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A water-solubilized, segmented, alternating block copolymer of a 1,4-bis-styrylbenzene with polyethylene glycol

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Abstract

The synthesis and characterization of a new segmented alternating copolymer is described, having monodisperse, partially methoxy-substituted bis-1,4-styrylbenzene chromophores linked with polyethylene glycol segments (average MW 1000) at the terminal aryl rings, so that the chromophore long axis lies along the polymerization vector. The product polymer is a blue-emitting material that is soluble in organic solvents and water. It is a waxy solid with a degree of polymerization of ∼3–6, a melting transition at 35 °C and good thermogravimetric stability up to 300 °C. It exhibits blue photoluminescence (PL) at 437 nm in chloroform, and at 445–465 nm in water, with relative PL quantum yields of 0.7 and 0.3, respectively. Its neat film luminescence maximum is 460 nm; solid state blending with PMMA blue shifts the emission to 440 nm at 10% polymer in PMMA.

Keywords: Water soluble polymer; Luminescent polymer; Segmented block copolymer

1. Introduction

An important strategy for making processible organic polymers for electronic properties' research has been the synthesis and characterization of segmented block copolymers (SBCs) consisting of well-defined, monodisperse fluorescent chromophores and flexible nonconjugating blocks. Karasz and coworkers showed in the 1990s that copolymer **1** incorporating rod-like 1,4-bis-styrylbenzene units linked by flexible polymethylene chains was effective for fabricating some of the first blue-emitting polymeric OLEDs [1]. Subsequent work has achieved wide variation of luminescence emission wavelength within this structural architecture using monodisperse chromophores, **2** [2], or modified variable chromophores (such as blue-modified phenylenevinylenes, BMPPV [3]) with a common flexible block, **3**. The growing interest in additional uses of organic electronic polymers – e.g., in photovoltaics, field effective transistors, sensor materials, etc. – provides continuing incentive to broaden the scope of properties for SBCs containing conjugated blocks.

Water solubilization of light emitting conjugated molecules is of considerable interest for biologically oriented work, and for methodologies where it is desirable to limit organic solvent use. Functionalizing conjugated organic polymers with ionic side chains has been a common strategy to make them water soluble [4]. An alternative strategy that avoids ionic substituents is to incorporate polyethylene glycol (PEG) units that are long enough to take advantage of hydrogen bonding in an extended conformation [5]. In this article, we report the synthesis and basic photophysical characterization of SBC **4** using architecture **2** with functionalized, monodisperse blue light emitting 1,4-bis-styrylbenzene chromophores, linked by polyethylene glycol (PEG) flexible units long enough to allow aqueous as well as organic solvent solubility.

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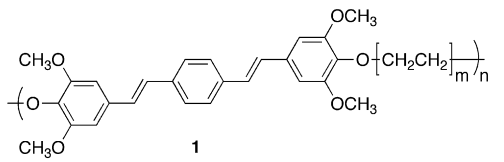

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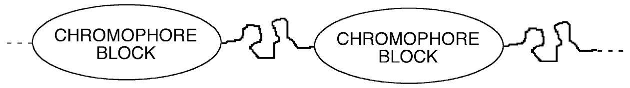
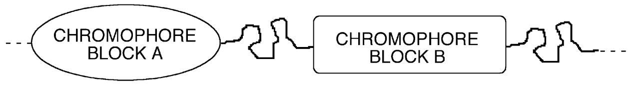
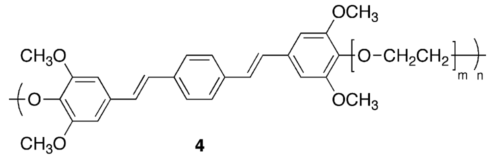


2 (monodisperse chromophores, alternating blocks)



3 (randomly modified chromophores, alternating blocks)



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2. Experimental section

2.1. Materials and methods

Commercially available reagent chemicals were used as received. PEG1000 was obtained from Acros, and used as received. Anhydrous grade *N*,*N*-dimethylformamide was obtained from EM Science in septa-sealed containers, and used as received. Tetrahydrofuran was distilled from calcium hydride, and then from sodium/benzophenone under nitrogen.

2.2. Instrumentation

Melting points were measured using a Melt-Temp™ melting point apparatus and are uncorrected. ^{1}H NMR spectra were obtained using a Bruker AVANCE-400 spectrometer. Peak positions are reported in ppm downfield relative to tetramethylsilane as a standard. FTIR spectra were obtained on a Midac M1200 spectrometer. UV–vis absorption spectra were recorded on a Shimadzu UV-2401PC system. Solution photoluminescence spectra were measured on JASCO FP-6500 spectrofluorimeter. Molecular weights of the polymer were measured using gel permeation chromatography (GPC) with a Knauer K-501 pump and a K-2301 refractive index detector. THF was used as the eluent, and linear polystyrene samples were used as molecular weight standards.

2.3. Synthesis

2.3.1. α,ω-Bis(2,6-dimethoxy-4-formylphenoxy)polyethylene glycol (5)

Into a dry flask under a nitrogen atmosphere, polyethylene glycol PEG_{1000} (average molecular weight 1000, 1.00 g, 10.0 mmol) was added, followed by 1 mL of anhydrous dimethylformamide and excess thionyl chloride (5 mL). The reaction mixture was stirred at 55 °C overnight, most of the thionyl chloride was removed under vacuum, and the reaction was quenched by carefully adding 0.1 M aqueous potassium carbonate solution. The reaction mixture was then extracted with dichloromethane. The organic layer was separated, dried over anhydrous magnesium sulfate, and evaporated to give crude α,ω-dichloro-PEG_{1000}, suitable for use in the next step.

The α,ω-dichloro-PEG_{1000} residue was put into a dry flask under a nitrogen atmosphere with 3,5-dimethoxy-4-hydroxybenzaldehyde (2.00 mmol, 0.36 g). Anhydrous dimethylformamide (6 mL) was added and the reaction mixture heated to 90 °C. Anhydrous potassium carbonate (2.25 mmol, 0.31 g) was then added in portions over a 1 h period. The reaction was stirred at 90 °C overnight, cooled to room temperature, poured into 40 mL of ice water, and extracted with dichloromethane. The organic layer was dried and evaporated to give the product as a waxy solid (0.97 g, 73%). ^{1}H NMR ($CDCl_3$): δ 3.64 (large s, internal poly-[CH_2CH_2O]), 3.70 (m, 4 H, $-OCH_2CH_2-$), 3.81 (t, 4 H, $J = 5.0$ Hz, aryl$-OCH_2\mathit{CH}_2-$), 3.91 (s, 12 H, OCH_3), 4.24 (t, 4 H, $J = 5.0$ Hz, aryl$-OC\mathit{H}_2CH_2-$), 7.12 (s, 4 H, aryl CH), 9.86 (s, 2 H, aldehyde CH).

2.3.2. α,ω-Bis(2,6-dimethoxy-4-ethylenylphenoxy)-polyethylene glycol (6)

Into a dry flask under a nitrogen atmosphere, methyltriphenylphosphonium bromide (2.00 mmol, 0.71 g) was added, followed by 25 mL dry tetrahydrofuran. The mixture was cooled to 0 °C and *n*-butyl lithium in hexanes (2.25 mmol, 1.20 mL) was added dropwise. After the reaction was allowed to warm to room temperature, a solution of **5** (0.73 mmol, 0.97 g) in dry tetrahydrofuran was added dropwise. The reaction was stirred at room temperature overnight. After quenching by water and dichloromethane extraction, the product was chromatographed (silica, 90:10 chloroform/methanol). The main product fraction was collected and evaporated to yield the product **6** as a viscous pale yellow liquid (0.77 g, 79%). ^{1}H NMR ($CDCl_3$): δ 3.64 (large s, internal poly-[CH_2CH_2O]), 3.7–3.8 (overlapping m, $-OC\mathit{H}_2CH_2-$), 3.86 (s, 12H, OCH_3), 4.13 (t, 4 H, $J = 5.2$ Hz, aryl$-OC\mathit{H}_2CH_2-$), 5.21 (d, 2H, $J = 10.8$ Hz, vinyl CH), 5.63 (d, 2H, $J = 17.4$ Hz, vinyl CH), 6.59–6.66 (overlapping s + m, 6H, aryl CH + vinyl CH).

2.3.3. Poly[ethylene glycol-(2,6-dimethoxy-1,4-phenylene)-1,2-(*E*)-ethenediyl-1,4-phenylene-1,2-(*E*)-ethenediyl-(3,5-dimethoxy-1,4-phenylene)] (4)

Into a dry flask under a nitrogen atmosphere, 1,4-diiodobenzene (0.50 mmol, 0.165 g), **6** (0.50 mmol, 0.662 g), palladium diacetate (0.08 mmol, 0.018 g), and tri(*o*-tolyl)phosphine (0.24 mmol, 0.073 g) were added. Anhydrous dimethylformamide (10 mL) was added and the reaction was heated to 95 °C. Triethylamine (2.60 mmol, 0.36 mL) was added and the reaction was then stirred at 95 °C overnight. After completion, the reaction was cooled to room temperature. Water was added, and the mixture was extracted with dichloromethane. The organic layer was separated, dried, and evaporated to give the crude product, which was purified by column chromatography (silica, 90:10 chloroform/methanol). The main product fraction was collected and evaporated to give crude **4** as a red viscous oil. This material was dissolved in dry tetrahydrofuran and treated with lithium aluminum hydride for 30 min. The reaction was then cautiously quenched by sequential, dropwise addition of propanol, ethanol, methanol, and water. The mixture was extracted with dichloromethane, separated, and the organic solvent layer evaporated to yield the final product polymer **4** as a waxy solid (0.27 g, 39%). ^{1}H NMR (DMSO-d_6): δ 3.56 (broadened s, internal poly-[CH_2CH_2O]), 3.67–3.8 (overlapping m, aryl–OCH_2CH_2–), 3.90 (s, 12H, OCH_3), 4.16 (t, 4H, $J = 4.6$ Hz, aryl–OCH_2CH_2–), 6.74 (s, 4 H, aryl CH), 7.02 (d, 2 H, $J = 16$ Hz, ethenyl CH), 7.04 (d, 2 H, $J = 16$ Hz, ethenyl CH), 7.50 (s, 4H, central aryl CH). FTIR (neat film, cm^{-1}): 2969–2872 (str, CH str), 1119 (str, C–O str), 950 (m, *trans* HC=CH out-of-plane bend). UV–vis (chloroform, λ_{max} [ε, M^{-1} cm^{-1}]): 367 nm [19,500]. Photoluminescence (chloroform, $\lambda_{exc} = 365$ nm): $\lambda = 418$ nm (shoulder), 437 nm (max).

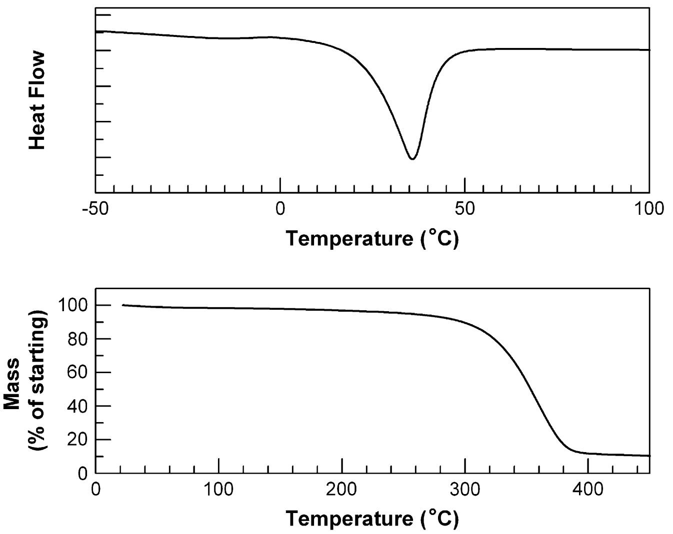
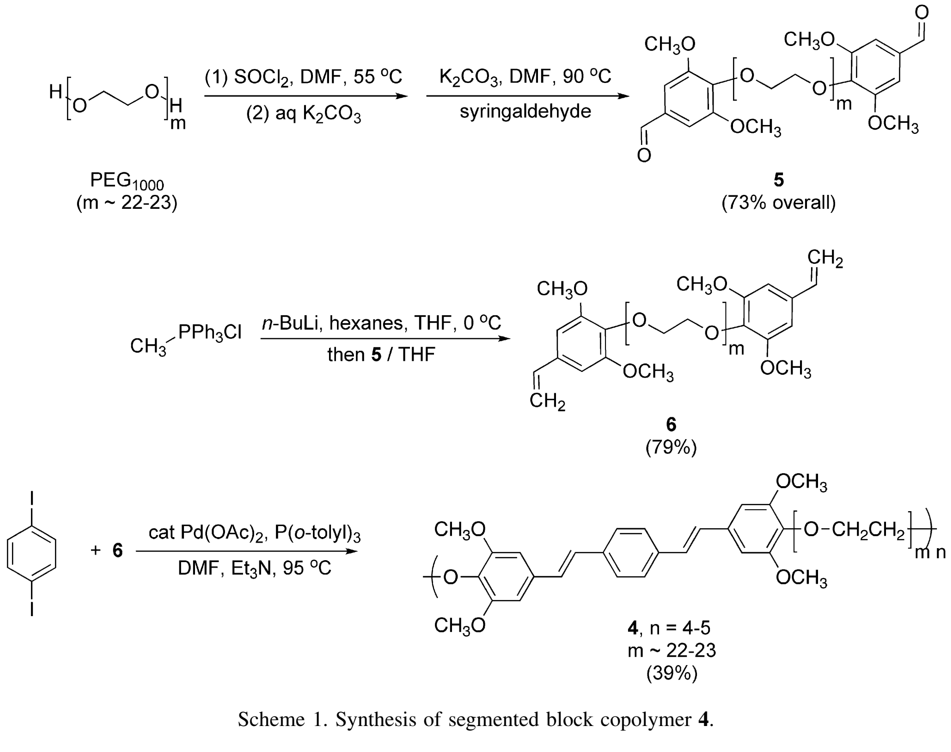


Fig. 1. DSC (above, endothermic down) and TGA (below) traces for copolymer **4**.

3. Results and discussion

Copolymer **4** was synthesized by modification of the procedure of Pasco et al. [6] for making PV-based SBCs (Scheme 1). Commercially available PEG with average MW = 1000 daltons (degree of polymerization 22–23) was converted to the α,ω-dichloride with thionyl chloride, and immediately coupled to two equivalents of syringaldehyde by Williamson etherification to make dialdehyde **5**. The dialdehyde was vinylated by the Wittig method to make **6**, then polymerized with 1,4-diiodobenzene using Heck methodology to give the desired polymer **4**. The crude polymer was treated with lithium aluminum hydride to reduce any aryl halide moieties. The final product appeared to have high purity by ^{1}H NMR spectrum; notably, no vinyl end group peaks were observed.

The purified copolymer was a waxy solid with a low melting point (35 °C) by differential scanning calorimetry, but with high thermal stability. It slowly loses about 11% of mass from room temperature to 300 °C, then decomposes to leave about 11% char above 380 °C (Fig. 1). Gel permeation chromatography (GPC) calibrated against polystyrene standards for multiple runs gave $M_w = 5000–8000$ and $M_n = 4600–7600$, indicating degrees of polymerization of roughly 3–6. The GPC trace typically had overlapping, bimodal peaks; an additional small amount of lower molecular weight fraction of about 2000 daltons was also frequently present,



Scheme 1. Synthesis of segmented block copolymer **4**.

corresponding roughly to two chromophores joined by one PEG_{1000} unit.

The low melting point of **4** is due to the long PEG flexible block used. However, the rigid chromophore segments do have an effect on the overall melting point, because PEG_{1000} itself is a liquid at room temperature. By comparison, the melting transitions of the original copolymer **1** with an octamethylene flexible block linker is 81 °C and the analogue where octamethylene is replaced by a *meta*-xylylene unit is 114 °C [7]. Most important for this study, not only is copolymer **4** soluble in typical organic solvents, but it is also soluble in water, as originally desired.

The UV–vis absorption spectra of **4** are very similar in chloroform and water, both with maxima at about 367 nm (Fig. 2). The solution photoluminescence (PL) excitation spectra match the absorption spectra very well, showing high chromophoric purity. However, the PL emission spectra show significant variability (Fig. 3). In chloroform, the PL maximum occurs at about 437 nm, and shows little change with concentration over 4–400 μmolar; a shoulder at about 418 nm suggests ill-resolved vibronic coupling, possibly with the out-of-plane bending mode of the *trans*-ethenyl groups. In water, the PL maximum is about 445 nm at 3 μmolar, but increases up to about 465 nm at 400 μmolar; the PL red shift in the high concentration range is about 0.18 eV relative to that in chloroform. The PL quantum yields in chloroform and water were measured to be 0.7 and 0.3, respectively, relative to quinine sulfate standard [8]. The quantum yields were obtained at concentrations of 3 μmolar in **4** to give low optical densities. Concentrations up to at least 20-fold high give essentially linear PL intensity increases, but a 100-fold increase in concentration gives significant self-quenching in both chloroform and water.

The similarity of the UV–vis spectra in the organic and aqueous solutions indicates that there is no significant aggregation in the concentration range (about 10 μmolar) having an optical density up to two. However, the concentration dependence of the PL emission maximum in water is consistent with some degree of interchain interaction, even before self-quenching becomes significant. The lack of significant PL emission lineshape variation in chloroform suggests better high concentration solubility. The lower quantum yield of **4** in water at low concentrations is probably not due to intrachain self-quenching from chain folding, since its water solubility depends upon extension of the PEG segments. Increased transient charge transfer quenching in the more polar water is a more likely mechanism.

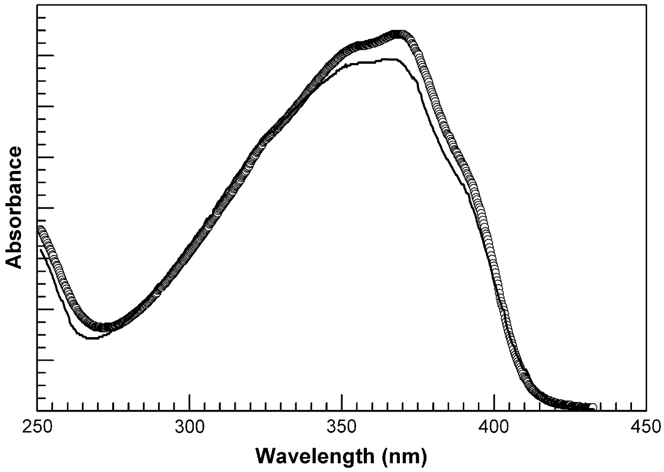


Fig. 2. UV–vis spectra for copolymer **4** in chloroform (○) and aqueous (—) solutions.

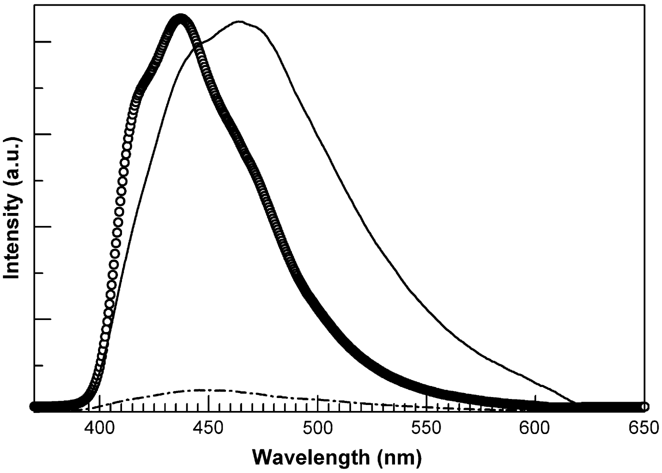


Fig. 3. Photoluminescence spectra for copolymer **4** in 77 μmolar chloroform (circles), 3.1 μmolar aqueous (broken line), and 80 μmolar aqueous (solid line) solutions; 365 nm excitation. The chloroform and aqueous spectra are scaled relative to one another for ease of viewing, but the two aqueous spectra are shown with the same relative ordinate scale.

A 15 μmolar solution of **4** in water was mixed with 0.2–0.8 M aqueous KBr, to investigate whether the PEG flexible chains might coordinate with the potassium ions, leading to folding of the individual copolymer chains. However, no significant change in the PL spectral maximum, lineshape, or emission intensity was observed in any of these experiments. This indicates that **4** does not readily aggregate by salting out in aqueous solution in this concentration range.

Copolymer **4** was tested as the emissive layer in test OLEDs fabricated with configuration ITO/PEDOT-PSS/**4**/Ca–Al. Unfortunately, none of the devices gave sufficiently long-lived electroluminescence for analysis. The heating that is typical when running an OLED can cause easy annealing of **4** due to its low melting point, with resulting device instability. Instead, solid film luminescence was tested using neat **4**, and blends of **4** in PMMA. Fig. 4 shows the solid PL results. For the neat film, the emission maximum is at 460 nm, similar to the maximum in aqueous solution. The neat film spectrum shows some poorly resolved fine structure that is observed in chloroform, but not water. As the amount of PMMA in the blend increases, the PL maximum blue shifts and loses the neat spectrum fine structure. At 10% w:w **4**/PMMA, the emission maximum is 440 nm, very similar to that for low concentrations of **4** in either chloroform or water. The results further support a lack of intrachain π-interactions between chromophores. However, the blends showed no improvement in OLED stability relative to the neat material.

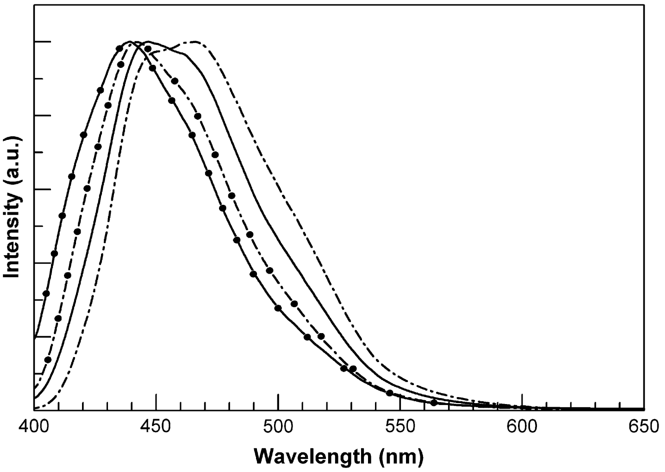
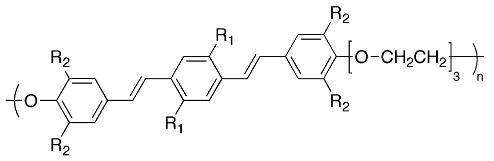


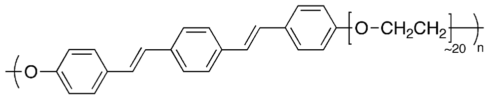
Fig. 4. Neat film photoluminescence spectra for copolymer **4** blended at various concentrations of PMMA: **4**/PMMA w:w100:0 (broken line), 50:50 (solid line), 30:70 (broken line with filled circles), 10:90 (broken line with filled circles). Intensities are scaled to the same ordinate maximum (in arbitrary units).

Other studies have been made using various blocky PPV units linked by flexible PEG units. Bianchi et al. gave a brief report about synthesis of somewhat ill defined SBCs (MW 5000) that incorporate variable *para*-phenylenevinylene (PPV) chain lengths (general architecture **3**); the evidence for variability in the PPV units comes from UV–vis absorbances suggesting up to 0.1% formation of hexameric phenylenevinylene (PV) units or higher [9]. Bianchi et al. subsequently demonstrated greater control in forming PPV blocks within the same architecture, by using different synthetic methods for the PPV polymerization step [10]. These systems achieve the goal of solubility in hydroxylic solvents, but have varying chromophore length (architecture **3** above) rather than monodisperse chromophores, and so are fundamentally different from **4**. They are not discussed further herein.

PEG side chain functionalized PPVs have also been proposed and synthesized, in order to improve ion transport qualities by comparison to PPV blends with PEGs, which often exhibit undesirable phase separation [11]. These are grafted copolymer architectures, and therefore also differ from block copolymer architectures **2** and **3**. The following brief discussion is limited to oligo-PV block copolymers with PEG segments.



7a $R_1 = H$ $R_2 = OCH_3$
7b $R_1 = R_2 = OCH_3$
7c $R_1 = OCH_3$ $R2 = H$



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Some model systems having oligo-PV blocks solublized with PEG moieties [12] have been studied. In higher polymer studies, Sun et al. have reported [13] that block copolymers composed of well-controlled bis-1,4-styrylbenzene segments having different substitutents, alternating with PEG trimers give **7**. This is a SBC of architecture **2**, as is **4**. These are not water soluble, because the PEG units are too short. They have similar absorption and emission spectra to **4**, because they have similar chromophores. Interestingly, Sun et al. reported the PL quantum yield to be 39% for **7a** having the very same chromophore unit as **4**, linked by PEG trimer flexible linkers, rather than by the 22- to 23-mer PEG linkers used in **4** itself. The 70% quantum yield for **4** shows how the longer PEG units allow the bis-1,4-styrylbenzene units to have a sufficiently large, average inter-chromophore distance to limit intrachain self-quenching. Yang et al. have reported studies of structures similar to **7** using PEG trimer linkers, but with less chromophore substitution [14].

Wang and Li have reported the linkage of substituted and unsubstituted bis-1,4-styrylbenzene units by double-chain PEG flexible units; the latter are basically cyclic crown ethers [15]. The electroluminescence behavior of these systems was reported. These systems, however, do not appear to be water soluble, judging by their purification procedure.

Benfaremo et al. have reported the synthesis and characterization of bis-1,4-styrylbenzene units without extra substitution, linked by PEG (MW 900) units to give **8** [16]. Its degree of polymerization ranged from ~2–9. This SBC is soluble in organic solvents, but interestingly is not soluble in water or alcohol, unlike **4**. This is probably due to a greater hydrophobicity of the unsubstituted bis-1,4-styrylbenzene units in **8**. By comparison, **4** has four methoxy substituents on the oligo-PV chromophore that may provide enough additional hydrogen bonding in water (beyond that provided by the PEG_{1000} units) to assist aqueous solubility. SBC **8**, like **4** gave OLED degradation problems when used as the emissive material. Recent work suggests that shortening the PEG segment to PEG200 or PEG600 helps with light emitting cell stability, if that is the primary goal as opposed to water solubilization [17].

4. Conclusions

A segmented block copolymer incorporating monodisperse, partly methoxy-substituted bis-1,4-styrylbenzene chromophores plus water solubilizing PEG_{1000} (D.P. = 22–23) segments (degree of polymerization 3–6) is soluble in both organic and aqueous solvents. The achievement of water solubility seems finely balanced. Based on the comparisons of similar systems made by others, water solubility in this structural architecture seems to need sufficiently long PEG blocks as well as substituents on the rigid chromophore that can provide some additional hydrogen bonding. The copolymer is low melting because of its PEG flexible blocks, but it has good thermal stability. The resulting system exhibits blue luminescence in solution and in solid films, with emission maxima in the range of 440–470 nm (2.64–2.82 eV), depending upon solvent or solid film composition. The synthetic strategy for this system should be readily extrapolated to make analogous luminescent systems having substantial water solubility.

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