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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 /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 Øfl=0.37 - 0.48, which is much higher than for PTE (Øfl = 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-alkylthienyl)ethyne **5** in high yield. Various attempts has been made to use **5** as an essential building block for developing novel poly(arylene ethynylene) materials.

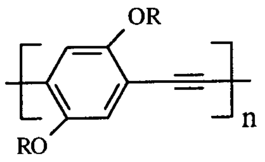
Regioregular poly(3-hexyl-2,5-thienylene ethynylene)s (P3HTE) have been synthesized in order to compare the steric interaction in the corresponding polymers. A systematic study has been carried out to evaluate the regioregularity effect of the polymer structure on the PL properties. P3HTE of a head-to-tail 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 λ_{max}) than the same polymers synthesized at high temperature. The copolymers exhibit a moderate rigidity with Mark-Houwink constant $\alpha = 0.8\text{-}0.9$, which is higher than poly(thienylene ethynylene) (PTE) **20** ($\alpha = 0.68$) but significantly lower than poly(phenylene ethynylene)

(PPE) **1** ($\alpha = 1.92$). The quantum efficiencies of PPETE copolymers are found to be ϕ_{fl} = 0.37 – 0.48, which is much higher than for PTE ($\phi_{fl} = 0.18$) 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.[2-5] 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 seperated 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**.



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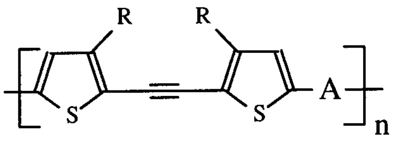

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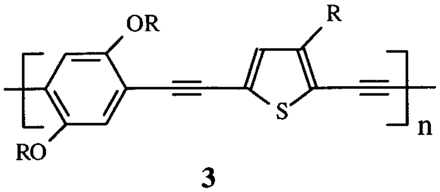

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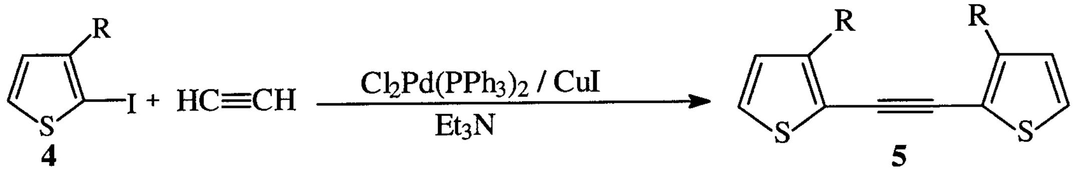
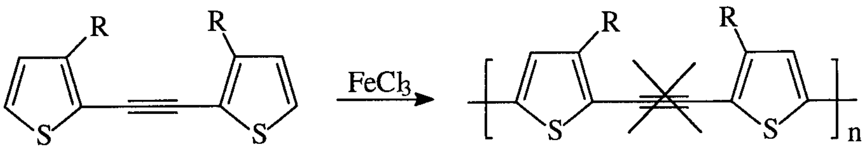
Results and Discussion

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.[6] 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**).[7]

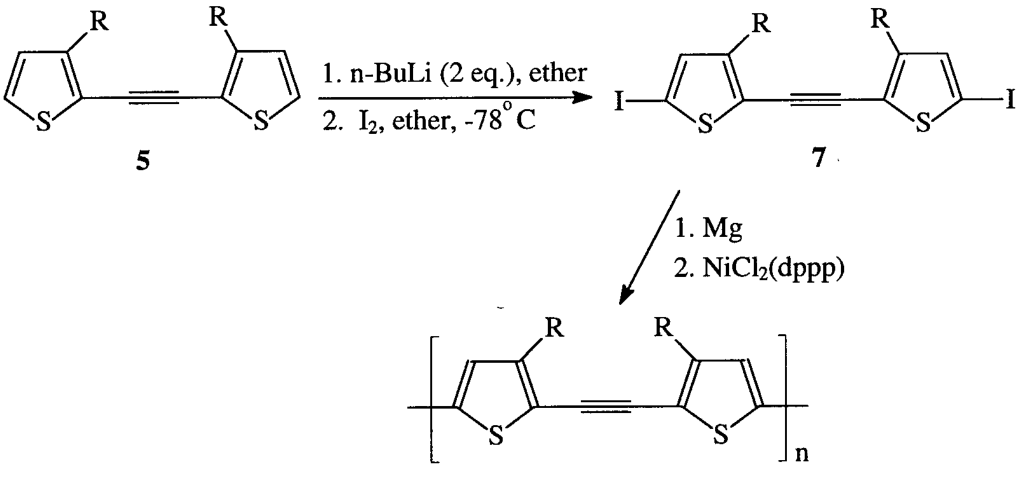


Polymerization study of bis(3-alkylthienyl)ethyne 5. In principle, any polymerization method for thiophene could be used to polymerize **5**. A common methodology for preparing polythiophene **7** is oxidizing thiophene[8] with $FeCl_3$. When bis(3-alkylthienyl)ethyne **5** was treated with $FeCl_3$ 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.



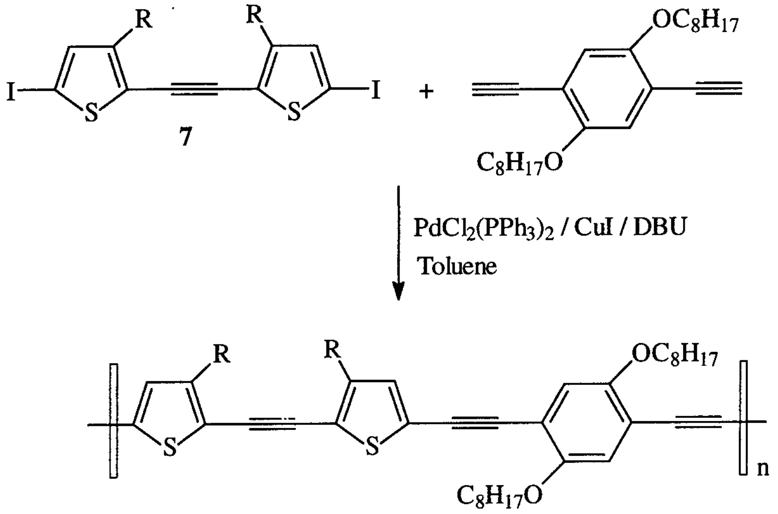
5 **6**

In order to circumvent the problem, bis(3-alkylthienyl)ethyne **5** was transformed to bis(5-iodo-3-alkylthienyl)ethyne **7** via the following reaction sequence.[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. ^{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**.



5 **7** **6**

In order to quickly access the polymer system containing bis(3-alkylthiophene)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 λ_{max} at 496 nm. The quantum efficiency(ϕ_{fl}) was estimated in THF to be about 0.33 when excited at 468 nm.



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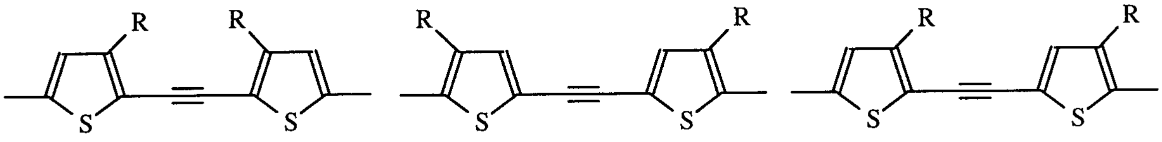
Section 2. Synthesis and Characterization of Regioregular Poly(3-Hexyl-2,5-thienyl ethynylene)s (P3HTEs).

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.



Head-to-Head (**HH**) Tail-to-Tail (**TT**) Head-to-Tail (**HT**)

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.

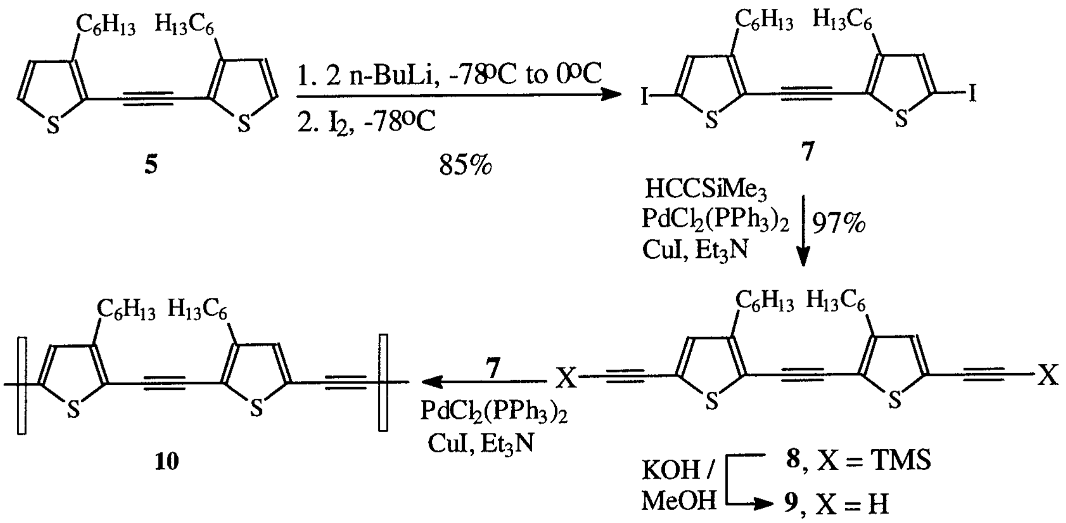
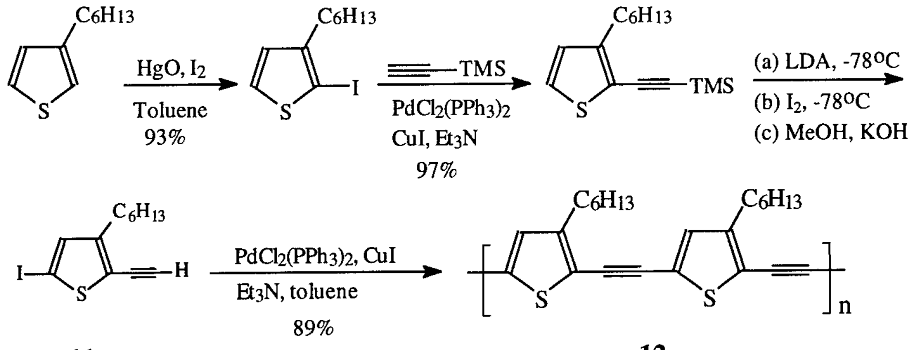


Figure 2. Regiocontrolled synthesis of poly(3-hexyl-2,5-thienyl ethynylene) with the head-to-head and tail-to-tail sequences.

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 necesssary to synthesize poly(3-hexyl-2,5-thienyl ethynylene) **12** with head-to-tail chain sequence, where less steric interaction between sustituents is expected. The desired head-to-tail linkage was achieved through polymerizing 2-ethynyl-5-iodo-3-hexylthiopnene (**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.



11 **12**

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 ^{1}H and ^{13}C NMR. No resonance signals near 3.48 ppm (acetylenic protons) were detected in the ^{1}H 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**. ^{1}H 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.

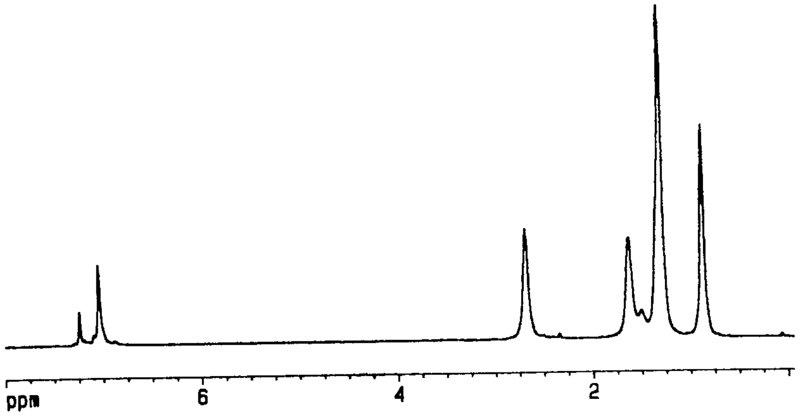
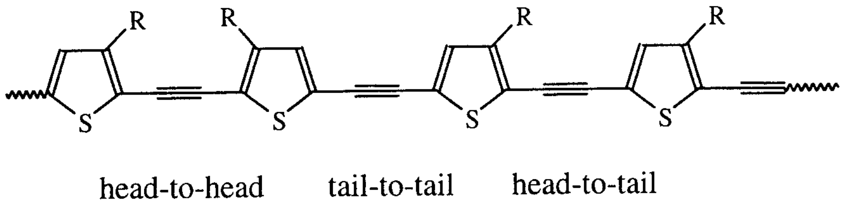


Figure 4. ^{1}H NMR ($CDCl_3$) spectrum of P3HTE **12**. The signal at 7.25 ppm is attributed to $CHCl_3$.

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**.



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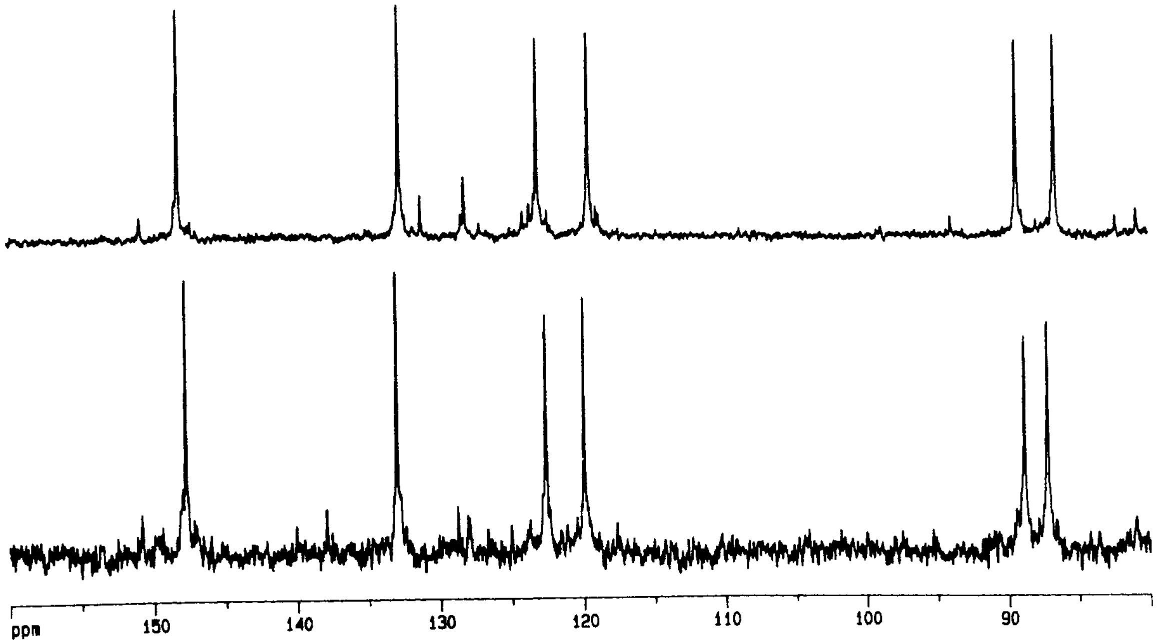
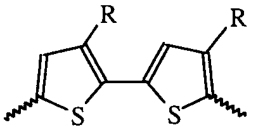


Figure 5. Quantitative ^{13}C NMR spectra of P3HTEs **10** (bottom) and **12** (top), where alkyl region is omitted for clarity.

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 π-conjugating polymers, a fundamental issue is how rigid these molecules are as a result of the extended π-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 $[\eta] = K\,\mathrm{M}^{\alpha}$, 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 α value is as high as 0.96. The striking low α 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.



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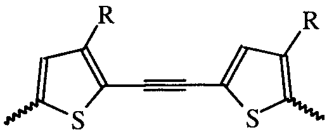

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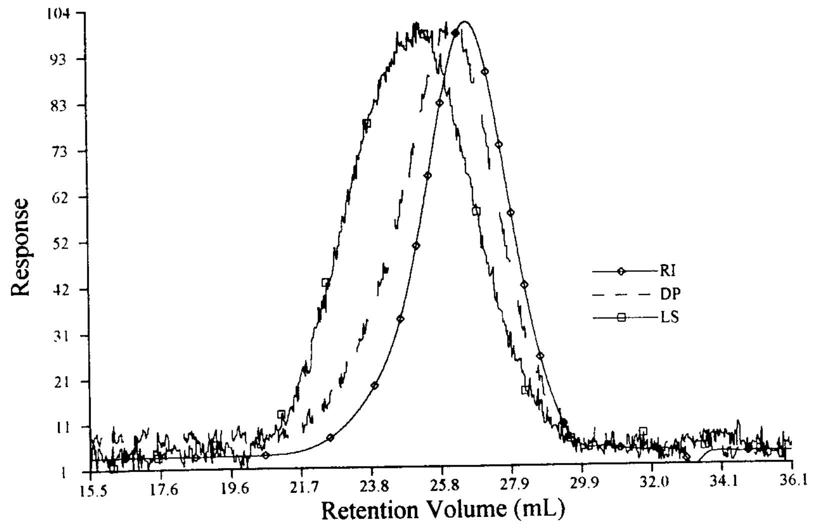


Figure 6. SEC^3 chromatogram of P3HTE **12**.

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 λ_{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 λ_{max} has been reported between regioregular (head-to-tail) and regiorandom poly(3-hexylthiophene)s in $CHCl_3$ solutions. The negligible difference in UV-vis absorption λ_{max} between **10** and **12** suggested that the arrangement of substituents had little effect on the π-π^* 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.

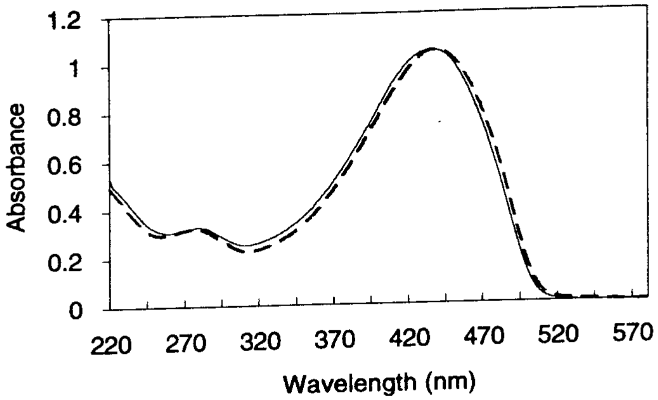
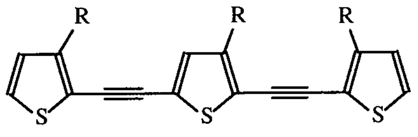


Figure 7. UV-visible spectra of P3HTEs **10** (solid line) and **12** (broken line) measured in the same concentration of THF solutions (0.1 g per liter concentration).

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[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[12,16] of terminal thienylacetylenes which generates the unwanted structural defects during the polymerization.

Different from P3HT[17] where only one emission band is observed, two emission bands were observed in the fluorescence spectra of P3HTE solutions (Figure 8) with λ_{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.



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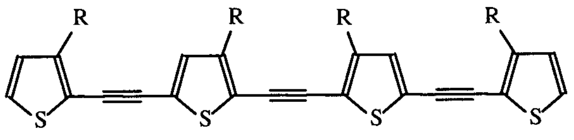

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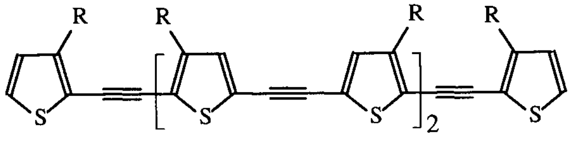

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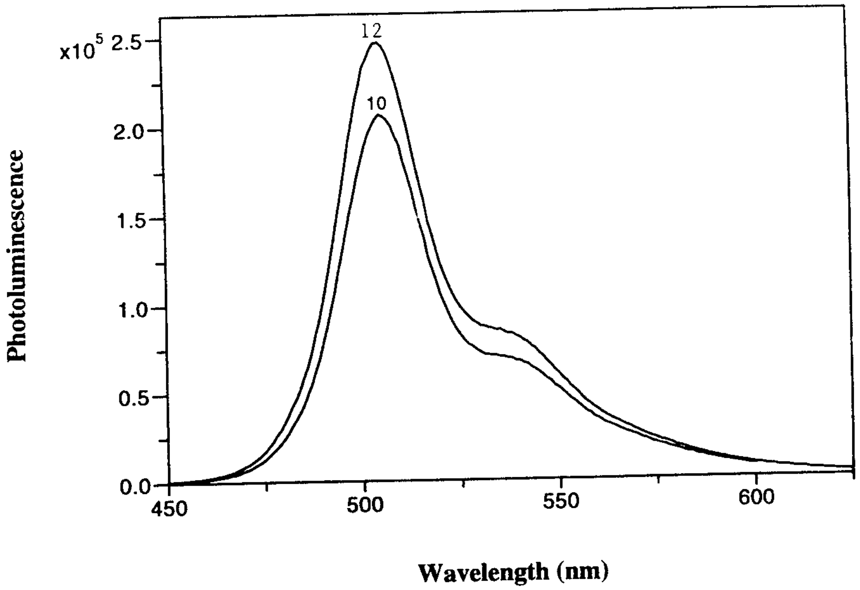


Figure 8. Fluorescence spectra of P3HTEs **10** and **12** showing structured emission bands at about 506 and 536 nm.

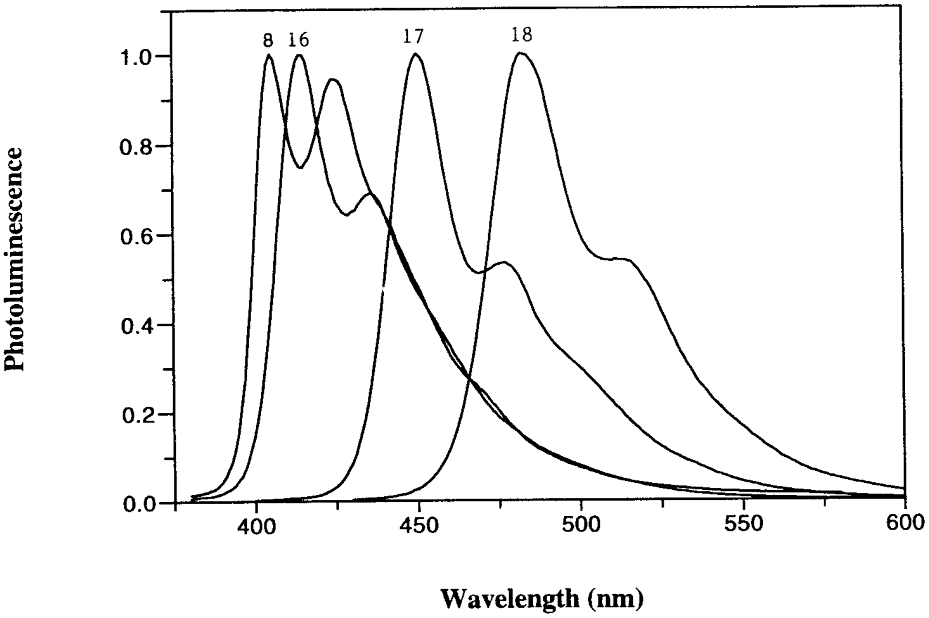


Figure 9. Normallized fluorescence spectra of oligomers **8, 16, 17** and **18**. The relative emission intensity of the low energy band decreases as the conjugation increases.

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 nonemissive 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.[18] Formation of the nonemissive excimer, which has been suggested in P3HT,[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[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[23] of the π-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 1. UV-vis, Fluorescence and ^{13}C NMR (δ(C≡C)) Data for P3HTEs

Compounds	absorption[a] λ_{max} (nm)	fluorescence[a] λ_{max} (nm)	Excitation [b] λ_{max} (nm)	ϕ_{fl}[c]	^{13}C NMR [C≡C] (δ)
12	440 (THF), 441 ($CHCl_3$), 486 (film)	506, 536 (THF) 575 (film)	430	0.20	86.54, 89.27
10	436 (THF), 437 ($CHCl_3$), 488 (film)	505, 535 (THF) 575 (film)	420	0.18	87.19, 88.81
13 (Random P3THE)	438 (THF) 437 ($CHCl_3$) 487 (film)	505, 535 (THF)	420	--	86.79, 87.46, 89.02, 89.61
Dimer **5**	320 (THF)			≈ 0	87.67
Dimer **8**	367,393 (THF)	408, 430 (THF)	370	0.07	88.07, 97.01, 99.73
Trimer **16**	371 (THF)	414, 436 (THF)	370	0.06	87.28, 87.92, 88.81
Tetramer **17**	391 (THF)	450, 476 (THF)	391	0.21	86.98,87.98, 88.57
Hexamer **18**	421 (THF)	484, 514 (THF)	421	0.18	86.79, 87.18, 87.21, 88.69, 89.21

[a] Solvent or the statement of measurement is shown in parenthesis. [b]Excitation spectrum is obtained by monitoring at λ_{max} of fluorescence. [c]Quantum efficiency is measured in THF solution.

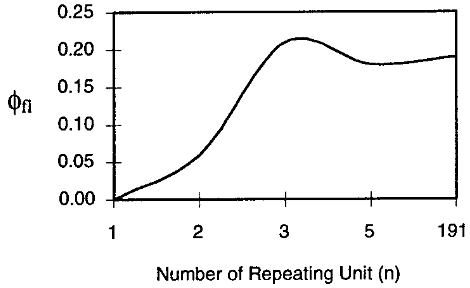
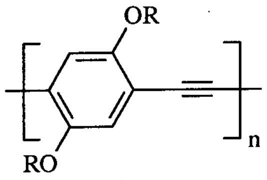


Figure 10. Photoluminescence quantum efficiencies (ϕ_{fl}) versus chain length of poly(3-hexylthienyl ethynylenes).

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

Poly(phenylene ethynylene) (PPE) **1** is a special class of π-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 (α=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 α constant is one of the important parameters to describe undisturbed polymer conformations in solution, correlation between the α values and solution quantum yields of π-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 ($\phi_{fl} \approx 0.2$).[23] As described in the section two of this report, the α 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 α-linked thiophene bridges has a large impact on the long range molecular rigidity and the corresponding physical properties.



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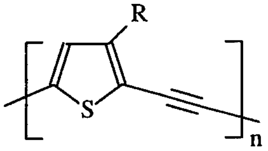

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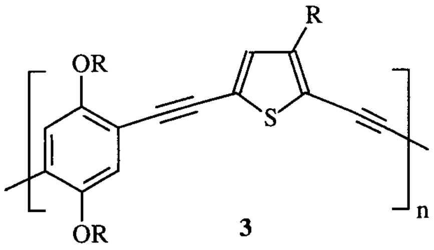

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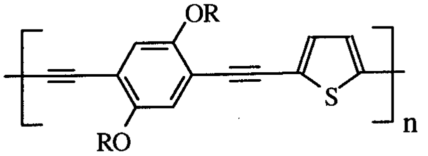
It is obviously desirable to develop poly(arylene ethynylene) materials which exhibit both the high luminescence of PPE **1** and processibility of PTE **20**. A standard approach is to place both *p*-phenylene-ethynylene and α- linked thiophene-ethynylene units into a single polymer chain as shown in **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 α- 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[10] and others,[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*-thienylene ethynylene)s (PPETEs **22-24**) were prepared by Heck-type coupling.[27] 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_3N 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.

$$\equiv\!-\mathrm{Ar}-\!\equiv \quad + \quad \mathrm{I}-\mathrm{Ar'}-\mathrm{I} \xrightarrow[\mathrm{Et_3N,\ Toluene}]{\mathrm{PdCl_2(PPh_3)_2\ /\ CuI}} \mathbf{PPETE}$$



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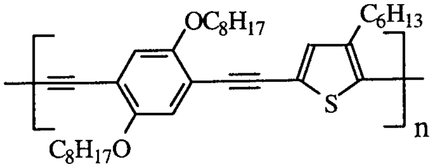

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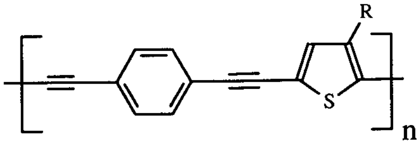

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Figure 11. Synthesis of alternating *co*-polymer PPETEs, where Ar and Ar' represent the corresponding phenyl and thiophene rings.

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 ^1H 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 λ_{max} values of the polymers are listed in Table 2. It is noted that the absorption λ_{max} values of PPETE **22** and **24** are at 444 and 413 nm, which are about 11 nm longer than the same polymers[20,26a] prepared at elevated temperature. Clearly the mild polymerization conditions are important in synthesizing poly(arylene ethynylene)s since phenylacetylenes[28] are susceptible to thermal reactions.

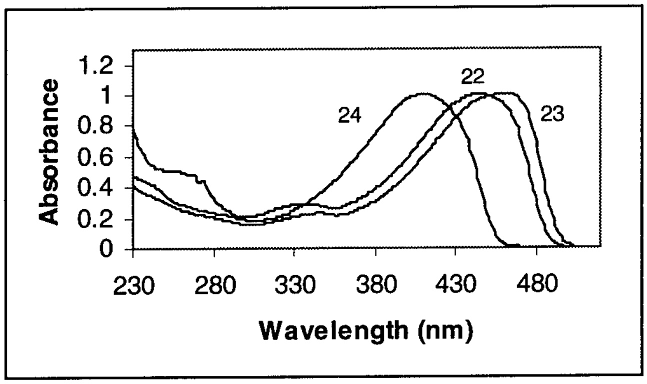

Figure 12. UV-vis absorption spectra of **22-24** measured in THF.

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^3). A typical SEC^3 chromatogram is shown in Figure 13, indicating a monomodel 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[29] for condensation polymerization and in agreement with the linear polymer structure.

For π-conjugated polymers, a fundamental issue is how much molecular rigidity is imparted by the extended π-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 α 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[24] ($\alpha = 0.68$) but significantly lower than PPE[20] ($\alpha = 1.92$). The low α 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.

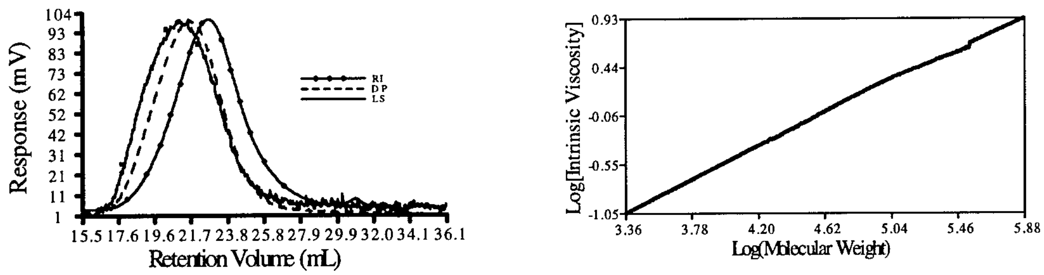

Figure 13. SEC^3 chromatogram (left) and Mark-Houwink plot (right) of PPETE **23**.

Table 2. UV-Vis, fluorescence and molecular weight data for PPETEs.

Polymer	Absorption[a] λ_{max} (nm)	Flluorescence[a] λ_{max} (nm)	Excitation λ_{max} (nm)[b]	ϕ_{fl}[c]	Mw (PDI)	Mark-Houwink constant α
22	444 (THF)	482, 514 (THF)	450 (THF)	0.37 (THF)	43,900	0.88
	444($CHCl_3$)	485,518($CHCl_3$)	450($CHCl_3$)	0.37($CHCl_3$)	(2.12)	
23	460(THF)	489, 520 (THF)	468 (THF)	0.48(THF)	61,600	0.82
	457($CHCl_3$)	492,524($CHCl_3$)	468(CHCl)	0.47($CHCl_3$)	(2.15)	
24	414 (THF)	451, 478 (THF)	398 (THF)	0.46(THF)	78,500	0.88
	413 ($CHCl_3$)	455,480 ($CHCl_3$)	398 ($CHCl_3$)	0.47($CHCl_3$)	(2.27)	
P3HTE[d]	438 (THF)	525, 535 (THF)	420 (THF)	0.18 (THF)	20,100	0.68
					(1.9)	

[a] Solvent is shown in parenthesis. [b] Fluorescence excitation λ_{max} observed while monitoring at fluorescence λ_{max}. [c] Quantum yields are measuured in $CHCl_3$ and THF solvent while excited at excitation λ_{max}. [d] Regiorandom Poly(3-hexylthienylene 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[3] and PTE[24], 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[30] (ϕ_{fl} = 0.35-0.40). The quantum yields (ϕ_{fl}) of PPETEs were measured in both THF and $CHCl_3$, giving very similar values (Table 1). It should be noted that the ϕ_{fl} values of PPETE are significantly larger than an isomeric structural analogue poly(*m*-phenylene ethynylene-*alt*-thienylene ethynylene)[31] whose ϕ_{fl} 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.[24] Only slight changes in the absorption λ_{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 (ϕ_{fl}=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.

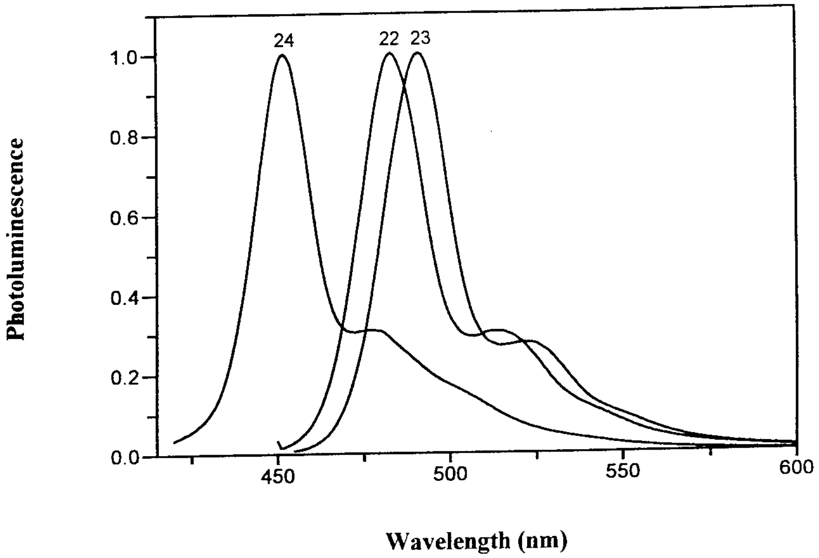

Figure 14. Normalized fluorescence spectra of PPETEs in THF solvent.

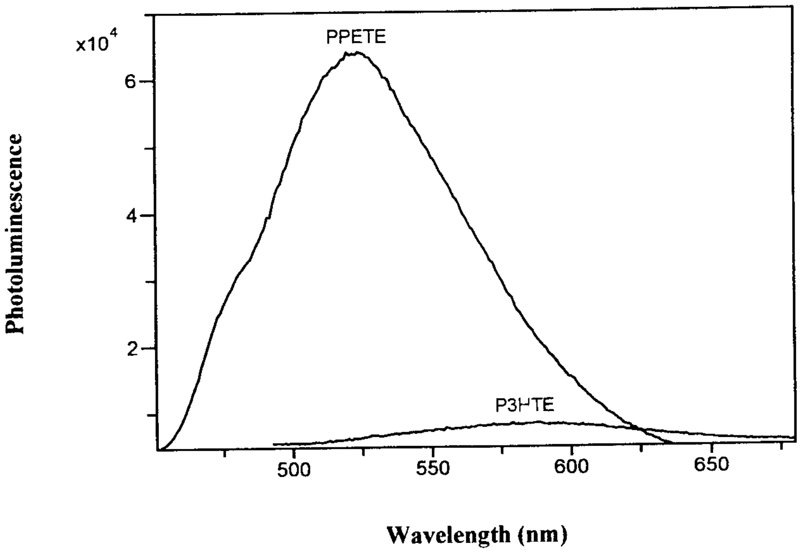

Figure 15. Fluorescence spectra of PPETE **24** and PTE **12** films.

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