NOVEL MACROMOLECULAR MATERIALS FOR ELECTRONIC AND OPTICAL APPLICATIONS

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A series of thiophene-containing poly(arylene ethynylene)s have been synthesized and their molecular structures and PL properties have been characterized. A convenient synthetic route has been developed to prepare bis(3-alkylthienyl)ethyne 5 in high yield. Various attempts have been made to use 5 as an essential building block for developing novel poly(arylene ethynylene) materials. Regioregular poly(3-hexyl-2,5-thienylene ethynylene)s (P3HTE) have been synthesized in order to compare the steric interaction in the corresponding polymers. A systematic study has been carried out to evaluate the regioregularity effect of the polymer structure on the PL properties. P3HTE of a head-to-tail chain sequence (12) showed stronger PL intensity than the corresponding polymer with a head-to-head chain sequence (10), although they exhibit the essentially same absorbance. The quantum efficiency of P3HTEs were found to increase sharply with the conjugation length of the molecules when the chain length is shorter than the tetramer. Further extending the conjugation length beyond the tetramer appeared to shift the fluorescence emission band to a longer wavelength, but to have little effect on the quantum efficiency of the molecule. Several alternating copolymers, poly[p-phenylene ethynylene]-alt-(2,5-thienylene)
ethylene)Js (PPETEs), have also been synthesized by using a Heck-type coupling reaction under mild conditions. PPETEs produced under the mild conditions exhibit longer conjugation length (ca. 10 nm in UV-vis absorption /max) than the same polymers synthesized at high temperature. The copolymers exhibit a moderate rigidity with Mark-Houwink constant @=0.8-0.9, which is higher than poly(thienylene ethynylene) (PTE) 20 (@=0.68) but significantly lower than poly(phenylene ethynylene) (PPE) 1 (@=1.92). The quantum efficiencies of PPETE copolymers are found to be Øf1=0.37 - 0.48, which is much higher than for PTE (Øf1 = 0.18) and comparable with PPE homopolymers. Synthesis of copolymer PPETE thus successfully combines both good solubility and processibility of PTE and high luminescence of PPE into a single polymer chain, making the material attractive for device applications.
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Abstract

A series of thiophene-containing poly(arylene ethynylene)s have been synthesized and their molecular structures and PL properties have been characterized. A convenient synthetic route has been developed to prepare bis(3-alkyl-thiencyl)ethyne 5 in high yield. Various attempts have been made to use 5 as an essential building block for developing novel poly(arylene ethynylene) materials.

Regioregular poly(3-hexyl-2,5-thienylene ethynylene)s (P3HTE) have been synthesized in order to compare the steric interaction in the corresponding polymers. A systematic study has been carried out to evaluate the regioregularity effect of the polymer structure on the PL properties. P3HTE of a head-to-tail chain sequence (12) showed stronger PL intensity than the corresponding polymer with a head-to-head chain sequence (10), although they exhibited the essentially same absorbance. The quantum efficiency of P3HTEs were found to increase sharply with the conjugation length of the molecules when the chain length is shorter than the tetramer. Further extending the conjugation length beyond the tetramer appeared to shift the fluorescence emission band to a longer wavelength, but to have little effect on the quantum efficiency of the molecule.

Several alternating copolymers, poly[(p-phenylene ethynylene)-alt-(2,5-thienylene ethynylene)]s (PPETEs), have also been synthesized by using a Heck-type coupling reaction under mild conditions. PPETEs produced under the mild conditions exhibit longer conjugation length (ca. 10 nm in UV-vis absorption $\lambda_{\text{max}}$) than the same polymers synthesized at high temperature. The copolymers exhibit a moderate rigidity with Mark-Houwink constant $\alpha = 0.8-0.9$, which is higher than poly(thienylene ethynylene) (PTE) 20 ($\alpha = 0.68$) but significantly lower than poly(phenylene ethynylene)
(PPE) 1 (α = 1.92). The quantum efficiencies of PPETE copolymers are found to be $\phi_n = 0.37 - 0.48$, which is much higher than for PTE ($\phi_n = 0.18$) and comparable with PPE homopolymers. Synthesis of copolymer PPETE thus successfully combines both good solubility and processibility of PTE and high luminescence of PPE into a single polymer chain, making the material attractive for device applications.
Introduction:

Conjugated polymers of rigid chain have been attracting considerable attention as recent studies indicate they can be used as an active layer in fabricating light-emitting diode (LEDs).\(^1\) The luminescent polymers, which have been used in LEDs, include poly(p-phenylene vinylene) (PPV), poly(p-phenylene) (PPP) and poly(thiophene). Recent achievement in this field has shown that acetylene-containing polymers, such as poly(p-phenylene ethynylene) 1, are strongly luminescent and promising for LEDs application.\(^2\) The objective of this research is to develop novel acetylene-containing conjugated polymers with improved luminescent properties. Based on the molecular structure, the targeted polymers can be separated into two categories: (1) polymers containig bis(3-alkylthienyl)ethyne unit (2) where “A” represents a molecular bridge to link the unit into polymers, alternating copolymers of thiophene-ethynylene and phenylene-ethynylene (3). This report summarizes the achievement in each categories during the grant-support period. Section one and two of this report focus on the polymer 2 while section three devotes to polymer 3.

![Chemical structures](image)

Results and Discussion

Section 1. Synthesis and Characterization of Polymers Containing Bis(3-alkylthienyl)ethyne Unit.
It is noticed that the substituents in bis(3-alkylthienyl)ethyne unit (2) point to each other, creating unique molecular geometry which may lead to a number of applications such as chemical sensors as illustrated in crown ether-containing polythiophene. Prior to the chemical sensor design, it is desired to learn the steric interaction of the substituents in 2. From the material science point of view, it is important to learn how the fluorescence properties of polymer 2 will be affected by the arrangement of substituent along the polymer backbone. In order to address these fundamental issues, a convenient synthetic route for the key monomer, bis(3-hexylthienyl)ethyne (5), has been successfully developed as shown below from the easily accessed starting material 3-hexyl-2-iodothiophene (4).

\[
\begin{align*}
\text{4} & \quad \text{I} + \text{HC} & \quad \text{Cl}_2\text{Pd(PPPh}_3\text{)}_2 / \text{CuI} & \quad \text{Et}_3\text{N} \\
\text{5} & \quad \text{R} & \quad \text{R}
\end{align*}
\]

**Polymerization study of bis(3-alkylthienyl)ethyne 5.** In principle, any polymerization method for thiophene could be used to polymerize 5. A common methodology for preparing polythiophene 7 is oxidizing thiophene with FeCl₃. When bis(3-alkylthienyl)ethyne 5 was treated with FeCl₃ under the same condition, however, an insoluble black powder was obtained. Solid state $^{13}$C (CPMAS) NMR of the black solid powder showed only alkyl and olefinic carbons, suggesting that the internal acetylene in 4 is susceptible to the reagent.
In order to circumvent the problem, bis(3-alkylthiophenyl)ethyne 5 was transformed to bis(5-iodo-3-alkylthiophenyl)ethyne 7 via the following reaction sequence.\textsuperscript{9} Polymerization of diiodothiophene 7 was attempted by using the nickel-catalyzed Grignard coupling method. Although 2-methyltetrahydrofuran was found to be a better solvent than THF for the polymerization, the reaction repeated failed to yield high molecular weight product. \textsuperscript{13}C-NMR of the obtained polymer resin, acquired under a quantitative condition, showed two acetylenic signals at 87.6 and 89.3 ppm in a ratio of about 1:2. The obtained polymer resin was dark brown in color, and polymer fibers could be formed from polymer melt. Clearly the system need to be further studied. At this stage we are continuing searching for proper polymerization conditions to increase the molecular weight of the polymer 6.

In order to quickly access the polymer system containing bis(3-alkylthiophenyl)ethyne, we have explored the possibility to couple diiodothiophene 7 with
diethynylbenzene. As expected the polymerization proceeded very well to lead to a solid product of orange color. Spectroscopic studies ($^1$H-, $^{13}$C-NMR, IR and UV-vis and GPC) confirm that the polymer had a chemical structure of 8. The polymer is highly luminescent with emission $\lambda_{\text{max}}$ at 496 nm. The quantum efficiency ($\phi_R$) was estimated in THF to be about 0.33 when excited at 468 nm.

Section 2. Synthesis and Characterization of Regioregular Poly(3-Hexyl-2,5-thienyl ethynylene)s (P3HTEs).

Design and Synthesis of Poly(3-hexyl-2,5-thienyl ethynylene) (P3HTE) with a head-to-head chain sequence. A feasible way to incorporate the bis(3-alkylthiophene)ethyne unit into the polymer systems appears to link the monomer 7 with carbon-carbon triple bonds, i.e. synthesizing polymer 10. Clearly the polymer 10 is a specific member of polymer 2 where the bridging unit “A” is a carbon-carbon triple bond. Direct coupling of acetylene with 7 appears to be not practical as it is difficult to control the required stoichiometry, which is necessary to obtain polymers of high
molecular weight. This problem can be avoided by polymerizing monomer 7 with 9.

Analyzing the chemical structure of 10, there exist two types of acetylene linkages, i.e. head-to-head and tail-to-tail shown in Figure 1. Synthesis of 10 requires to build the two linkage in different stages.

![Diagram of chain sequences](image)

**Figure 1.** Illustration of chain sequences of head-to-head (HH), tail-to-tail (TT) and head-to-tail (HT).

Our strategy in building the regioregular poly(3-hexyl-2,5-thienyl ethynylene) (P3THE) 10 is to form the head-to-head linkage in the monomer synthesis, leaving the tail-to-tail linkage in the polymerization step. Thus bis(3-hexyl-2-thienyl)ethyne 5 can serve as a perfect starting material, in which the head-to-head linkage has been built in. Iodination of 5 by using n-butyllithium followed by treatment with iodine at -78°C afforded bis(3-hexyl-5-iodo-2-thienyl)ethyne 7 in a combined yield of 85%. Subsequent coupling of 7 with (trimethylsilyl)acetylene lead to a crystalline product 8, which after desilylation provided bis(5-ethynyl-3-hexyl-2-thienyl)ethyne (9). Polymer 10 was eventually obtained in high yield via coupling monomers 7 and 9 at room temperature with formation of the tail-to-tail linkage.
Figure 2. Regiocontrolled synthesis of poly(3-hexyl-2,5-thienyl ethynylene) with the head-to-head and tail-to-tail sequences.

**Design and Synthesis of Poly(3-hexyl-2,5-thienyl ethynylene) (P3HTE) with a head-to-tail chain sequence.** It is noticed that all alkyl substituents on thiophene rings in 10 are pointed toward each other. A fundamental question is whether such spacial arrangement of alkyl substituents could cause severe steric interaction among the substituents, and thus affecting the physical properties of the corresponding materials. To assess such steric interaction, it is necessary to synthesize poly(3-hexyl-2,5-thienyl ethynylene) 12 with head-to-tail chain sequence, where less steric interaction between substituents is expected. The desired head-to-tail linkage was achieved through polymerizing 2-ethynyl-5-iodo-3-hexylthiophene (11) at room temperature. In this monomer a terminal acetylene was connected to 4-position of the thiophene ring, thus leaving head-to-tail linkage as only possibility during polymerization. Synthesis of 9 was accomplished in five steps from 3-hexylthiophene by selective mono-iodination at 2-
position, then coupling with (trimethylsilyl)acetylene, followed by iodination at 5-position of thiophene ring.

![Chemical reaction diagram]

(a) LDA, -78°C
(b) I₂, -78°C
(c) MeOH, KOH

Figure 3. Regiocontrolled synthesis of poly(3-hexyl-2,5-thienyl ethynylene) with the head-to-tail sequence.

**Characterization of Regioregular P3HTEs.** Both P3HTEs 10 and 12 were dark brown resins, which were soluble in organic solvents such as THF, toluene, and chloroform. Polymer films could be cast from their corresponding solutions. Polymer structures were characterized by solution ¹H and ¹³C NMR. No resonance signals near 3.48 ppm (acetylenic protons) were detected in the ¹H NMR spectra of P3HTEs 10 and 12. Complete polymerization in both 10 and 12 was further supported by disappearance of the absorption band near 3309 cm⁻¹ (C-H stretching) in IR spectra, which is strong and characteristic in acetylene-containing monomers 9 and 11. ¹H NMR spectra of both regioregular P3HTEs revealed very similar resonance signals. In comparison with regiorandom P3HTE,¹⁰,¹¹ the resonance signals for methylene protons between 1-3 ppm (Figure 4) are sharp and well resolved, attributing to the regioregularity in the polymer chain structures.
Figure 4. $^1$H NMR (CDCl$_3$) spectrum of P3HTE 12. The signal at 7.25 ppm is attributed to CHCl$_3$.

Quantitative $^{13}$C NMR provides a sensitive probe for the alkyl substitution patterns in the polymer backbone. Our previous report$^{10}$ has shown that four acetylenic carbons of about equal intensity are observed in the regiorandom P3HTE 13. With aid of the model compounds, two signals are assigned to head-to-tail linkage, and the other two to head-to-head and tail-to-tail linkages. Quantitative $^{13}$C NMR spectra of 10 and 12 are shown in Figure 5. In the top spectrum of Figure 5 two acetylenic carbons at 86.54 and 89.27 ppm are corresponding to the head-to-tail linkage in P3HTE 10. The bottom spectrum shows another set of acetylenic carbons at 87.19 and 88.81 ppm, attributing to head-to-head and tail-to-tail linkages in P3HTE 8. Lack of overlapping in the two sets of acetylenic carbons confirms the regioregular structures in both 10 and 12.
Molecular Weights and Chain Stiffness of Regioregular P3HTEs. The molecular weights of P3HTEs were measured in THF eluent by using size exclusion chromatography with on-line refractive index, viscosity and light-scattering detectors (referred to as SEC$^3$). By using the SEC$^3$ setting the true molecular weights of the polymers were obtained versus the elution volume. A typical SEC$^3$ chromatogram is
shown in Figure 6, indicating that P3HTE 12 has a monomodel distribution. The peak molecular weights from refractive index (RI), viscosity (DP) and light scattering (LS) detectors were quite comparable, suggesting a linear polymer structure. The weight-average molecular weights determined were 20,100 ($M_w/M_n = 1.9$) for 12 and 116,400 ($M_w/M_n = 7.8$) for 10. The broader molecular weight distribution of 10 could be due to the side reaction$^{12}$ of the terminal thienylacetylenes occurring during the polymerization.

For $\pi$-conjugating polymers, a fundamental issue is how rigid these molecules are as a result of the extended $\pi$-conjugation. Evaluation of their unperturbed molecular dimensions in dilute solutions will help to gain an insight into the extended chain stiffness of these polymers. The Mark-Houwink coefficients in $[\eta] = K M^\alpha$, measured by the on-line viscometer, were $\alpha = 0.68$ and $K = 3.52 \times 10^{-4}$ cm$^3$/g for 12. It is intriguing to make comparison with poly(3-hexylthiophene) (P3HT)$^{13}$ whose $\alpha$ value is as high as 0.96. The striking low $\alpha$ value for 12 indicates that P3ATE polymers may not have a rigid linear conformation in the dilute solution, which is the minimum-energy conformational form$^9$ for an oligomer of 16 repeating units. In other words, the conformation for P3ATE could be more coil-like in comparison with P3HT. The observed conformational difference between P3HT and P3HTE may originate from the reduced steric and coulombic interactions between the adjacent thiophenes in the latter. In light of the energy difference between the molecular fragments 14 and 15, the probability for 15 to occur in P3HTE is expected to be higher than the one for 14 in P3HT. Random occurrence of 15 along the polymer backbone could be one of the major reasons responsible for P3HTE to deviate from the rigid linear conformation,$^5$ in which
the thiophene rings have to be placed with the sulfur atoms pointing alternately up and down along the entire polymer chain.

![Chemical structures](image)

**Figure 6.** SEC\(^3\) chromatogram of P3HTE 12.

**Photoabsorbance and Photoluminescence.** UV-vis spectra of P3HTEs 5 and 10 were measured from THF solutions (Figure 7) and thin films on glass substrates. Under the same conditions both polymers 10 and 12 showed very similar UV-visible absorbance. Comparing with P3HTE 10, the absorption \(\lambda_{\text{max}}\) of P3HTE 12 was slightly shifted to a longer wavelength (about 4 nm). The regioregularity effect in P3HTEs appeared to be much smaller than poly(3-hexylthiophenes) (P3HTs),\(^{14}\) where a difference
of 28 nm in $\lambda_{\text{max}}$ has been reported between regiorregular (head-to-tail) and regiorandom poly(3-hexylthiophene)s in CHCl$_3$ solutions. The negligible difference in UV-vis absorption $\lambda_{\text{max}}$ between 10 and 12 suggested that the arrangement of substituents had little effect on the $\pi-\pi^*$ absorption band and the conjugation length of P3HTE. The diminished regioregularity effect in P3HTE could be explained in terms of the reduced steric interactions between substituents on adjacent thiophene rings, and of reduced interaction between the alkyl side chain and the sp$^2$ lone pair on the sulfur atoms of the neighbour thiophenes.

Figure 7. UV-visible spectra of P3HTEs 10 (solid line) and 12 (broken line) measured in the same concentration of THF solutions (0.1 g per liter concentration).

Regioregular P3HTE 12 in CHCl$_3$ solvent showed a maximum absorption wavelength at 441 nm (Table 1), which is essentially same as for poly(3-ethylthiophene ethynylene).$^9$ It appears that the length of the alkyl substituents has a negligible influence on the conjugation length of P3ATE materials. Regiorandom P3HTE,$^{10}$ prepared at room temperature as reported previously, exhibited a remarkably longer conjugation length (ca.
35 nm in solution and 41 nm in solid) than the same polymer\textsuperscript{15} prepared at an elevated temperature. Thus the polymerization temperature could play an important role in synthesizing P3HTE materials with low electronic gaps. This temperature effect might originate from the instability\textsuperscript{12,16} of terminal thienylacetylenes which generates the unwanted structural defects during the polymerization.

Different from P3HT\textsuperscript{17} where only one emission band is observed, two emission bands were observed in the fluorescence spectra of P3HTE solutions (Figure 8) with $\lambda_{\text{max}}$ at about 506 and 536 nm. The emission ratios of the two bands for both 10 and 12 were essentially not changed over a wide concentration range ($10^{-6}$-$10^{-3}$ M of the repeating unit). Three thiophene-capped model compounds, trimer 16, tetramer 17 and hexamer 18, were synthesized to explore the possible conjugation length effect on the fluorescence characteristics. Fluorescence spectra of 16-18 exhibited structured emissions with two resolved bands (Figure 9). The relative fluorescence intensity of the low energy band appeared to decrease as the conjugation length of the molecule increases.
Figure 8. Fluorescence spectra of P3HTEs 10 and 12 showing structured emission bands at about 506 and 536 nm.

Figure 9. Normalized fluorescence spectra of oligomers 8, 16, 17 and 18. The relative emission intensity of the low energy band decreases as the conjugation increases.
Quantum Yields of Fluorescence. Fluorescence quantum yields of P3HTEs are listed in Table 1. Since both 10 and 12 have very similar conjugation length and the same absorbance, the difference between fluorescent intensities are due primarily to the arrangement of alkyl substituents along the polymer backbone, which affects the non-radiative decay process of the excited states. This regioregularity effect on fluorescence intensity is even larger in the solid state, as polymer 12 of HT linkages fluoresces about ten times stronger than 10 of HH and TT linkages. The low fluorescence in 10 might be due to relative ease in forming a non emissive excimer from symmetrically substituted HH and TT linkages, as the TT linkage allows closer face-to-face proximity interaction with a planar excited state molecule.\textsuperscript{18} Formation of the non emissive excimer, which has been suggested in P3HT,\textsuperscript{17} is consistent with our observation that the fluorescence of P3HTEs decreases by more than an order of magnitude from solution to film states. In summary, P3HTE of HT linkage exhibits stronger fluorescence than the one of HH and TT linkages in both the solution and film states.

It is well documented that conjugation length\textsuperscript{19} of a molecule plays an important role in affecting the quantum yield. Bis(3-hexyl-2-thienyl)ethyne 6 gave essentially no fluorescence when excited in its entire photoabsorbance range (300-450 nm), due primarily to the small size\textsuperscript{23} of the \pi-system. Addition of two triple bonds to the thiophene rings made the molecule fluorescent as shown in bis[3-hexyl-5(trimethylsilyl)ethynyl-2-thienyl]ethyne (8). The quantum yield of trimer 13 was still low (about 6\%). Interestingly the quantum yield of tetramer 14 sharply increased to 21\% in repeated measurements, a value which is comparable with P3HTE polymers. Further extending the conjugation length beyond 14 appeared to have little effect on the
fluorescence quantum efficiency of the molecule, but to shift the fluorescence emission to longer wavelength.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>absorption¹</th>
<th>fluorescence¹</th>
<th>Excitation</th>
<th>$\phi_n$ ⁶</th>
<th>$^{13}$C NMR $^{[\text{C} \equiv \text{C}]} (\delta)$</th>
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<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$^b \lambda_{\text{max}}$ (nm)</td>
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<tr>
<td>12</td>
<td>440 (THF), 506, 536 (THF)</td>
<td>430</td>
<td>0.20</td>
<td>86.54, 89.27</td>
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<td></td>
<td>441 (CHCl₃), 575 (film)</td>
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<td></td>
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<td></td>
<td>486 (film)</td>
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<td>10</td>
<td>436 (THF), 505, 535 (THF)</td>
<td>420</td>
<td>0.18</td>
<td>87.19, 88.81</td>
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<tr>
<td></td>
<td>437 (CHCl₃), 575 (film)</td>
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</tr>
<tr>
<td></td>
<td>488 (film)</td>
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<tr>
<td>13</td>
<td>438 (THF)</td>
<td>505, 535 (THF)</td>
<td>420</td>
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<td>86.79, 87.46,</td>
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<td>408, 430 (THF)</td>
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<td>87.21, 88.69, 89.21</td>
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</tbody>
</table>

¹ Solvent or the statement of measurement is shown in parenthesis. ²Excitation spectrum is obtained by monitoring at $\lambda_{\text{max}}$ of fluorescence. ⁶Quantum efficiency is measured in THF solution.
Figure 10. Photoluminescence quantum efficiencies ($\phi_R$) versus chain length of poly(3-hexylthienyl ethynlenes).

Section 3. Alternating Copolymers of Thiophene-Ethynylene and Phenylene-Ethynylene.

Poly(phenylene ethynylene) (PPE) 1 is a special class of $\pi$-conjugated polymers in which para-substituted phenyl rings alternate with carbon-carbon triple bonds. The linear rod-like bonding geometry of the triple bond (in comparison with the corresponding double bond) has the advantage to extend the molecular rigidity in both short and long ranges. Resulting from its linear rod molecular structure, PPE 1 has a characteristically large Mark-Houwink ($\alpha$=1.92) constant$^{20}$ in comparison with $\alpha = 0.96$ for polythiophene.$^{21}$ The increased molecular rigidity in PPEs could be responsible for their high solution PL quantum efficiencies.$^3$ Since the $\alpha$ constant is one of the important parameters to describe undisturbed polymer conformations in solution, correlation between the $\alpha$ values and solution quantum yields of $\pi$-conjugated polymers could be a very useful probe to study the effect of the molecular rigidity of a polymer in solution on its PL efficiency.

Another example of a poly(arylene ethynylene) is poly(thienyl ethynylene) (PTE) 20 which exhibits green photoluminescence$^{22,23}$ with moderate solution quantum
efficiency ($\phi_n = 0.2$).\textsuperscript{23} As described in the section two of this report, the $\alpha$ value of PTE 20 measured in THF solvent is only about 0.68, which is typical for a random-coil molecular conformation. Clearly the presence of the $\alpha$-linked thiophene bridges has a large impact on the long range molecular rigidity and the corresponding physical properties.

![Chemical structures](image)

It is obviously desirable to develop poly(arylene ethynylene) materials which exhibit both the high luminescence of PPE 1 and processibility of PTE 20. A standard approach is to place both $p$-phenylene-ethynylene and $\alpha$- linked thiophene-ethynylene units into a single polymer chain as shown in 3. By doing so the short-range chain rigidity of PTE is increased via extending the linear rod-like chain segment from thiphene-ethynylene-thiophene in 20 to thiophene-ethynylene-phenylene-ethynylene-thiophene in 3, and the PL efficiency of 3 is expected to be significantly higher than 2. Inclusion of $\alpha$- linked thiophenes in 3 will modify the rigid-rod backbone of PPE so as to improve the solubility and processibility relative to PPE 1. Although a few examples of co-polymer 3 have been synthesized by this group\textsuperscript{10} and others,\textsuperscript{25,26} no systematic study has been carried out to evaluate their PL efficiencies and their dependence on chain rigidity. Here we report our results on the synthesis of three variously substituted
examples of 3 under mild conditions, and characterization of their photoluminescent properties and molecular chain rigidities.

**Polymer Synthesis and Characterization.** Poly(p-phenylene ethynylene-alt-thiénylene ethynylene)s (PPETEs 22-24) were prepared by Heck-type coupling. Typically a substituted 2,5-diiodothiophene reacted with a diethynylbenzene in toluene in the presence of a catalytic system PdCl$_2$(PPh$_3$)$_2$/CuI/Et$_3$N to lead to a polymer backbone where α-thiophene and benzene rings alternately occur along the polymer chain. Using diiodothiophene (as opposed to dibromothiophene) allows the polymerization to be carried out at room temperature, thus minimizing the unwanted side reactions.

\[
\begin{align*}
\text{Ar} & \quad + \quad \text{Ar}'-\text{I} \quad \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_2/\text{CuI/ Et}_3\text{N, Toluene}} \quad \text{PPETE} \\
\end{align*}
\]

![Diagram of PPETEs 22-24](image)

Figure 11. Synthesis of alternating co-polymer PPETEs, where Ar and Ar' represent the corresponding phenyl and thiophene rings.

PPETEs were yellow-orange in color in the solid state. The polymers showed good solubility in common organic solvents such as toluene, THF and chloroform.
Uniform films could be cast from their solutions. IR and $^1$H NMR spectra of the polymers detected no trace of acetylenic groups, indicating the polymerization was complete under the mild conditions used.

Figure 12 shows the UV-vis absorption spectra of PPETEs. The absorption $\lambda_{\text{max}}$ values of the polymers are listed in Table 2. It is noted that the absorption $\lambda_{\text{max}}$ values of PPETE 22 and 24 are at 444 and 413 nm, which are about 11 nm longer than the same polymers\textsuperscript{20,26a} prepared at elevated temperature. Clearly the mild polymerization conditions are important in synthesizing poly(arylene ethynylene)s since phenylacetylenes\textsuperscript{28} are susceptible to thermal reactions.

![Graph](image-url)

Figure 12. UV-vis absorption spectra of 22-24 measured in THF.

**Molecular Weight and Chain Stiffness.** The molecular weights of the polymers were measured in THF eluent by using size exclusion chromatography with on-line refractive index, viscosity, and light-scattering detectors (referred to as SEC\textsuperscript{3}). A typical SEC\textsuperscript{3} chromatogram is shown in Figure 13, indicating a monomodal distribution in molecular weight. The comparable peak molecular weights from refractive index (RI), viscosity (DP) and light-scattering (LS) detectors suggest a linear structure without branching. The polydispersities of the polymers (listed in Table 2) are about 2, which is
typical\textsuperscript{29} for condensation polymerization and in agreement with the linear polymer structure.

For \(\pi\)-conjugated polymers, a fundamental issue is how much molecular rigidity is imparted by the extended \(\pi\)-conjugation. Evaluation of their unperturbed molecular dimensions in dilute solutions will help to gain an insight into the extended chain stiffness of these polymers. The \(\alpha\) values in Mark-Houwink equation \([\eta] = K M^\alpha\), as measured by the on-line viscosity detector, are about 0.8 for PPETEs which is only moderately higher than P3HTE\textsuperscript{24} (\(\alpha = 0.68\)) but significantly lower than PPE\textsuperscript{20} (\(\alpha = 1.92\)). The low \(\alpha\) value implies that the polymer chains of PPETEs are far less stiff than the rigid-rod polymer PPE as a result of the main chain modification. In other words, alternatively replacing phenyl in PPE by thiophene ring has a large impact in reducing the long-range chain stiffness of PPE. This is in agreement with the observed good solubility for PPETE 24 in which there is no substituent on the phenyl ring.

![Graphs](image_url)

Figure 13. SEC\textsuperscript{3} chromatogram (left) and Mark-Houwink plot (right) of PPETE 23.
Table 2. UV-Vis, fluorescence and molecular weight data for PPETEs.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Absorption&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Fluorescence&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Excitation</th>
<th>Mw</th>
<th>Mark-Houwink</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>( \lambda_{\text{max}} ) (nm)&lt;sup&gt;b&lt;/sup&gt;</td>
<td>( \phi_{\text{f}} )&lt;sup&gt;c&lt;/sup&gt;</td>
<td>(PDI)</td>
</tr>
<tr>
<td>22</td>
<td>444 (THF) 444(CHCl₃)</td>
<td>482, 514 (THF) 485,518(CHCl₃)</td>
<td>450 (THF) 450(CHCl₃)</td>
<td>0.37 (THF) 0.37(CHCl₃)</td>
<td>43,900</td>
</tr>
<tr>
<td>23</td>
<td>460(THF) 457(CHCl₃)</td>
<td>489, 520 (THF) 492,524(CHCl₃)</td>
<td>468 (THF) 468(CHCl₃)</td>
<td>0.48(THF) 0.47(CHCl₃)</td>
<td>61,600</td>
</tr>
<tr>
<td>24</td>
<td>414 (THF) 413 (CHCl₃)</td>
<td>451, 478 (THF) 455,480(CHCl₃)</td>
<td>398 (THF) 398(CHCl₃)</td>
<td>0.46(THF) 0.47(CHCl₃)</td>
<td>78,500</td>
</tr>
<tr>
<td>P3HTE&lt;sup&gt;d&lt;/sup&gt;</td>
<td>438 (THF)</td>
<td>525, 535 (THF)</td>
<td>420 (THF)</td>
<td>0.18 (THF)</td>
<td>20,100</td>
</tr>
</tbody>
</table>

<sup>a</sup>Solvent is shown in parenthesis. <sup>b</sup>Fluorescence excitation \( \lambda_{\text{max}} \) observed while monitoring at fluorescence \( \lambda_{\text{max}} \). <sup>c</sup>Quantum yields are measured in CHCl₃ and THF solvent while excited at excitation \( \lambda_{\text{max}} \).

<sup>d</sup>Region random Poly(3-hexylthiénylene ethynylene).²⁴

**Photoluminescence.** PPETEs exhibited strong green luminescence in organic solutions. The fluorescence spectra were obtained from diluted and deoxygenated THF solutions (Figure 14). All spectral data are summarized in Table 2. Similar to the fluorescence of PPE<sup>3</sup> and PTE<sup>2⁴</sup>, two well-resolved bands (high and low energy emissions) were observed in PPETEs, suggesting the existence of similar pathways for the radiative decay of the excited states. The PL quantum yields were determined relative to quinine sulfate. The PPETEs were found to be highly luminescent in solutions with quantum efficiencies ranging from 0.37 to 0.48, which are quite comparable with those of
PPE homopolymers\textsuperscript{30} ($\phi_n = 0.35$-$0.40$). The quantum yields ($\phi_n$) of PPETEs were measured in both THF and CHCl$_3$, giving very similar values (Table 1). It should be noted that the $\phi_n$ values of PPETE are significantly larger than an isomeric structural analogue poly($m$-phenylene ethynylene-$alt$-thienylene ethynylene)\textsuperscript{31} whose $\phi_n$ value in CHCl$_3$ is reported to be only 0.18. The greater enhancement observed in the $p$-phenylene-containing PPETE is presumably due to the longer conjugation length permitted by $p$-phenylene than by $m$-phenylene in the PPETE polymers.

It is also interesting to make a comparison between the photophysical properties of PPETE and P3THE.\textsuperscript{24} Only slight changes in the absorption $\lambda_{\text{max}}$ are observed between P3HTE and PPETEs (Table 2), indicating similar conjugation lengths between the two polymer system. The PL quantum efficiencies of PPETEs, however, are about 2.5 times as high as P3HTE ($\phi_n=0.18$). Clearly alternate replacement of the thiophene rings along the P3HTE chain with phenyl rings has a large impact on the nonradiative decay process. The enhancement is even more pronounced in the solid state, as the film of PPETE emitted about 15 times stronger than P3THE with a head-to-tail chain sequence (Figure 15) under the identical conditions. In summary, synthesis of copolymer PPETE successfully combines both good solubility and processability of PTE and high luminescence of PPE into a single polymer chain, making the material attractive for device applications.
Figure 14. Normalized fluorescence spectra of PPETEs in THF solvent.

Figure 15. Fluorescence spectra of PPETE 24 and PTE 12 films.
References and Notes:


12. Upon standing at room temperature for a five days, neat 2,5-diethynyl-3-hexylthiophene and thiienylacetylene 11 were gradually polymerized to insoluble dark brown resins. IR and solid $^{13}$C NMR (CPMAS) of the solid indicated that most acetylenic carbons had been converted to olefinic carbons. Solutions of thiienylacetylenes ca. 20% in hexanes, however, can be stored in refrigerator for a few weeks without significant change.


