Macromolecules

Well-Defined Alternating Copolymers of Oligo(phenylenevinylene)s and Flexible Chains

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Supporting Information

ABSTRACT: A series of alternating copolymers containing oligomeric bis(2-ethylhexyl)-*p*-phenylenevinylene (BEH-PPV) chromophores and conformational-flexible *n*-decyl or tetra-ethylene glycol chains were prepared. The polymerization was carried out using Sonogashira coupling conditions between monomers composed of an iodo-terminated PPV oligomer (trimer, pentamer, or septamer) and a bis(phenylacetylene)-containing flexible chain. Polymers containing the *n*-decyl





chain attained higher molecular weights compared to the tetraethylene glycol-containing polymers. 4-Ethynylanisole-capped oligomers (trimer, pentamer, or septamer) were prepared, and their solution photophysical properties were compared to the analogous polymeric materials. The solution optical properties of the polymers were primarily determined by chromophore length of the constituent oligomers. In contrast, the thin film fluorescence spectra of the polymers showed substantial differences between *n*-decyl and tetraethylene glycol containing materials, suggesting significant changes in the degree of interchain coupling in the solid state. The control of effective conjugation length afforded by these materials makes them a promising system for understanding electronic trap states in conjugated polymers.

■ INTRODUCTION

The morphology of conjugated polymers plays a critical role in determining the electronic properties of the thin films utilized in devices such as organic photovoltaics, organic light-emitting diodes, and field effect transistors.^{1,2} The transition from a single polymer molecule into a useful polymer film depends on the macromolecule's structural characteristics including molecular weight, backbone composition, and solubilizing-chain structure. To develop rational control over morphology of bulk materials, it is imperative to understand the fundamental factors that determine structure in conjugated polymer materials. To accomplish this goal, we set out to create and study well-defined polymers whose structure and energetics can be systematically controlled at the synthetic level.

Recently, we synthesized a series of polymers that can access predetermined conformations in the single polymer chain.³ Our initial strategy utilized the random incorporation of morphology directing ("morphon") chemical groups into the backbone of the prototypical conjugated polymer poly(2-methoxy-5-(2'ethylhexyloxy)-*p*-phenylenevinylene) (MEH-PPV). By using single molecule spectroscopy (SMS),^{4,5} we found that morphons that re-enforce the linear nature of the PPV⁶ chain actually improve the alignment of chromophores in the polymer⁷ while, consistent with previous work,⁸ morphons that direct the polymer chain into a bent structure create globular architectures. Control over single chain structure was an important step toward ground-up control of film properties, as highly aligned single polymer nanodomains facilitate ultralong-range energy transfer.⁹⁻¹¹ In this work, we report the synthesis and photophysical properties of a new series of polymerized oligomers, providing even finer synthetic control of both structure and optical properties.

Although the polymers we described previously provided access to varying morphologies, the Horner-Wadsworth-Emmons polymerization that was utilized has several disadvantages. The polymerization leads to low molecular weights and a regiorandom copolymer with a broad distribution of effective chromophore lengths. Here we report an updated strategy that utilizes a Sonogashira polymerization to create high molecular weight polymers with known oligomeric bis(2ethylhexyl)-p-phenylenevinylene (BEH-PPV) chromophores between morphons (Figure 1). We have investigated two flexible morphons (alkyl and tetraethylene glycol) that provide conformational freedom and may allow single polymer chains to fold into ordered sheets. Solution absorption and emission measurements revealed that the photophysics of the polymers were primarily determined by the conjugation length of the constituent oligomers, allowing for rational control of their optical as well as their structural properties.

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Figure 1. Flexible-morphon BEH-PPVs prepared in this work.

RESULTS AND DISCUSSION

Synthesis. The synthesis of polymerizable BEH-PPV oligomers¹² (**10**, **13**, and **16**) was carried out through repetitive Horner–Wadsworth–Emmons reactions¹³ according to Scheme 1. The oligomer series consisted of a trimer (**10**), pentamer (**13**), and septamer (**16**) with terminal iodo functionality and were easily synthesized owing to their symmetry. The sequence began with the synthesis of previously known monomers 7, 8, and 9 (Supporting Information).^{14–16} **10** was prepared by the Horner coupling of 2 equiv of aldehyde 7 and the diphosphonate **8** with stoichiometric KOtBu. To create an oligomeric chromophore that better resembles the subsequent polymeric chromophores, the iodos were substituted with 4-ethynylanisole via a Sonogashira coupling to produce **11**. To access the higher oligomers, an elongation of the aldehyde chromophore was accomplished by coupling of 7



with the phosphonate 9. Deprotection of the acetal provided the aldehyde PPV dimer 12, which was converted into pentamer 13 through coupling with 8. Alternatively, 12 could be further elongated to create aldehyde PPV trimer 15 and ultimately 16 through analogous chemistry. Similar to 11, the higher oligomers were capped with 4-ethynylanisole to access pentamer (14) and septamer (17) chromophores. All oligomers prepared via the Horner reaction were refluxed in toluene with catalytic iodine and then purified by silica gel chromatography to ensure all vinyl groups adopted the more stable trans configuration.¹⁷

Two flexible morphons based on an *n*-decyl chain $(C_{10}H_{20})$ and a tetraethylene glycol $(CH_2CH_2O)_4$ chain with terminal phenylacetylenes were chosen to complement the BEH-PPV oligomers for a Sonogashira polymerization (Scheme 2). Such a strategy was previously employed with PPV trimers of varying compositions.^{18,19} Here we have also employed the tetraethylene glycol chain that may allow for greater conformational flexibility in solution and the solid state by way of the preferred gauche conformation around the C-C bond in ethylene glycols.^{20,21} The synthesis of the alkyl-chain morphon began with a Friedel-Crafts acylation of sebacoyl chloride (18) with bromobenzene to provide the diketone 19. Wolff-Kishner reduction using hydrazine and KOH in diethyelene glycol at 180 °C gave the completely aliphatic 20. Sonogashira coupling of trimethylsilylacetylene (TMS-acetylene) followed by deprotection with aqueous KOH provided the desired bis-(phenylacetylene) with alkyl linker 21. The synthetic procedure for the tetraethylene glycol morphon utilized a nucleophilic substitution of tosylated tetraethylene glycol 22 with 4bromophenol. Similar Sonogashira coupling utilizing TMSacetylene followed by deprotection provided the desired bis(phenylacetylene) with ethylene glycol linker 24.

Our interest in incorporating defined oligomers and morphons into the polymer backbone limited our strategy to step-growth polymerization conditions, which can lead to low molecular weights without exact stoichiometric control.²²



^aReagents and conditions: (i) KOtBu, THF, 0 °C; (ii) 4-ethynylanisole, Pd(PPh₃)₄, HNⁱPr₂, toluene, 85 °C; (iii) HCl, THF, H₂O, 50 °C.

Scheme 2. Synthesis of Flexible Morphons 21 and 24^a



^aReagents and conditions: (i) bromobenzene, AlCl₃, CH₂Cl₂, 40 °C; (ii) NH₂NH₂, KOH, diethylene glycol, 180 °C; (iii) TMS-acetylene, PdCl₂(PPh₃)₂, CuJ, PPh₃, NEt₃, THF, 60 °C; (iv) 20% KOH(aq), THF, methanol; (v) 4-bromophenol, K₂CO₃, acetone, reflux.

Scheme 3. Synthesis of Polymers $1-6^a$



^aReagents and conditions: (i) Pd(PPh₃)₄, CuI, HNⁱPr₂, toluene, 85 °C, 3 days.

	$M_{ m n}$	PDI	oligomer length	no. chromophores ^a	$\lambda_{\rm abs,max}~({\rm nm})$	$\lambda_{\rm em,max} (\rm nm)$	Φ^b	τ (ns)
polymer								
1	78 300	1.7	3mer	56	442	504	0.75	1.167
2	61 600	1.5	5mer	29	467	539	0.27	0.557
3	87 500	1.2	7mer	31	482	550	0.27	0.393
4	42 400	1.4	3mer	29	441	506	0.62	0.509
5	34 100	1.4	5mer	16	463	539	0.27	0.526
6	46 000	1.3	7mer	16	479	547	0.18	0.442
oligomer								
11	1 312	1.0	3mer	1	443	504	0.42	1.251
14	2 029	1.0	5mer	1	475	535	0.23	0.851
17	2 746	1.0	7mer	1	485	544	0.20	0.412
^a Avorago baso	d on the M	and woight	of repeat unit b_{AII}	properties were mass	rad in taluana. C	wantum violde wa	ro colculator	l rolativo to

"Average based on the M_n and weight of repeat unit." All properties were measured in toluene. Quantum yields were calculated relative to Rhodamine 123 in ethanol ($\Phi = 0.96$) and are accurate to $\pm 10\%$.

However, it has been shown that polymerizations based on the Sonogashira coupling reaction can produce extremely high molecular weights (>1500 kDa).²³ The key to accessing these

high degrees of polymerization depends on the use of a slight excess (1.03 equiv) of acetylene monomer to compensate for the minor, yet unavoidable, Glaser coupling between alkynes.

Article



Figure 2. ¹H NMR spectra (CD₂Cl₂) of trimer oligomers 10 (A) and 11 (B) and trimer polymers 4 (C) and 1 (D).

We polymerized the BEH-PPV oligomers (10, 13, and 16) with both flexible morphons (21 and 24) to create six different polymers (1-6) by employing the catalytic system of $Pd(PPh_3)_4$, CuI, and HN^iPr_2 in toluene at 85 °C for 3 days (Scheme 3). The molecular weights, PDIs, and average number of BEH-PPV chromophores per polymer chain are summarized in Table 1. As a consequence of the large, predefined monomers that are used in the reaction, the PDIs are lower than expected from a step-growth polymerization. It is interesting to note that the alkyl morphon led to higher molecular weights (almost double) for each of the respective oligomer polymerizations. It is unclear at this time if the reduction in the degree of polymerization is due to a less efficient Sonogashira coupling of a para-alkoxy substituent (24) compared to a para-alkyl substituent (21) on the phenylacetylene or if the catalyst activity is reduced due to chelation from the tetraethylene glycol functionality.

NMR Analysis. Figure 2 shows a representative example of the BEH-PPV oligomers before and after polymerization. The top spectrum (A) is of the iodo-terminated trimer **10**, and the aromatic region shows three singlets (7.11, 7.18, and 7.32 ppm) for the aryl hydrogens and an AB quartet at 7.49 ppm for the internal alkene protons. The methylene hydrogens adjacent to the oxygen do not provide well-resolved signals; rather, the slightly different protons are clustered around 3.91 ppm. Capping the trimers with 4-ethynylanisole leads to **11** (B),

which displays a reduced coupling constant of the AB quartet, two new aromatic doublets at 6.90 and 7.46 ppm, and a new singlet at 3.83 ppm for the methoxy group. Upon incorporation into polymer 4 (C), the aromatic region remains relatively unchanged from 11; however, new signals arise between 3.5 and 4.2 ppm owing to the new tetraethylene glycol linker. Integration shows that the trimer oligomers and flexible morphons are incorporated into the polymer in a 1:1 ratio. For polymer 1 (D), the aromatic region again stays relatively unchanged except for a shift of the flexible linker aromatic group doublets, which now overlap at 7.20 ppm. The alkyl region shows the alkoxy protons associated with the trimer at 3.91 ppm as well as the aliphatic protons associated with the hydrocarbon flexible linker at 2.62 ppm. Again the integration between the alkyl flexible linker and the trimer show a 1:1 polymer backbone incorporation. Although not shown here, the NMR analysis of polymers 2, 3, 5, and 6 shows the correct 1:1 incorporation of each building block into the polymer repeat unit (Supporting Information). Finally, it is important to note the lone signal at 3.91 ppm for the alkoxy protons. As previously shown,^{24,25} multiple signals in this region suggest the presence of cis-alkenes in the conjugated polymer backbone. In our previous work utilizing the Horner polymerization method,³ we found that large cis-alkene content was present upon polymerization. Even after refluxing in toluene with catalytic iodine, not all of the cis-alkene was removed. This

highlights the value of the presently described system in that all chromophores are identical and maintain the all-trans alkene arrangement upon polymerization.

Solution UV-vis and Fluorescence. The absorption spectra of capped oligomers (11, 14, 17) as well as polymers (1-6) were obtained in toluene. The active chromophore of the oligomer and its corresponding polymers (i.e., 11 vs 1 and 4) are very similar, and only small changes in the λ_{max} were observed between the materials (Table 1). Figure 3 shows an



Figure 3. Absorbance (top) and emission (bottom) of *n*-decyl morphon copolymers 1, 2, and 3 in toluene.

overlay of the absorption spectra of the *n*-alkyl morphon polymers 1–3 while the remaining spectra can be found in the Supporting Information. As expected,^{26,27} the $\lambda_{abs,max}$ showed a bathochromic shift upon increasing the conjugation length from trimer (1, $\lambda_{abs,max} = 442$ nm) to pentamer (2, $\lambda_{abs,max} = 467$ nm) to septamer (3, $\lambda_{abs,max} = 482$ nm). The $\lambda_{abs,max}$ of 3 is slightly lower than native BEH-PPV ($\lambda_{max} = 505$ nm).²⁸ The emission spectra displayed a similar bathochromic shift from trimer (1, $\lambda_{em,max} = 504$ nm) to pentamer (2, $\lambda_{em,max} = 539$ nm) to septamer (3, $\lambda_{em,max} = 550$ nm).

Consistent with the expected trends for phenylenevinylenes,^{29,30} the fluorescence lifetimes of the compounds generally decreased with increasing conjugation length due to the stronger oscillator strength of the longer chromophores. An exception to this general trend was found for 4, which had a substantially shorter lifetime (0.509 ns) than other trimer materials (1 = 1.167 ns and 11 = 1.251 ns). Similarly, both pentamer polymers (2 and 5) showed shorter lifetimes than the corresponding oligomer 14.

The quantum yields (Φ) , measured against a reference standard of Rhodamine 123 in ethanol, did not show the same strong correlation with oligomer length. The trimer compounds displayed substantially higher quantum yields than the pentamers or septamers. Previous reports have found that the relationship of oligomer conjugation length on quantum yield depends on the specific structure of the side chains and endcaps, with some compounds displaying a similar drop in Φ with increasing conjugation length³⁰ and others displaying Φ values which are essentially independent of conjugation length.³¹ Additionally, there were significant differences between 1, 4, and 11 (Φ = 0.75, 0.62, and 0.42, respectively), likely a result of the shortest chromophores being the most susceptible to nonradiative decay channels that result from changes in the periphery of the compound. While there are differences in the lifetimes and quantum vields between the oligomers and polymer, the excited state energies of the polymers are essentially identical to those of the oligomers. Thus, the oligomers-morphon approach provides the opportunity to explore the origin of changes in excited state energies observed in the solid state and develop improved control of conjugated polymer materials.

Thin Film Fluorescence. The linked oligomers described above allow us to probe the chain interactions governing film electronic properties in systems with well-defined conjugation length. The septamer compounds **3** and **6** in particular provide a useful comparison point to the well-characterized PPV derivatives, as their solution absorption peak is close to that of MEH-PPV and BEH-PPV.^{32,33} The fluorescence spectrum of MEH-PPV is well-known to undergo a substantial bath-ochromic peak shift between solution and the solid state due to the formation of low-energy traps.^{32,34,35} Electronic traps present a critical performance issue for devices based on conjugated polymer materials, limiting the efficiency of exciton harvesting and charge transport in devices.^{36–38}

Several possible mechanisms exist for the formation of lowenergy sites and red-shifted fluorescence spectra in conjugated polymers. Red-shifted emission in the β -phase of poly(9,9dioctyl)fluorene relative to solution or amorphous phases is ascribed to planarization of polymer chains due to interchain steric interactions that lead to a corresponding increase in effective conjugation length or hyperextended conjugation.³ Closely packed polymer chains can also lead to the formation of excited state interactions (excimers).⁴¹ Additionally, recent spectroscopic studies of aggregates of random MEH-PPV/ terphenyl copolymers have suggested that ground state electronic interactions are the source of low-energy red sites.7 By studying materials with controlled conjugation lengths, we can distinguish between these different scenarios because the limited conjugation of the oligomer units eliminates the possibility of hyperextended conjugation.

To probe the effects of the flexible morphons on the solid state properties of these materials, we measured the fluorescence spectra of thin films of **3** and **6** prepared by spin-coating on glass (Figure 4). Despite the identical conjugation lengths of the two polymers, there were substantial differences in the spectra. The fluorescence spectrum of **3** could be well fit to a Franck–Condon model with a single 0-0 energy and 3 quanta for the CC progression of Gaussian broadened vibronic lines:

$$I_{\rm em}(\omega) = A\omega^3 \sum_{n_i=0} \left(\prod_i \frac{{\rm e}^{-S_i} S_i^{n_i}}{n_i!} \right) {\rm e}^{-\left[(\omega - E_0 + n_i \hbar \omega_i)/\sigma\right]^2}$$
(1)

where ω is the energy of the emitted light, *A* is the amplitude of the 0–0 transition, *E*₀ is the energy of the 0–0 transition, and $n_{\nu} S_{\nu} \hbar \omega_{\nu}$ and σ are the quanta, Huang–Rhys factor vibrational



Figure 4. Thin film fluorescence spectrum of 3 (solid) and fit to single CC progression of vibronic peaks (red-dashed) (top). Thin film fluorescence spectrum of 6.

frequency of the *i*th mode, and peak width, respectively.^{42–44} The fit values for S_{ii} $\hbar\omega_{ii}$ and σ (Table 2) are consistent with

Table 2. Best Fit Parameters for Thin Film Fluorescence Spectra of 2 and 3

polymer	$E_0 ({\rm cm}^{-1})$	S	$\sigma~({ m cm}^{-1})$	$\hbar\omega_i ~(\mathrm{cm}^{-1})$
2	18 160	0.988	840	1500
3	17 700	0.939	866	1503

emission from a relatively uniform set of chromophores. The 0-0 transition for 3 at 17 700 cm⁻¹ (565 nm) is bathochromically shifted 472 cm⁻¹ from the solution peak. The magnitude of this shift is comparable to that observed in MEH-PPV and BEH-PPV. Thin films of 2 could also be well fit by a single Franck–Condon progression with a 0-0 energy at 18 160 cm⁻¹, which represents a bathochromic shift of only 393 cm⁻¹ relative to solution (Supporting Information). The larger bathochromic shift for the longer oligomers could be indicative of better coupling between the polymers as a result of stronger interactions of the individual chromophores.

In contrast to the *n*-alkyl morphon-containing polymers, the spectrum of **6** is not well fit by either one or two Franck–Condon progressions (similar to **5**, Supporting Information). Nor does the spectrum appear to be a single progression in which the 0–0 peak has been suppressed as has been observed previously for solution aggregates of PPV-oligomers.⁴⁵ The first peak in the spectrum is at 565 nm, which is the same energy as the 0–0 transition in the spectrum of **3**. If a single Franck–Condon progression with a 0–0 transition at this energy is constrained in the fit, the remainder of the spectrum is a very

broad emission peaked at \sim 645 nm. Such a fit does not agree with the two transitions centered at 623 and 669 nm in the experimentally obtained spectrum. This fitting suggests that while some portions of the film behave similarly to 3, others exhibit even stronger interchromophore interactions that yield the red-shifted emission. This result is consistent with the hypothesis that the greater length or flexibility of the alkoxy linkers allows more extensive chain folding in the solid state, facilitating these interchromophore interactions.

Broad, red-shifted fluorescence peaks can result from both excimers or a distribution of overlapping Franck-Condon progressions. These two sources of red-shifted emission can be distinguished by their fluorescence lifetime, with excimers typically being much longer lived ($\tau > 1$ ns).⁴⁶ Fluorescence lifetime measurements of films of 6, fit to biexponential decay functions, showed that greater than 97% of the signal came from a relatively short-lived component ($\tau = 0.580$ ns). Repeating this measurement with a 670 nm long pass filter in front of the detector yielded a similar result ($\tau = 0.670$ ns for 97% of the decay curve). As these lifetimes are too short for excimers, we assign this broad red-shifted emission to a heterogeneous distribution of low-energy peaks. This distribution in energies for emissive sites is likely a result of differences in interchromophore coupling that arise from heterogeneity of the packing within the films. Studies of aggregated oligomers in solution have observed species that are composed of varying degrees of both monomer-like and aggregated species.^{45,47} The predominance of these lower energy sites in the polymers with the alkoxy linkers is evidence that they are folding in the solidstate into structures that allow the oligomers to interact at closer distances.

In summary, we have successfully synthesized a series of welldefined BEH-PPV polymers with flexible morphons composed of either a *n*-decyl or tetraethylene glycol chain. High molecular weight polymers were obtained using a step-growth polymerization based on the Sonogashira coupling. Owing to the presynthesized PPV oligomers, each chromophore in the polymer backbone was identical and contained no cis-alkene linkages. The solution photophysical properties of 4-ethynylanisole-capped PPV oligomers and polymer-incorporated PPVs were very similar and demonstrate that the polymer chromophores behave similarly to the free oligomers. By varying the flexibility of the morphon linkers, the extent of interchain interactions could be varied in the solid state. These materials provide a powerful new platform for continuing studies in the evolution of structure and properties from single molecules to thin films.

ASSOCIATED CONTENT

S Supporting Information

Detailed experimental procedures are available, including experimental equipment, synthetic procedures, and NMR characterization; solution absorption and fluorescence spectra of compounds 4, 5, 6, 11, 14, and 17 as well as the thin film fluorescence of 2 and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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