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Synthesis and Characterization of Luminescent Polymers of Distyrylbenzenes with Oligo(ethylene glycol) Spacers

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ABSTRACT: A luminescent polymer **3**, consisting of a distyrylbenzene (PPV model oligomer) moiety and an oligo(ethylene glycol) (PEO oligomer) moiety has been synthesized by two independent methods: a polymer-analogous Mitsunobu reaction and conventional double displacement reaction. This new polymer is soluble in a variety of organic solvents, forms excellent, optically clear films, and exhibits strong fluorescence. A solution of the polymer exhibits amplified stimulated emission with an emission bandwidth of 3 nm (fwhm) when pumped with a nitrogen laser. Initial experiments to use this new polymer in light-emitting devices are described.

Introduction

In recent years, poly(*p*-phenylenevinylene) (PPV)-based polymers have been extensively investigated because they exhibit efficient photoluminescence and potentially useful electroluminescent properties.[1,2] In an effort to improve stability and processability and to affect the emission wavelength, numerous PPV derivatives and analogues have been synthesized.[3−9] In an electroluminescent device, light is generated by the combination of holes and electrons.[10,11] The holes and electrons in the valence and conduction band are injected by electrodes. In a light-emitting electrochemical cell (LEC),[12] emission occurs because of a hole−electron combination, from electrochemically generated p-type and n-type carriers. In this case good counterion mobility is required. This concept has been used to fabricate numerous devices using poly(ethylene glycol) as the ion transporting medium mixed with a photoluminescent material.[12] A potential problem with this approach has been phase separation of a hydrophobic chromophore and the poly(ethylene glycol). One approach to avoid the phase separation problem is to incorporate the ethylene glycol segments into the polymer with the luminescent chromophore. Only one other electroluminescent polymer, in which glycol units are attached as side chains on a PPV backbone, has so far been reported.[13]

In this paper we report the first synthesis of a polymer containing a photoluminescent distyrylbenzene chromophore separated by poly(ethylene glycol) spacers. This polymer exhibits efficient solution fluorescence and was characterized by ^{1}H and ^{13}C NMR, IR, elemental analysis, X-ray powder diffraction, TGA, and DSC.

Experimental Section

Measurements. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DRX500 spectrometer (500 MHz ^{1}H; 125 MHz ^{13}C). Fourier transform infrared (FT-IR) spectra were obtained on a Perkin-Elmer 1760x spectrometer. UV−visible spectra were recorded on a Perkin-Elmer Lambda 9 spectrometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out on Thermal Analysis TGA2950 and 2910 instruments, respectively, at a rate of 10 °C/min. Fluorescence was measured on a SLM 8100 emission spectrometer. X-ray powder diffraction was carried out on a Rigaku Rotaflex RU-300 X-ray diffractometer equipped with a Dmax-B controller and employing a Cu Kα source. Melting points were determined on an Electrothermal Digital Melting Point Apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories (Woodside, NY).

Materials. All solvents and materials were used as received unless otherwise noted. α,α′-*p*-Xylylene dichloride and poly(ethylene glycol) were purchased from Aldrich. Poly(ethylene glycols) were dried at 45 °C under vacuum over P_2O_5 for a minimum of 3 days. Tetrahydrofuran (THF) was distilled from sodium under an inert atmosphere. All reactions were performed under a dry argon atmosphere.

Preparation of Tetraethyl-*p*-xylylenediphosphonate (1). To a 100 mL round-bottom flask fitted with a reflux condenser and gas bubbler and containing triethyl phosphite (38 g, 228 mmol) was added the α,α′-*p*-xylylene dichloride (20 g, 114 mmol). The reaction mixture was flushed with Ar and then heated at 150 °C for 7 h. After cooling, the solid white mass was

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broken up and the product recrystallized from petroleum ether (2.5 L). The cooled product was filtered off and stored in a desiccator under vacuum. Yield: 27 g, 62%. Mp: 75.4−76.3 °C (lit. 74−75 °C[14]).

Synthesis of 4,4′-(*p*-phenylenedi-1,2-ethenediyl)-diphenol (2). In a 500 mL round-bottom flask heat dried under vacuum, equipped with a bubbler and flushed with argon, was added sodium hydride (60% in oil, 5.1 g, 0.13 mol). It was washed three times with hexane via syringe and the remaining hexane was removed under vacuum. Anhydrous DMF (50 mL) was added. To the sodium hydride suspension was added a solution of the bis(phosphonate) (8.0 g, 21.2 mmol) in 50 mL of anhydrous DMF over 20 min. The solution turned pale yellow (presumably due to the monoanion) and then red (the dianion). Stirring was continued for 2 h. A solution of *p*-hydroxybenzaldehyde (5.68 g, 46.5 mmol) in anhydrous DMF (50 mL) was then added over 40 min. The reaction mixture was allowed to stir overnight. Water was added dropwise to the thick reaction mixture to neutralize any remaining sodium hydride. The reaction mixture was acidified with 1 N HCl to pH 6, cooled to −10 °C, filtered, washed with water, and dried in a vacuum desiccator. Recrystallization from DMF gave the chromophore as fluorescent yellow plates. Yield: 3.7 g, 56%. Mp: >300 °C (lit. 360 °C[14,15]).

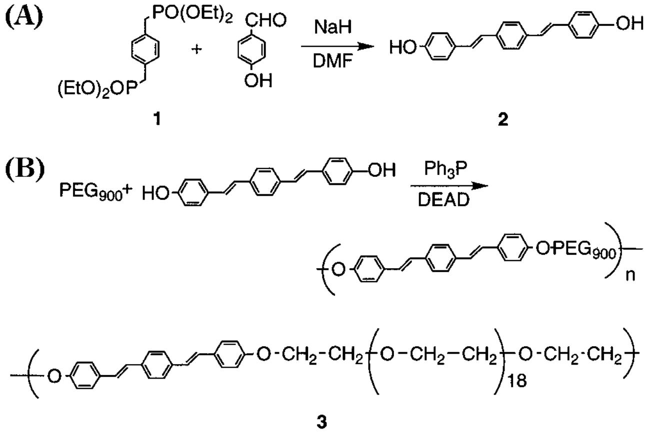
Polymerization

Via Mitsunobu Reaction. In a 500 mL round-bottom flask heat dried under vacuum, equipped with a bubbler and flushed with argon, was placed poly(ethylene glycol) (M_n 900) (7.5 g, 8.3 mmol), triphenylphosphine (6.5 g, 25 mmol), and the chromophore (**2**) (2.62 g, 8.3 mmol). The reaction flask was flushed with argon, and freshly distilled THF was added (100 mL). Diethyl azodicarboxylate (DEAD) (1.5 mL, 9.5 mmol) was added dropwise over 20 min, and the reaction mixture was then warmed to 45 °C. After 1 h, most of the chromophore had dissolved and an additional 1.5 mL of DEAD was added over 1 h. The reaction mixture was heated over 3 days in which an additional 1.5 mL of DEAD was added. THF (200 mL) was then added and the warm reaction mixture precipitated into 5 volumes of ethanol. Isolation of the polymer was then easily achieved by centrifugation (4 °C, 7000 rpm, 10 min), decanting off the supernatant, washing the precipitated polymer with ether, and filtration through a sintered glass funnel. The product was dried in a vacuum desiccator over P_2O_5. Yield: 9.0 g, 90%.

^{1}H NMR (DMSO-d_6) δ 7.55 (s, 4H, Ar central ring), 7.43 (d, 4H, Ar), 7.23−7.05 (dd, 4H, olefinic), 4.06 (s, 2H, **CH**$_2$OAr), 3.76 (s, 2H, **CH**$_2$CH$_2$OAr), 3.52 (s, 18H, OCH$_2$CH$_2$O). ^{13}C NMR (DMSO-d_6) δ 159.1, 137.2, 130.8, 128.6, 127.4, 126.8, 115.7, 70.7, 69.9, 68.2. FT-IR (film) 3500, 3333, 2910, 1740, 1700, 1605, 1540, 1105 cm^{-1}. UV−vis (film): λ_{max} 318 nm.[5] Fluorescence (film thickness: 1130 Å) λ_{max} = 456, 484 nm. Anal. Calcd for $C_{62}H_{96}O_{21}$: C, 63.25; H, 8.22. Found: C, 62.22; H, 8.25; N, 0.77.

Via Oligoethylene Glycol Bis(mesylate). To a 50 mL heat dried, three neck, round-bottom flask under argon was added the PEG bis(mesylate)[19] (0.95 g, 0.90 mmol). The distyrylbenzene chromophore **2** (0.26 g, 0.82 mmol) was added followed by freshly ground, anhydrous potassium carbonate (0.34 g, 2.45 mmol). The reaction vessel was alternately evacuated and flushed three times with dry argon. Dry DMF (9 mL) was added, and the reaction mixture was heated to 95 °C for 64 h. The reaction mixture was cooled to room temperature and degassed, deionized water (75 mL) was added, and the resulting solution saturated with sodium chloride and extracted with methylene chloride (3 × 10 mL), while exposure to the atmosphere was kept to a minimum. The organic extracts were washed with water (2 × 50 mL), and then dried over anhydrous sodium sulfate, and filtered, and the solvent was evaporated under vacuum. Yield: 1.1 g (95%), ^{1}H NMR (DMSO-d_6): δ 7.54 (s, 4H, Ar central ring), 7.43 (d, 4H, Ar), 7.20−6.94 (dd, 4H, olefinic), 4.01 (s, 2H, **CH**$_2$-OAr), 3.64 (s, 2H, **CH**$_2$CH$_2$OAr), 3.55 (s, 18H, OCH$_2$CH$_2$O). ^{13}C NMR (DMSO-d_6) δ 158.1, 136.4, 129.8, 127.5, 126.3, 125.2, 114.7, 72.3, 70.1, 68.9, 67.2, 60.1, 39.7. FT-IR (film) 3490, 3287, 2900, 1610, 1514, 1447, 1305 cm^{-1}. Anal. Calcd for $C_{62}H_{96}O_{21}$: C, 63.25; H, 8.22. Found: C, 61.66; H, 8.53; N, <0.10.

Scheme 1. Synthesis of the Distyrylbenzene Chromophore (A) and the Mitsunobu Polymerization (B)



Results and Discussion

Chromophore. Numerous phenylenevinylene model oligomers and derivatives have been synthesized in order to optimize their materials' properties.[3,5] Interruption of the π-conjugation and/or suitable structural modifications have been used to improve the solubility and stability of these materials as well as to tune their emission frequency.[6,16] We chose the distyrylbenzene chromophore (**2**) (Scheme 1) as the simplest phenylenevinylene oligomer that would be expected to exhibit the desired properties and also provide synthetic versatility. Polycondensation of the distyrylbenzene segment (**2**) with poly(ethylene glycol) was carried out via a Mitsunobu reaction and was the first example of what seems to be a new and useful method of polymerization.[17,18]

The chromophore itself was a yellow, crystalline material, very sparingly soluble in most organic solvents at room temperature. It exhibited a fluorescence in the solid state, and even very dilute solutions exhibited an extremely strong blue fluorescence. The material has been reported to melt at 360 °C with decomposition; however, we have noticed only a slow, continuous darkening of the material at temperatures greater than 280 °C. Over time in light, particularly UV in air, the material turned green. TGA measurements under nitrogen and in air showed an initial decomposition at approximately 305 °C. Further, in the presence of air, an apparently rapid reaction took place that seemed to produce a new, more stable material. Similar investigations of bis(4,4′-dimethoxydistyrylbenzene)[15] did not show this effect. This uncommon behavior is currently under investigation.

Spacer. Poly(ethylene glycol) (PEG) was chosen as the intended spacer, as it was expected that it would facilitate ion transport in an LEC device and would also have an important solubilizing affect. In addition, its availability in a variety of molecular weights and

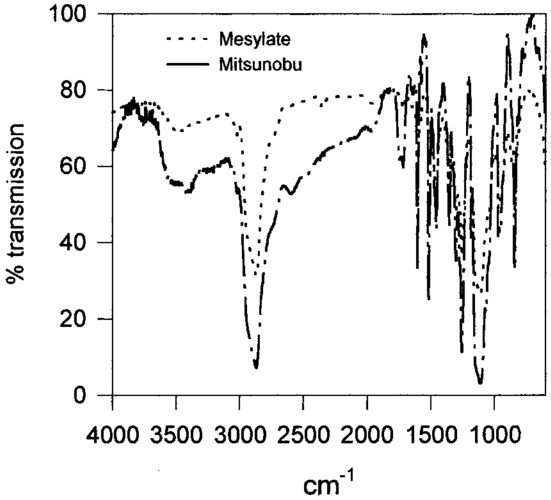
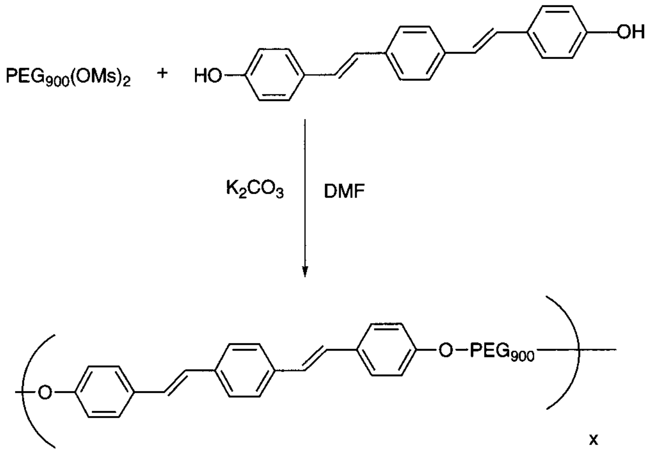


Figure 1. IR spectra of the polymers **3** prepared (a) by the Mitsunobu reaction and (b) from the mesylate.

Scheme 2. Alternate Polycondensation



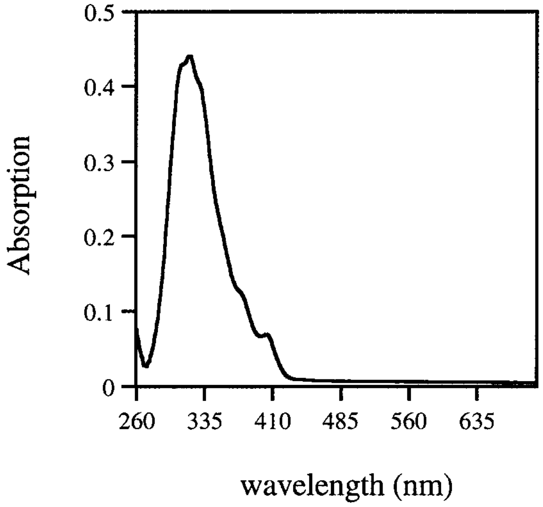


Figure 2. Absorption spectrum of a spin-coated film of polymer **3**.

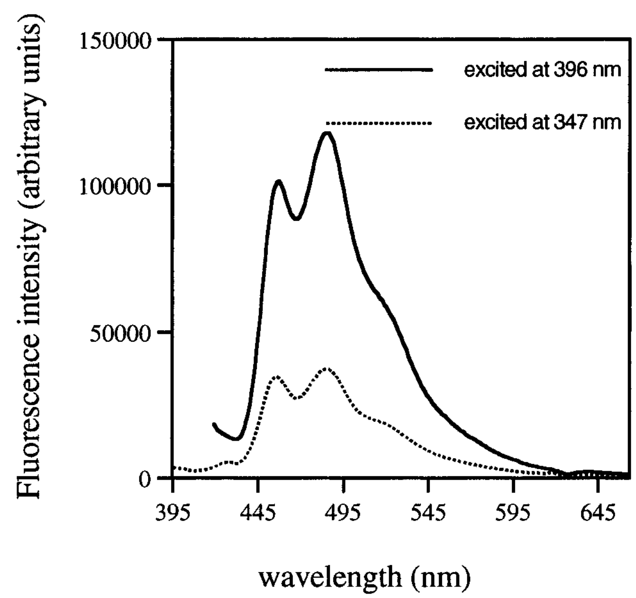


Figure 3. Emission spectra of a spin-coated film of polymer **3**.

molecular weight distributions, as well as its low cost, contributed to its attractiveness. The commercially available PEG material that was used in this study (M_n 900, PDi 1.1) corresponds to approximately 20 ethylene glycol units.

Polymer. We chose to perform the polymerization of our preformed PPV segment with commercially available PEG (M_n 900). Our first materials were obtained using the Mitsunobu reaction. Upon addition of diethyl azodicarboxylate (DEAD) to a suspension of the chromophore in a solution of poly(ethylene glycol) and triphenylphosphine in THF at 45 °C, the chromophore slowly dissolved. Extended heating over 2 days gave a viscous solution. Precipitation into ethanol and drying under vacuum over P_2O_5 gave the desired polymer as a yellow rubbery powder in 90% yield. To our knowledge, this is the first example of the use of the Mitsunobu reaction to carry out a condensation polymerization. We used this reaction to also prepare a number of end-functionalized poly(ethylene glycols) and poly(ethylene glycol) copolymers on which we will report in subsequent publications. It should be noted, however, that significant IR absorption (Figure 1) at 1740 and 1700 cm^{-1} was observed and suggested an undesired carbonyl-containing component. Preparation of a sample by an alternate route (Scheme 2) from poly(ethylene glycol) bis(mesylate)[19] gave a product with no detectable absorptions in the carbonyl region. Elemental analyses of the two polymers showed a significant nitrogen content (0.77%) in the Mitsunobu reaction prepared sample. Comparison of the IR spectrum of **3** to that of diethyhydrazine dicarboxylate in the 1700–1800 cm^{-1} region indicated the incorporation of hydrazino carboxylate residues in the Mitsunobu prepared polymer.

The polymer was not soluble in water, alcohol and ether, but easily soluble in THF, DMF, chloroform, and acetonitrile. ^{1}H NMR and ^{13}C NMR in DMSO-d_6 (Figures 2 and 3) were in good agreement with those expected for the desired material. In addition, the lack of any detectable peak at 4.56 ppm indicated <1.0% of ethylene glycol end groups.[20] The ratio of peaks from the chromophore to those from the ethylene glycol segment was also in good agreement with a 1:1 copolymer. The known sparing solubility of the chromophore suggested that we have a reasonably high molecular weight product. Molecular weight determination was extremely solvent dependent. Size exclusion chromatography (SEC) analysis of the polymer in chloroform, however, gave good agreement with commercially available PEG samples of known molecular weight and indicated a clean monomodal distribution with M_n 7400,

M_w 18 700, PDI 2.5. The peak molecular weight was 10 800 and corresponded to a DP of 9.

The polymer exhibited a fluorescence in the solid state and very dilute solutions also exhibited an extremely strong blue fluorescence. In DMF solution, when excited in the wavelength range 320−400 nm, the polymer exhibited strong fluorescence in the range 410−470 nm. When pumped with a 347 nm, 3 ns nitrogen laser pulse, a solution of the polymer exhibited laser action due to the amplified spontaneous emission. The intensity of this laser action was comparable to that found when only the chromophore at comparable number densities was used. This clearly indicated that the chromophore did not have any significant loss in quantum efficiency when incorporated into a polymer with poly(ethylene oxide) segments. The absorption spectrum of a spin-coated film on a quartz substrate is shown in Figure 2 and its fluorescence emission spectra are presented in Figure 3; the spectrum from 396 nm excitation is more intense than that from 347 nm excitation. The structure observed in both the absorption and fluorescence emission spectra is attributed to vibronic effects and has a frequency separation of approximately 1300 cm^{-1}. Experiments to establish evidence of stimulated emission when pumped in the UV are in progress.

Thermal Properties. The thermogravimetric analysis (TGA) of polymer **3** was conducted in air and under N_2. Although there seemed to be a gradual weight loss above 50 °C, 98.18% of the material was still present at 258 °C and nearly 95% at 336 °C (under N_2). In air, significant weight loss occured at a much lower temperature, 314 °C, and a slight shoulder was observed in the thermogram at approximately 375 °C. The slow weight loss starting at 50 °C might be due to low molecular weight materials or to strongly bound solvent. The change in decomposition rate of the polymer in air at 375 °C was noteworthy. This was similar to that noted in the TGA of the chromophore in air as described above. These observations were indicative of oxidation or oxygen-catalyzed rearrangement to somewhat more stable species and this effect is currently under investigation.

Ober and co-workers[14] prepared a number of alkyl derivatives of the same chromophore and showed that several of them demonstrated liquid crystalline behavior. X-ray powder diffraction analysis revealed only two peaks ($d = 4.27$ and $d = 3.91$) on a hump, indicating a semicrystalline material. The initial DSC trace showed a transition at approximately 55 °C, which was unobserved in subsequent traces. This transition might also be caused by PEG segment melting. No liquid crystalline properties have, as yet, been observed in this system.

Device Experiments. Preliminary attempts to fabricate devices consisting of spin-coated films of **3** sandwiched between an indium tin oxide (ITO) anode and an aluminum cathode, to date, have been unsuccessful. As anticipated, the devices turned-on at low voltages (around 2 V) and emitted blue light but degraded quickly, making it difficult to determine device characteristics. We have found, however, that this new polymer could be used to dramatically improve the device performance of the sulfonated tris(phenanthroline)ruthenium(II) complex that we have recently examined as an electrochemically active light emitter.[21] For example, a layer spun onto a 300 Å thick layer of polymer **3** was found to produce a luminance level of approximately 40 cd/m^2 at 6 V. The light emission (red-orange) was from the Ru(II) complex, and the external device efficiency of this material was improved by a factor of 10 (to a value of 0.1%) via the use of polymer **3**. Thus, the use of this new segmented copolymer as a hole transporting material in a light-emitting electrochemical cell appears promising.

Conclusions

We have prepared the first polymer with a PPV model chromophore containing a known ion transport moiety (PEG). The polymer was synthesized via a Mitsunobu reaction, and this approach should be applicable to a wide variety of substrates. The polymer had fluorescence properties related to the distyrylbenzene chromophore, and amplified spontaneous emission of 3 nm bandwidth was observed. In addition to the materials reported here, we have prepared other polymers with more soluble PPV segments, various PPV to PEG ratios, and even a diphenyloxadiazole−PEG copolymer, which might be useful as an electron injection or hole-blocking material.[22]

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