) of **1** and 34.51 mg (0.273 mmol) of 1,4-diethynyl benzene **2** were dissolved in a three-necked round-bottom flask containing a mixture of 8 ml of DMF, 2 ml of diisopropylamine, and 4 ml of water. 1.51 mg (0.0013 mmol) of $Pd(PPh_3)_4$ and 0.25 mg (0.0013 mmol) of CuI were added into the flask. The reaction mixture was stirred under nitrogen at 50°C for 48 h. After the reaction, the reaction mixture was cooled and slowly poured into 500 ml of methanol/acetone/ether mixture (10:40:50 by volume%). The precipitates were isolated by filtration. The polymer was dissolved in water/methanol and reprecipitated from methanol/acetone/ether twice. Finally, the polymer was dissolved in 150 ml of water, 0.05 g of sodium cyanide was added, and resulting solution was dialyzed against water (Millipore Nanopure^{TM}) using a 1 kD MWCO cellulose membrane for 3 days. After the dialysis, the polymer solution was freeze-dried to obtain 86 mg of the yellow solid (yield 61%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.61 (d, 4H), 7.22 (s, 2H), 4.06 (t, 4H), 2.76 (t, 4H), 2.35 (m, 4H), 2.05 (m, 4H) ppm.

Synthesis of P2

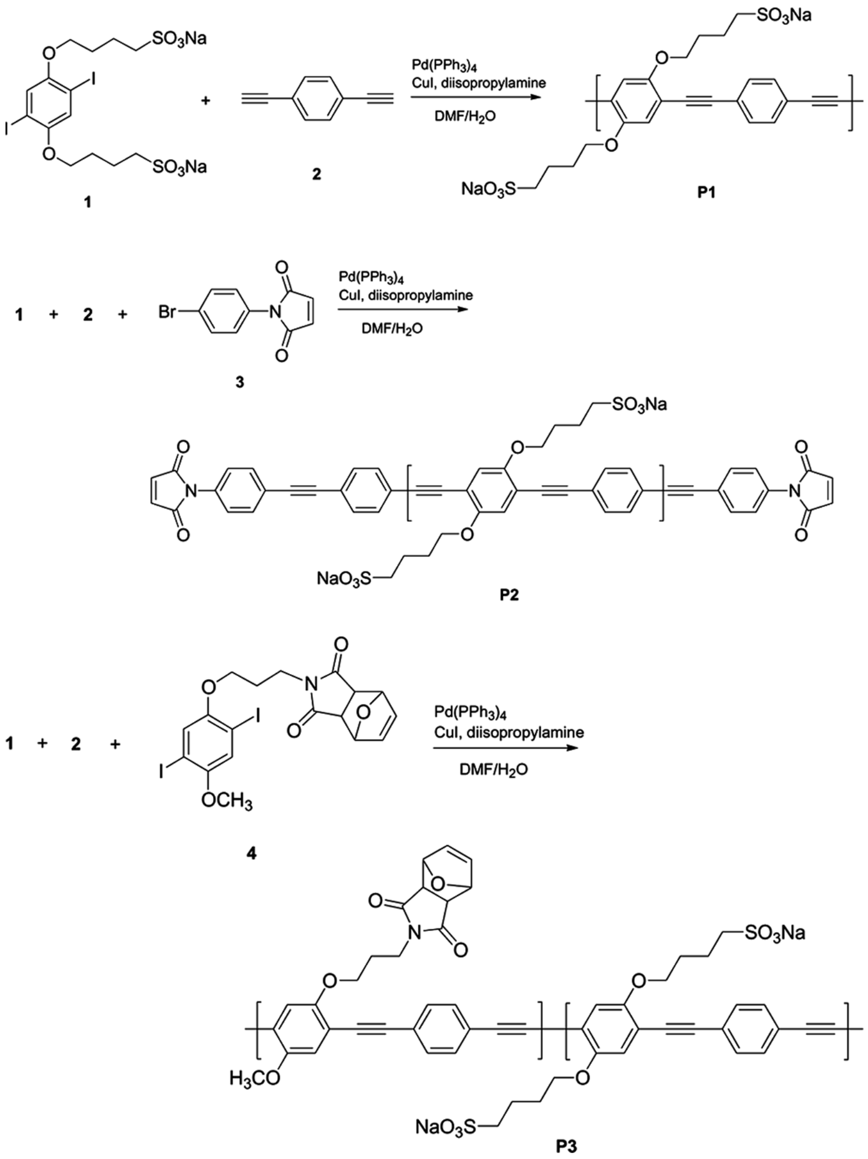
201.80 mg (0.297 mmol) of **1** and 42.63 mg (0.325 mmol) of **2** were dissolved in a mixture of 8 ml of DMF, 2 ml of diisopropylamine, and 4 ml of water in a three-necked round-bottom flask. 1.71 mg (0.0015 mmol) of $Pd(PPh_3)_4$ and 0.32 mg (0.0015 mmol) of CuI were added to the flask. The reaction mixture was stirred under nitrogen at 50°C for 48 h. 310.07 mg (1.23 mmol) of **3** and 2.75 mg of $Pd(PPh_3)_4$ were added to the flask. After additional 24 h, the reaction mixture was cooled to room temperature. The same purification method was employed as described for **P1**. 84 mg of the yellow solid was obtained in 54% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.60 (d, 4H), 7.52 (d), 7.49 (d), 7.22 (s, 2H), 4.11 (t, 4H), 3.26 (t, 4H), 2.67 (m, 4H), 2.32 (m, 4H) ppm.

Synthesis of P3

174.21 mg (0.258 mmol) of **1**, 61.97 mg (0.491 mmol) of **2**, and 150.3 mg (0.258 mmol) of **4** were dissolved in a mixture of 8 ml of DMF, 2 ml of diisopropylamine, and 4 ml of water in a three-necked round-bottom flask. 1.39 mg (0.0012 mmol) of $Pd(PPh_3)_4$ and 0.23 mg (0.0012 mmol) of CuI were added to the flask. The reaction mixture was stirred under nitrogen at 50°C for 48 h. The same reaction and purification methods were employed as described for **P1** and **P2**. 65 mg of the yellow solid was obtained in 14% yield. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.56 (d, 4H), 7.50(d, 4H), 7.45 (s, 2H), 7.32 (s, 1H), 7.08 (s, 1H), 6.57 (t, 2H), 4.34 (t, 6H), 3.76 (s, 3H), 3.37 (t, 4H), 3.33 (t, 2H), 2.65 (d, 4H), 1.75–1.73 (m, 10H) ppm.

RESULTS AND DISCUSSION

The synthetic routes for polymers **P1**, **P2**, and **P3** are shown in Scheme 1. Monomers **1**, **3**, and **4** for the preparation of the polymers were synthesized according to the literature procedures. Poly(arylene ethynylene)s are typically prepared by palladium-catalyzed Sonogashira-Hagihara cross-coupling of 2,5-dialkoxy-1,4-diiodobenzenes and 1,4-diethynyl benzene. For the preparation of control **P1**, 1,4-diethynyl benzene **2**



SCHEME 1 Synthetic methods for polymer **P1**, **P2**, and **P3**.

and a slight excess of aryl diiodide in the presence of catalytic amount of palladium tetrakis(triphenylphosphine) and copper iodide are dissolved in DMF with an amine base.

It is already reported that if the maleimide groups were present in the polymer backbone during the Sonogashira-Hagihara type polymerization, only low molecular weight oligomers were obtained due to Heck-type side reaction [14]. Thus it was necessary to mask the maleimide during the polymerization to get a high molecular weight **P3**. We used furan to protect the maleimide group via Diels-Alder reaction. As an alternative method for maleimide functionalization, a slight excess of the aryl dialkyne was introduced for the preparation of **P2**, thereby incorporation of alkyne-end group was successfully accomplished for further reaction with maleimide-bearing molecule **3**. Thus we have prepared three types of poly(arylene ethynylene)s such as control **P1**, maleimide-end-capped **P2**, and polymer with maleimide group in each repeat unit **P3**.

All the poly(arylene ethynylene)s were characterized by ^{1}H NMR spectroscopy. The *in situ* end-capping reaction with maleimide was undertaken by adding 4-bromophenyl-*N*-maleimide with additional palladium catalyst, and the presence of maleimide group at the ends of polymer chain **P2** was also found around 7.5 ppm. GPC revealed that the three polymers had molecular weights ranging from 11,000 to 14,000 as shown in Table 1. All the polymers are readily soluble in water, methanol, and dimethyl sulfoxide (DMSO), but insoluble in tetrahydrofuran (THF) and chloroform.

The UV-vis absorption and emission spectra of **P1**, **P2**, and **P3** in water, methanol, and mixture of water and methanol (concentration 10^{-5} M) are shown in Figures 1 and 2. Absorption bands of **P2** and **P3** were blue-shifted in both methanol and water compared to those of **P1**. As shown in Figure 1(a), **P1** exhibits an absorption maximum at 407 nm with a weak one at 349 nm in methanol solution. Appreciable extent of red shift can be observed by addition of water into the methanol solution, suggesting that aggregation was induced in aqueous phase. Red shifts of absorption in aqueous solution of **P2** and **P3** can be also seen in Figures 1(b) and (c).

Upto now, there have been two reliable explanations on the red shift of poly(arylene ethynylene) absorption and emission spectra

TABLE 1 Molecular Weights^a of the Poly(arylene ethynylene)s

	M_n	M_w	Polydispersity
P1	14,100	24,300	1.72
P2	14,650	16,650	1.13
P3	11,250	11,920	1.06

^{a}Molecular weights were determined by GPC with DMAc as an eluent.

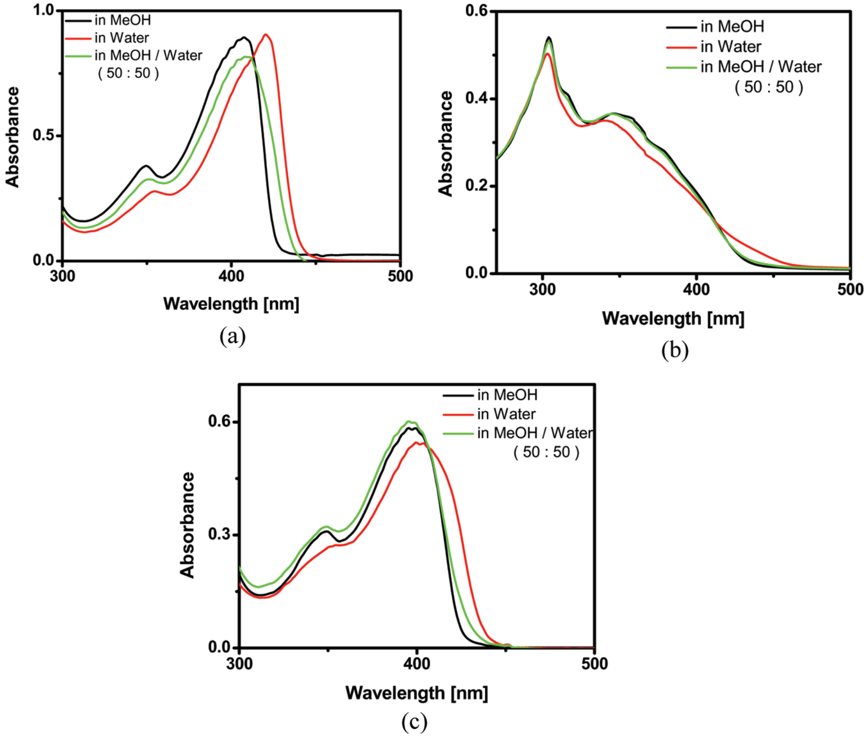
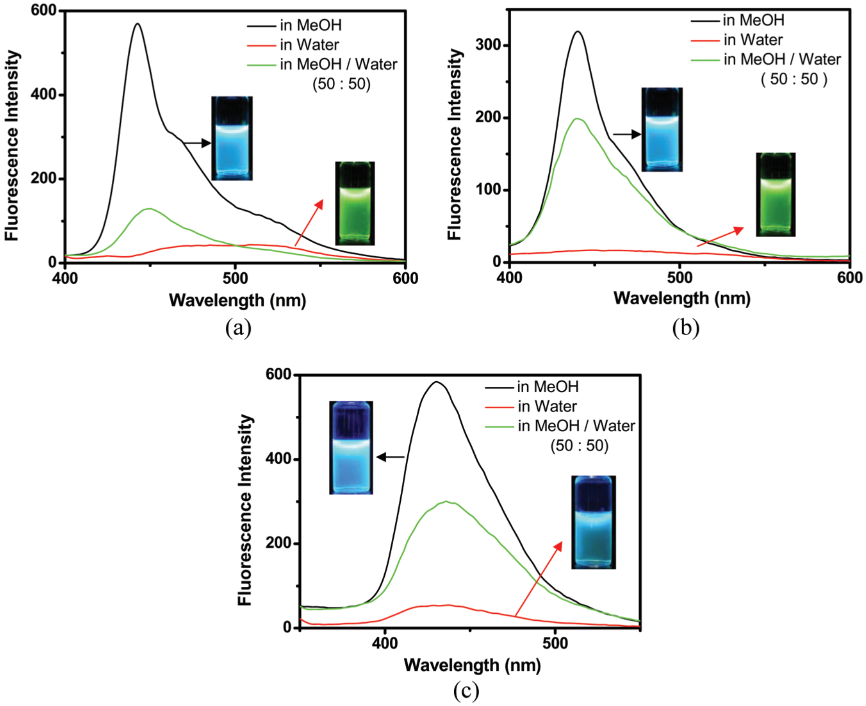


FIGURE 1 UV-vis spectra of the polymers: (a) **P1**; (b) **P2**; (c) **P3**.

due to the relatively free rotation of their alkyne-aryl single bonds. One is connected with interchain co-facial aggregation, that is, tight $\pi-\pi$ stacking of many poly(arylene ethynylene) chains, and the other is related to the aggregation-induced planarization of the conjugated backbone [15,16]. Moreover, previous investigations have suggested that the planarization of the conjugated backbone give rise to a relatively modest red shift of 10–20 nm, which preserve the vibrational structure of the molecules, whereas co-facial aggregation induces larger shifts (>50 nm) and the loss of the vibrational structure [17,18].

In fact, with the gradual addition of water to methanol, the emission intensity of **P1** and **P2** gradually decreased with red shift of emission bands. As can be seen inset photographs of emission colors in Figure 2, green emission color was developed in 100% aqueous solution of **P1** and **P2**. On the while, in the case of **P3**, red shift of emission band was not observed, only intensity decrease appeared, indicative of aggregation-induced emission decrease.



(a) (b) (c)

FIGURE 2 Fluorescence spectra of the polymers: (a) **P1**; (b) **P2**; (c) **P3**.

CONCLUSION

We synthesized a series of blue-emitting anionic water-soluble conjugated poly(arylene ethynylene)s with maleimide in its main chain or end group via Sonogashira-Hagihara cross-coupling reaction. The polymers showed similar absorption and emission bands with slight blue shift of absorption according to incorporation of maleimide moiety. According to investigations on their optical properties, aggregation in aqueous solution was inevitable in terms of emission intensity decrease and red shift of absorption and emission bands.

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