GRAFTED AND CROSSLINKABLE POLYPHENYLENEETHYNYLENES: SYNTHESIS, PROPERTIES AND THEIR APPLICATIONS

A Dissertation
Presented to
The Academic Faculty

By

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In Partial Fulfillment
Of the Requirements for the Degree
Doctor of Philosophy in Chemistry

Georgia Institute of Technology
December, 2005
GRAFTED AND CROSSLINKABLE POLYPHENYLENEETHYNYLENES: SYNTHESIS, PROPERTIES AND THEIR APPLICATIONS

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ACKNOWLEDGEMENTS

Thank God for His blessing and guiding. I can’t imagine that I could complete all those on my own. Also, I wish I can express my appreciation to the following people who have been supporting and helping me through these three year’s hard time: My advisor, Uwe Bunz, for allowing me to join his group and guiding me; my wife, Liqun Wang, and my parents, Zaizhong Wang and Meiyu Wu for their unconditional support; all Bunz’s group members, especially, James Wilson, Sandra Shotwell, for their helping on my research and three year’s happy time; my committee members and everyone else.
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List of Abbreviations

CD  circular dichroism
CV  cyclic voltametry
CPPL circularly polarized photo luminescence
DSC differential scanning calorimetry
eV  electron volts
Fc  Ferrocene
FTIR  Fourier transform infra red
GPC  Gel Permeation Chromatography
HOMO highest occupied molecular orbital
IR  infra-red
LED light emitting diode
LUMO lowest unoccupied molecular orbital
Mₐ  number average molecular weight
Mp  melting point
MS  mass spectrum
Mₕ  weight average molecular weight
NBS  N-bromosuccinimide
NLO  non-linear optics
NMR  nuclear magnetic resonance
OLED organic light emitting diode
PAE poly(aryleneethynylene)
PDI polydispersity index
<table>
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<td>PE</td>
<td>polyester</td>
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<tr>
<td>PL</td>
<td>photoluminescence</td>
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<tr>
<td>PPE</td>
<td>poly(paraphenyleneethylene)</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(paraphenylenevinylene)</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
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<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
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<tr>
<td>TCE</td>
<td>tetrachloroethane</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscope</td>
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<tr>
<td>$T_g$</td>
<td>glass transition</td>
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<tr>
<td>TLC</td>
<td>thin layer chromatography</td>
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<tr>
<td>UV-vis</td>
<td>ultraviolet-visible</td>
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<td>V</td>
<td>volts</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>$\Phi$</td>
<td>quantum yield</td>
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Summary

This thesis presents the first reported grafted PPE - polycaprolactone-g-PPE; the first PPE based sensing model: biotinylated grafted PPE/streptavidin coated sphere; the first photocrosslinkable PPE – allyloxy PPE; and the new mechanism which demonstrates morphology control on a single molecular level.
Chapter 1
Grafted and Crosslinkable PPEs: Background and Proposed Research

1.1 Introduction

Conjugated Polymers are semiconducting materials, with potential applications covering all the opto-electronic areas, such as light emitting diodes (LEDs), lasers, photovoltaic cells, and transistors.

As an important member of the conjugated polymer family, poly(paraphenyleneethynylene)s (PPEs) have been intensely studied during the last decade. There are three major synthetic approaches to PPEs: metathesis, acetylene gas, and diiodo/dialkyne coupling. PPEs with different side chains have been successfully synthesized. The primary function of side chains such as alkyl and alkoxy groups are to provide solubility for the polymers. Side chains also can give PPEs specific functions such as sensing proteins or metal ions, tuning energy gaps, changing morphologies in the solid state, etc.

Polymers with rigid-coil structures are expected to form self-assembling morphologies. PPEs have rigid backbones, therefore, not surprisingly self-assembly is observed for PPE-containing copolymers. Several PPE-containing AB and ABA block copolymers have been made and investigated for their phase behavior, optical properties and self-assembly. Such AB block copolymers can form spectacular morphologies, fibrous and self-assembled conjugated nanotubes.
The exciting results from the studies of PPE block copolymers motivated us to investigate grafted PPEs before we entered the field. Due to the difficulty of synthesis, PPEs with macromolecular substituents were less studied. Compared with block copolymers, grafted PPEs have more complicated structures, therefore, the morphologies and properties of grafted PPEs are more difficult to be predicted. There are several reasons for studying grafted PPEs: 1.) achieve novel structures by self-assembly of suitable grafted PPEs—e.g. mesoscopic nanospheres, nanowires, bicontinuous networks, bubble arrays; 2.) improve solubility—e.g. water solubility, and 3.) study the influence of morphology on their solid state optical properties.

Crosslinkable PPEs are useful for device applications such as light emitting diodes, photovoltaic cells, transistors, sensory laminates and potentially waveguides. These PPEs can achieve a designed microstructure by UV irradiation or thermal crosslinking. After crosslinking, their thermal and chemical stability can be greatly improved.

1.2 General Synthesis of PPEs

There are three major synthetic approaches to obtain PPEs: 1.) the classic synthesis of PAEs is the Pd-catalyzed coupling of dihaloarenes (Br, I) with diethynylarenes (Scheme 1.1). The polymers obtained from this method normally do not have high molecular weight, and they also contain butadiyne defects. However, the mild reaction conditions tolerate many functional groups such as hydroxyl, azide, and TEMPO.
Scheme 1.1. Synthesis of PPEs by the Pd-catalyzed reaction of aryldihalides with dialkynylarenes.

2.) A similar way of making PPEs is the Pd-catalyzed reaction of aromatic dihalides with acetylene gas (Scheme 1.2). Higher molecular weight polymers are easier to achieve. The reaction conditions are similar to those described for route 1, in that they tolerate many functional groups. The reaction is performed under exclusion of air to prevent defect formation.

Scheme 1.2. Synthesis of PPEs by the acetylene gas method.

3.) Alkyne metathesis is the best method to prepare defect-free dialkyl and dialkoxy PPEs (Scheme 1.3).
Scheme 1.3. Synthesis of PPEs by alkyne metathesis utilizing in situ catalysts.

The third method—alkyne metathesis produces the highest quality PPEs: defect free and of high molecular weight. However, the reaction conditions are too harsh to tolerate functional groups such as hydroxyl and ester. Therefore, to make grafted PPEs and crosslinkable PPEs, the synthesis was restricted to Pd catalyzed methods.

Scheme 1.4. Catalytic cycle. I oxidative addition; II transmetalation; III reductive elimination
From studying the catalytic cycle (Scheme 1.4)\textsuperscript{5b}, it is found that Pd(0) is the active species which catalyzes the polymerization.

1.3 Grafted PPEs: Synthesis and their applications

The first and the most important question here we are facing is: how to synthesize the grafted PPEs? As mentioned previously in this chapter, syntheses of grafted PPEs are restricted to the Heck-Cassar-Sonogashira-Hagihara coupling reaction method. The mild reaction conditions tolerate functional groups such as hydroxyl and TEMPO which are essential for synthesizing grafted PPEs. Controlled “living” polymerization is chosen to attach macromolecular substituents to the PPE backbones. This polymerization method furnishes polymers with narrow polydispersities.

Polycaprolactone-g-PPE\textsuperscript{7}, which will be discussed in chapter 2, was the first grafted PPE ever reported (Scheme 1.5). Since then, other grafted PPEs have been synthesized. The synthetic approaches can be divided into two major methods: 1.) synthesize macromolecular monomers first, and then polymerize them. Polycaprolactone-g-grafted PPE, polylactide-g-PPE, polyoxazoline-g-PPE and polycaprolactone diethylhexyl PPEs copolymers were successfully prepared by this method (Figure 1.1). 2.) Synthesize PPEs first, and then graft polymer onto the PPE backbone by post polymerization. Polystyrene grafted PPEs\textsuperscript{9} were made by this method (Scheme 1.6). Other grafted PPEs such as polychloromethylstyrene-g-PPE and polylactide-g-ethylhexyl PPE copolymers were obtained by this method (Figure 1.2).
Scheme 1.5. Synthesis of the PPE with a macromolecular polycaprolactone substituents.

Scheme 1.6. Synthesis of polystyrene grafted PPE
Figure 1.1. Grafted PPEs synthesized by method 1

Figure 1.2. Grafted PPEs synthesized by method 2
The polycaprolactone grafted PPEs has been investigated. As a grafted polymer, this PPE not only combines properties from both polycaprolactone and PPE, but also displays characteristics that can neither be obtained from polycaprolactone nor from PPE, e.g., it shows the strong blue fluorescence from the conjugated main chains in solution which is identical to the regular PPEs, but in the solid state, it is less aggregated or non-aggregated, depending on the length of polycaprolactone side chains. It inherits its crystalline structure in the solid state from the polyester side chains.

Polycaprolactone grafted PPEs have been successfully synthesized and their optical properties are investigated. The second most important question to ask is “how to make it” is: “What can it be used for?”

As a result of “living” polymerizations, the reactive hydroxyl end groups on the polyester side chains enable the grafted PPEs to be reacted with a biotin attached acid chloride (Chapter 3). The polyester side chains improve the water solubility of the PPE. By attaching a biotin functional group, polyester grafted PPEs were used as bio-sensing materials in water. Biotinylated PPE/streptavidin coated polystyrene spheres which were used as sensing model is the first PPE based biosensing model, and it provides convincing evidence that PPEs can be used as biosensors. Based on this conclusion, further investigation of bio and metal ion sensing by PPE deriveds were carried out in our group which lead to several good quality publications from the Bunz group.

However, the polyester side chain made from caprolactone does not confer true water solubilities, although it can become soluble in water with the help of a surfactant. Water solubility is a basic requirement for bio-applications, because most bio-materials will be either insoluble or denatured in organic solvents. To improve the water solubility,
polylactide grafted and polyoxazoline grafted PPEs (Chapter 4) were synthesized. Compared with polycaprolactone grafted PPEs, the density of the hydrophilic ester groups on the polylactide side chain is doubled, and the polylactide grafted PPE dissolves well in a 10:1 mixture of water and acetone. Polyoxazoline grafted PPEs show a much better solubility in water, but its emission spectrum in water shows slight aggregation.

Polystyrene was grafted onto PPEs by nitroxide initiated controlled living radical polymerization (Chapter 5). When chloromethylstyrene was utilized, a more complex structure could be obtained by double grafting. This hydrophobic polystyrene grafted PPEs is an important addition to the hydrophilic polyester grafted PPEs.

In Chapter 6, self-assembly of partially grafted PPEs are discussed. PPEs are rigid rod-like polymers, so if their macromolecular grafted side chains are relatively flexible and within a particular weight percentage, nanophase separation is expected. PPEs with 40%-50% (by weight) polylactide and polycaprolactone were synthesized and as we expected, nanophase separation was observed by AFM (Figure 1.3). Surprisingly, the mechanism of self-assembly in this case is different from Hillmyer’s systems. Doughnut-like circles were proven to the result of the bending of single or a few molecules.
1.4 Crosslinkable PPEs: Synthesis and their applications

Photocrosslinkable conjugated polymers are of interest. They can be easily microstructured utilizing photolithography. The mild conditions of Pd-catalyzed Heck-Cassar-Sonogashira-Hagihara coupling reactions allow us to attach crosslinkable functional groups onto the backbone of PPEs.\(^{10}\)

![Scheme 1.7. Synthesis of AllyloxyPPE](image)
AllyloxyPPE can be thermal or photo crosslinked. After crosslinking, the polymer becomes insoluble in organic solvents, but it is still fluorescent, which indicated that the backbone of the PPE survive.

2D and 3D microstructures were fabricated as a demonstration of photocrosslinking, and picoliter beaker as demonstration of thermal crosslinking.

![Images of 2D pattern, 3D photonic crystal, and picoliter beaker]

Figure 1.4. (a) 2D pattern; (b) 3D photonic crystal and (c) picoliter beaker

1.5 Conclusion and Proposed Research

Grafted and crosslinkable PPEs show desirable properties that make them attractive materials for biological sensing and for device fabrication. The chemical properties of PPEs can be tuned by different macromolecular side chains. The crosslinking capability makes fabricating plastic semiconducting devices possible for the material scientists. Based on all the data we have obtained so far, we propose the following goals as further developments for the grafted PPEs and crosslinkable PPEs:

1) Investigate the function of long macromolecular side chains in the solid state, and determine how the properties of those side chains effect the excimer formation.

2) Partially grafted PPEs can form nanoscale phase separation. How we can control the phase separation?

3) Investigate the post-modification of crosslinked PPE bubble arrays.
1.6 References


Chapter 2
Synthesis and Characterization of Polyester Side Chain Substituted Poly (p-phenyleneethynylene)s

2.1 Introduction

Poly(paraphenyleneethynylene)s (PPEs)\(^1\) are a specific class of conjugated polymers in which benzene groups are linked by alkyne units. Their high fluorescence quantum yield and their well developed chromicity\(^2,3\) make PPEs attractive as sensors\(^4\) and as active layers in semiconductor devices.\(^5,6\) While structural variations on PPEs\(^7-11\) have been reported, to our knowledge, PPEs with macromolecular substituents have not been described. Such graft copolymers would be of interest a) as novel macromolecular architectures, b) as a means to obtain the optical properties of PPEs in the solid state at high intrinsic backbone dilution, and c) as embedded, nanoscale separated materials with potentially unusual mechanical and solubility properties.

2.2 Results and Discussion

The synthesis of a grafted PPE was started by reacting 2.1 with \(\varepsilon\)-caprolactone catalyzed by Sn(O–C=OCHEtBu)\(_2\). As in a typical ring opening reaction, the resulting telechelic macromonomer 2.2 (Scheme 2.1) had a very narrow polydispersity index (PDI) (< 1.5) and its molecular weight could be well controlled by the ratio of 2.1 and \(\varepsilon\)-caprolactone. The yield of 2.2 (48%) was not very high because 2.2 partially soluble in
methanol. An acetylene gas route was chosen to synthesize polyester grafted PPEs because this method could tolerate hydroxy and ester functional groups. As a base, both piperidine and triethylamine were tested, and piperidine gave better results. The chemical stability of 2.2 in pipridine was checked by mixing 2.2 (1.0 g) and piperidine (10 mL) together and stirring at room temperature for 24 h. By $^1$H NMR, no decomposition of 2.2 observed. To synthesize 2.3, 2.2 was dissolved in THF and piperidine. The solution of this macromonomer was extremely difficult to degas because of its high viscosity. Addition of a trace amount of (Ph$_3$P)$_2$PdCl$_2$ (0.2 mol%), CuI, and a measured quantity of acetylene gas$^{12}$ furnished a deep-yellow, flaky, material after
precipitation from acidified methanol. The color and the following gel permeation chromatography (GPC, vs. polystyrene) showed that 2.3 had formed in 78% yield. The GPC trace of 2.3 was monomodal but with a broad distribution of molecular weights. The polydispersity index (PDI) was 5.3 and the $M_n$ of 2.3 was recorded to $3.36 \times 10^5$. The polymer had a degree of polymerization ($P_n$) of 140 repeating units. In the $^{13}$C NMR spectra of 2.3 the resonances of the grafted-on polyesters were prominent, but the signals attributable to the conjugated main chain were weak and thus difficult to discern. Due to the substitution pattern at the benzene ring and the innate non-regioselectivity of the Pd coupling, the alkyne carbons in 2.3 should show four resonances and the benzene rings should show six resonances in its $^{13}$C NMR spectrum, exacerbating the problem of the low signal to noise ratio of the backbone carbon resonances.

Scheme 2.2. Synthesis of a PPE 2.5 with TIPS substituents. i. Yield of 2.4 = 98%. ii. See Scheme 1. Yield of 2.5 = 98%, $M_n = 37 \times 10^3$ (GPC), PDI = 3.9, $P_n = 117$
To demonstrate that Pd-catalysis works well for this substitution pattern (Scheme 2.2) we prepared a model polymer that shares the backbone with 2.3 but features simpler solubilizing groups. The microwave-mediated coupling (5 min reaction time) of 2.1 with chlorotriisopropylsilane in imidazole furnished the monomer 2.4 in a 98% yield a colorless oil after chromatography. Treatment of 2.4 under conditions optimized for the synthesis of 2.3 gave a high molecular weight polymer 2.5 that was soluble in halogenated organic solvents. At concentrations higher than 2.5 wt% 2.5 slowly formed a blue-fluorescent but clear jelly in dichloromethane or in chloroform. The aromatic and alkyne regions of the $^{13}$C NMR spectrum of 2.5 are superimposable with that of 2.3 and shown in Fig. 2.1. As expected, the signals of the alkyne carbons and the benzene rings are split due to the non-equivalency of the side chains in the monomer 2.4 and the inset shows the split of the alkyne resonances at 92 ppm into four signals.

Fig. 2.1. $^{13}$C NMR of model polymer 2.5. Visible are the four alkyne peaks at $\delta = 92$ (see inset) and the five resolved signals for the benzene rings. The large signal at $\delta = 77$ is due to CDCl3. TIPS signals are not shown. The signal at $\delta = 31$ is a hydrocarbon impurity.
The UV-vis and emission spectra of polymers 2.3 and 2.5 in chloroform solution and in thin films are shown in Fig. 2.2. Their optical properties are similar to each other and in accord with the spectroscopic data recorded for dialkyl-PPEs\(^1\) where \(\lambda_{\text{max}}\) (solution) is 388 nm and \(\lambda_{\text{max}}\) (thin film) is 439 nm. The silyloxy substituent in 2.5 seems to have a slight electron withdrawing effect. As a consequence, \(\lambda_{\text{max}}\) (absorption) is somewhat blue shifted in 2.5. The optical properties of 2.3 in the solid state are unusual. As-spun films
show a $\lambda_{\text{max}}$ (absorption) of 436 nm, typical of dialkyl-PPEs. Upon annealing (4 h, 100 °C) these thin films, their absorption changes back to $\lambda_{\text{max}} = 406$ nm, which is similar to the absorption of 2.3 recorded in chloroform (Fig. 2.2). In addition, the absorption loses almost all structure. The emission of the films changes much less upon annealing and only a small shift from 519 to 504 nm is observed when going from the pristine to the annealed films. The fluorescence intensity does not change visibly upon annealing. At the same time the annealed thin films of 2.3 are now insoluble in common organic solvents. We assume that the insolubility of the polymers upon annealing is due to an increased order in the polyester side chain.

![Fig. 2.3. X-Ray diffraction of different polyester substituted PPEs. Bottom curve: gel phase. Middle curve: pristine powder. Top curve: annealed powder.](image)

Powder X-ray diffraction (Fig. 2.3) shows that the intensity of the polyester diffraction peaks at 5.6, 4.14, 3.74, and 3.0 Å increases upon annealing, while a diffuse
intensity of diffraction that is visible as a hump at $2\theta = 20–22^\circ$ disappears during the annealing process. This broad diffraction peak at $2\theta = 20–22^\circ$ is typical for the $\pi$-$\pi$-stacking of the PPEs and is the most intense diffraction in these materials.\textsuperscript{13,14} The annealing increases the ordering of the polyester side chains, but it seems to decrease the ordering of the PPE main chain, \textit{i.e.} in the competition of main chain and side chains, the side chains win and lead to a twist and a gross disorder of the PPE main chain in the solid. In the powder diffraction of the annealed sample there are no signs of the diffraction of the main chain left.

A drop-cast film of 2.3 shows crystalline features (Figure 2.4) which are often seen from polyester types polymer. Upon annealing, the size of crystals grow much larger. This is further evidence that the order of polyester side chain is increased during the annealing.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image.png}
\caption{Crystalline structure of 2.3}
\end{figure}

Nonemissive interchain excitons are responsible for low quantum yields of conjugated polymers in solid state.\textsuperscript{15} Mixtures of conjugated polymer with other
nonconjugated polymer such as polystyrene suffer from phase separation, and conjugated polymers with dendritic sidegroups was found to prevent interchain interaction from two dimensions. A grafted PPE was designed to solve this problem.

Scheme 2.3. Synthesis of PPE with super long macromolecular polyester side chain.
The emission spectra of the thin film made from polymer 2.3 still shows aggregation, so 20 polyester repeat units apparently do not enough steric bulk to the PPE chain to prevent interchain interactions. To achieve longer polyester side chain grafted PPEs (i.e., \( P_n = 60 \)), the method used in Scheme 2.1 is no longer suitable. There are two reasons, first is the high viscosity of reaction mixture, and the second is steric hinderance from the large side chain. Due to this reason, Scheme 2.1 was slightly modified. Instead of synthesizing macromonomer 2.2, which has 20 repeated units, 2.6 was synthesized through the same procedure but only had 1-2 repeat units which could provide the desired solubility for the next step. After obtaining 2.7, the polymer was dried under vacuum for 24 h, and then reacted with \( \varepsilon \)-caprolactone. The GPC data showed that 2.8 had a long polyester side chain with 60 repeated units.

A preliminary test was carried out to investigate how the length of the polyester side chain could affect the fluorescence properties in the solid state. Diethylhexyl PPE was used as a reference. Polyester grafted PPE 2.8 and diethylhexyl PPE respectively were dissolved in dichloromethane and their UV absorption and fluorescence intensity were adjusted to the same level. Since their quantum yield is very close (\( \Phi_{\text{diethylhex }} = 100\% \), \( \Phi_{\text{peppe}} = 89\% \)), so the equal fluorescence intensity of polymer solution ensured that the concentrations of PPE repeat units are similar. Emission of spin-cast films with identical absorbance those solutions were checked again. The results showed that PPE with long polyester side chains display higher fluorescence intensity than the fluorescence of diethylhexyl PPE (Figure 2.5). There is less than 10 nm red shift of the solid state fluorescence spectra of polymer 2.8 which compared to its spectrum in
chloroform. The interchain interaction of PPE backbone is dramatically reduced by the macromolecular side chains.

Figure 2.4. Emission spectra of polymer 2.8 and diethylhexyl PPE. Top: emission in the chloroform solution; bottom: emission of thin film.
The mechanical properties of **2.8** are also different from those of regular PPEs. The flexible polyester side chains give this grafted PPE a much improved tensile strength, **2.8** easily forms fluorescent fibers (Figure 2.5)

![Fluorescence Microscope images of fiber prepared from polymer 2.8 with different filters. a.) no filter; b.) blue filter used (allow light with a wavelength under 400 nm to pass); c.) green filter used (between 400-500nm); d.) red filter used (over 500nm)]
2.3 Conclusion

In conclusion we have developed methods to synthesize grafted PPEs. As a demonstration, two new dialkyl-PPE derivatives 2.3 and 2.5 with macromolecular polyester substituents and triisopropylsilyloxy side groups have been prepared and fully characterized by GPC, NMR, DSC. The attachment of the polyester side chain to the PPE leads to a graft copolymer that shows an unusual chromic behavior, in that its $\lambda_{\text{max}}$ (UV-vis) blueshifts upon annealing. The interchain interaction can be prevented or reduced by increasing the length of polyester side chain. The reduced interchain interaction might be very useful and important for conjugated polymer device applications where high fluorescence efficiency is needed.

2.4 Experimental

To a nitrogen purged flask were added 4-methylphenethyl alcohol (21.2 g, 156 mmol), acetic anhydride (79.6 g, 780 mmol), pyridine (400 mL) and 4-dimethylaminopyridine (catalytic amount). The mixture was stirred at room temperature for 6 h. The solvent and excess acetic anhydride were removed in vacuo to afford the desired product as a colorless liquid. The acetate was purified by column
chromatography by using hexane / dichloromethane (1:3) as an eluent. The product was obtained as a colorless oil (25.9 g, 93%). IR (KBr, cm\(^{-1}\)): ν 3460, 2864, 2732, 2073, 1900, 1740, 1514, 1365, 1223, 976, 908, 812, 718, 640, 606, 550. \(^1\)H NMR (CDCl\(_3\)) \(\delta = 7.13\) (s, 4H), 4.30-4.26 (t, 2H, \(J_{3H,H} = 7.0\) Hz), 2.94-2.89 (t, 2H, \(J_{3H,H} = 7.0\) Hz), 2.35 (s, 3H), 2.05 (s, 3H) \(^1\)C NMR (CDCl\(_3\)) \(\delta = 170.82, 135.88, 134.56, 129.04, 128.62, 64.92, 34.50, 20.87, 20.79\).

![Chemical structure](image)

To a nitrogen purged flask, 4-methylphenethylacetate (25.0 g, 140 mmol), iodine (39.1 g, 154 mmol), periodic acid (0.639 g, 2.81 mmol), acetic acid (500 mL), \(\text{H}_2\text{O}\) (100 mL) and \(\text{H}_2\text{SO}_4\) (15.0 mL) were added. The mixture was heated up to 80 °C for 3 h under \(\text{N}_2\). The solvent was removed in vacuo. The residue was dissolved in ethylacetate and washed with \(\text{H}_2\text{O}\), then 1N (aq) \(\text{K}_2\text{CO}_3\) and 1N (aq) \(\text{Na}_2\text{SO}_3\). The organic phase was dried over \(\text{MgSO}_4\) and the solvent was evaporated. The resulting solid was purified by silica gel chromatography using 1:3 kexane / dichloromethane to give product as a colorless solid (51.7 g, 78%). Mp = 55 °C IR (KBr, cm\(^{-1}\)): ν 2945, 2870, 1738, 1516, 1452, 1369, 1232, 1041, 984, 878, 802, 700, 656, 606. \(^1\)H NMR (CDCl\(_3\)) \(\delta = 7.65\) (s, 1H), 7.62 (s, 1H), 4.24–4.19 (t, 2H, \(J_{3H,H} = 7.0\) Hz), 2.98–2.94 (t, 2H, \(J_{3H,H} = 7.0\) Hz), 2.33 (s, 3H), 2.03 (s, 3H) \(^1\)C NMR (CDCl\(_3\)) \(\delta = 170.73, 141.76, 139.76, 139.70, 139.60, 100.76, 100.01, 63.16, 38.48, 26.90, 20.87\).
2,5-diiodo-4-methylphenethyl alcohol (50.0 g, 116 mmol) was dissolved in 65 mL of dichloromethane. After addition of 1.5 L of MeOH and K₂CO₃ (161 g, 1.16 mol), the mixture was stirred at room temperature for 16 h. The solvent was evaporated and the resultant solid was transferred into funnel and washed with H₂O. Recrystallized from hexane, the product was a colorless solid (41.9 g, 93%). Mp = 118 °C. IR (KBr, cm⁻¹): ν 3273, 2950, 2874, 1439, 1371, 1342, 1163, 1041, 1018, 995, 876, 781, 704, 654, 606. ¹H NMR (CDCl₃) δ = 7.66-7.65 (d, 2H), 3.83-3.79 (t, 2H, J₃H,H = 6.8 Hz), 2.93-2.88 (t, 2H, J₃H,H = 6.8 Hz), 2.33 (s, 3H), 1.42 (bs, 1H). ¹³C NMR (CDCl₃) δ = 141.65, 140.39, 139.86, 139.76, 100.91, 100.23, 62.02, 42.49, 26.93.

2,5-diiodo-4-methylphenethyl alcohol (2.00 g, 5.16 mmol), triisopropylsilylchloride (3.96 g, 20.7 mmol), and imidazole (0.975 g, 15.5 mmol) were placed into a pressure tube and capped. The tube was placed in a microwave oven.
(Emerson, 600 watt) and irradiated for 4 x 1 minute pulses. The progress of the reaction was monitored by TLC. The reaction mixture was separated by flash column (hexane: ethyl acetate, 80:20) and excess triisopropylsilyl chloride was removed by vacuum distillation. The silyl ether was obtained as a light yellow oil. Yield 2.75 g (98%). IR (KBr, cm\(^{-1}\)): \(\nu\) 2939.3, 2889.2, 2862.2, 1506.3, 1461.9, 1446.5, 1379.0, 1365.5, 1247.9, 1188.1, 1103.2, 1068.5, 1012.6, 996.2, 921.9, 881.4, 746.4, 680.8, 657.7.  \(^1\)H-NMR (CDCl\(_3\), 300 MHz): \(\delta\) = 7.71 (s, 1H), 7.65 (s, 1H), 3.83 (t, 2H, J\(_{3H,H} = 6.9\) Hz), 2.88 (t, 2H, J\(_{3H,H} = 6.9\) Hz), 2.34 (s, 3H), 1.55-0.99 (m, 21H). \(^1^3\)C-NMR (CDCl\(_3\), 400 MHz): \(\delta\) = 141.47, 141.43, 140.69, 139.74, 100.87, 100.35, 62.81, 43.18, 27.16, 18.24, 12.16.

An oven-dried Schlenk flask cooled under nitrogen was charged with 2,5-diiodo-4-methylphenethylalcohol (2.00 g, 5.16 mmol), \(\varepsilon\)-caprolactone (11.8 g, 103 mmol), and tin(II)-2-ethylhexanoate (127 mg, 313 \(\mu\)mol). The flask was heated while stirring to 110°C. The reaction was stopped after 12 h. The highly viscous product was diluted with 10.0 mL chloroform, then precipitated into 300 mL of methanol. The diiodo-polyester was obtained as a colorless solid. Yield 6.56 g, 48%. GPC (vs. polystyrene standards in chloroform): \(M_n = 2400, M_w/M_n = 1.3\) IR (KBr, cm\(^{-1}\)): \(\nu\) 2941.2, 2893.0, 2866.0, 1722.3, 1683.7, 1652.9, 1506.3, 1471.6, 1456.2, 1394.4, 1294.1, 1244.0, 1190.0, 1107.1, 1045.3, 962.4, 933.5, 877.6, 840.9, 731.0, 709.8. \(^1^H\) NMR (CDCl\(_3\), 400 MHz): \(\delta\) = 7.67 (s, 1H), 7.63 (s, 1H), 4.24 (t, J\(_{3H,H} = 6.8\) Hz, 2H), 4.05 (t, J\(_{3H,H} = 6.8\) Hz, 3H), 3.64 (t, J\(_{3H,H} = 6.6\) Hz, 2H), 2.88 (t, J\(_{3H,H} = 6.9\) Hz, 2H), 2.34 (s, 3H), 1.55-0.99 (m, 21H). \(^1^3\)C-NMR (CDCl\(_3\), 400 MHz): \(\delta\) = 141.47, 141.43, 140.69, 139.74, 100.87, 100.35, 62.81, 43.18, 27.16, 18.24, 12.16.
Hz, 2H), 2.98 (t, J_{3\text{H},H} = 6.8 \text{ Hz}, 2H), 2.30 (t, J_{3\text{H},H} = 7.5 \text{ Hz}, 40H), 1.68-1.60 (m, 80H), 1.41-1.33 (m, 40H) \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 400 MHz): \delta = 173.73, 173.54, 173.29, 141.91, 139.91, 139.87, 139.82, 100.76, 100.03, 64.54, 64.14, 63.95, 63.10, 62.62, 38.64, 34.23, 34.12, 33.95, 33.82, 33.34, 28.53, 28.35, 28.18, 26.96, 25.93, 25.53, 25.31, 24.98, 34.69, 24.58, 24.39.

Figure 2.7 DSC of 2.2 showing 13.3 kJ/mole repeat.

![DSC graph]

A Schlenk flask of known volume (37 mL) was charged with \textbf{6.5} (0.761 g, 1.39 mmol), THF (1.5 mL), piperidine (1.5 mL), (PPh\textsubscript{3})\textsubscript{2}PdCl\textsubscript{2} (2.0 mg, 2.8 \mu mol, 0.2 mol\%) and CuI (1.0 mg, 5.3 \mu mol, 0.4 mol\%). The flask was degassed by three freeze-pump-
thaw cycles. The acetylene gas (34 mL, 1.4 mmol) was added through the purged sidearm by a balloon. The reaction was allowed to stir at room temperature for 48 h during which time the reaction mixture solidified. The reaction mixture was filtered over a small volume of silica (~10 mL) on a fritted funnel with hexane as solvent. The hexane was evaporated, the polymer re-dissolved and precipitated into methanol. A bright yellow polymer (0.514 g, 62%) was obtained. GPC (vs. polystyrene standards in chloroform): $M_n = 37200$, $M_w/M_n = 3.9$. IR (KBr, cm$^{-1}$): ν 2941.2, 2891.1, 2864.1, 2194.8, 1504.4, 1461.9, 1360.9, 1103.2, 1070.4, 1012.6, 996.2, 918.1, 883.3, 742.5, 680.8, 569.6. $^1$H NMR (300 MHz, CDCl$_3$): 7.45 (2H, term. Ph-H), 7.42-7.36 (bm, 2H), 3.94 (bs, 2H), 3.07 (bs, 2H), 2.47 (bs, 3H). $^{13}$C-NMR (400 MHz, CDCl$_3$): δ = 138.39, 138.00, 133.69, 123.36 (broad—2 carbons), 93.58, 63.77, 37.99, 20.53, 18.24, 12.22.

The diiodo polyester was combined with (3.29 g, 1.39 mmol), piperidine (1.5 mL), THF (1.5 mL), (PPh$_3$)$_2$PdCl$_2$ (2.0 mg, 2.8 μmol, 0.2 mol%) and CuI (1.0 mg, 5.3 μmol, 0.4 mol%) in a Schlenk flask (37 mL). Acetylene gas (34 mL, 1.4 mmol) was added through the purged side arm with a balloon. The reaction solidified after 36 h. The resultant polymer was filtered over a cotton plug using dichloromethane as a solvent before precipitating into methanol. The polymer was collected over a fritted funnel, re-
dissolved in dichloromethane and precipitated again. A bright yellow polymer was obtained (2.31 g, 78 % yield). GPC (vs. polystyrene standard in chloroform): 336,000 M_n vs polystyrene standards. Repeat = 2400 g/mol, P_n = 140, M_w/M_n = 5.3 IR (KBr, cm\(^{-1}\)): \(\nu\) 2941.2, 2864.1, 1718.5, 1419.5, 1363.6, 1292.2, 1238.2, 1174.6, 1047.3, 960.5, 933.5, 840.9, 732.9, 709.8. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.41 (bs), 4.36 (bs, 2H), 4.04 (bt, J_{3H,H} = 6.6 Hz, 38H), 3.62 (bs, 2H), 2.94 (bs, 2H), 2.28 (bt, J_{3H,H} = 7.4 Hz, 40H), 1.62 (bm, 80H), 1.36 (bm, 40H). \(^13\)C NMR (400M Hz, CDCl\(_3\)): \(\delta\) = 173.69, 173.50, 13.83, 136.73, 133.40, 132.84, 123.85, 123.18, 93.18, 92.54, 65.15, 64.09, 63.05, 62.55, 34.06, 32.27, 28.29, 25.47, 25.25, 24.52, 20.29.

Figure 2.8 DSC of polymer 6.3 showing 216 kJ/mol repeat for the total curve and 124 kJ/mol repeat for the “peak” of the curve.
XRD

Samples were prepared for powder XRD (Rigaku D\Max-2100 Powder X-Ray Diffractometer, Bragg-Bretano geometry, Cu Kα radiation. All samples utilized the same plate to maintain a consistent background and sample thickness. The samples were run at a step of 0.04° 2θ from 5° to 42°, 2θ. The precipitated PE-PPE was packed into the well and pressed smooth with a glass slide to obtain the plot for “packed aggregates”. A concentrated chloroform solution of the polymer was layered onto the sample holder. This gelatinous sample was run under identical conditions to obtain the “gel” plot. This gel was then annealed at 100 °C for 4h to produce the plot for “annealed gel”.

2.5 References


Chapter 3
Biotinylated Grafted PPEs: the First PPE Based Biosensor*13

3.1 Introduction

Conjugated materials are valuable sensors1 that just begin to penetrate the biological world.2 Spectacular examples are the sensing of DNA strands by cleverly designed polythiophenes, water soluble poly(para-phenylenevinylene) derivatives,3–5 and the use of polydiacetylene vesicles for toxin detection.6

Efficient fluorescence7 and chromic behavior8 make poly-(para-phenyleneethynylene)s (PPE) attractive as candidates in sensory schemes1 and water soluble PPE-derivatives are known.9 However, PPEs substituted with biogenic moieties are largely uncharted waters,5,10 and we were interested in a biotin substituted PPE as a model compound to study interactions of suitably functionalized conjugated polymers with bacterium. In this study, a streptavidin coated polystyrene bead is a primitive model for a cell/bacterium and the biotin/streptavidin interaction mimics the recognition process between conjugated polymer and a “cell surface”. The binding between biotin and streptavidin is very strong. If biotinylated PPEs shows no interaction with streptavidin, there is not worth further investigated biosensing capability of PPEs.

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3.2 Results and Discussion

To obtain a biotinylated PPE, the polymer 3.1 was dissolved in dry THF and treated with the biotin-attached acid chloride 3.2 at 0 °C (Scheme 3.1). The acid chloride 3.2 was prepared according to literature procedures. After allowing the reaction mixture to reach ambient temperature stirring was continued for 4 h. The reaction mixture was precipitated into 250 mL of methanol under vigorous stirring. The polymer 3.3 was isolated by suction filtration, redissolved in 1 mL of THF and precipitated into water to remove all excess of biotin. The successful biotinylation was qualitatively evidenced by IR spectroscopy of the polymer 3.3, while its approximate degree of biotinylation was determined by an agglutination assay utilizing free streptavidin. Based upon this assay every 15th to 20th monomer unit in the PPE chain ($P_n = 140$, gel permeation chromatography) was biotinylated. As a consequence only 7–14 biotin units are attached
to a single polymer chain. This low “loading” of the PPE made it impossible to evidence the presence of biotin by $^1$H NMR spectroscopy. However, the agglutination studies showed convincingly the presence of biotinylated PPEs.

![Image](image.png)

**Fig. 3.1.** Left: composite of polymer 3.3 and streptavidin-coated microspheres agglutinated at the bottom of the Eppendorf cap. The blueish fluorescence is innate to the Eppendorf cap. Right: control experiment in which polymer 3.2 and streptavidin coated microspheres are mixed. No agglutination is observed.

It was of interest to see if the biotinylated PPE 3.3 and its precursor 3.1 would behave differently when exposed to streptavidin-coated microspheres. In a first experiment polymer 3.1 was mixed with streptavidin-covered microspheres. Fig. 3.1 (right) shows that the polymer solution is unchanged and does not alter its emission color. If a solution of 3.3 was mixed with a suspension of streptavidin-coated microspheres (Fig. 3.1, left), the polymer precipitated out as a consequence of the tight binding of the polymer bound biotin to the immobilized streptavidin.
The precipitate obtained by the reaction of 3.3 with streptavidin-coated beads was examined by fluorescence microscopy (Fig. 3.3 a,b,d). The formation of dense “mats” of beads was observed. Surprisingly the beads appeared both blue and red fluorescent when viewed through a DAPI or Texas Red filter respectively (Fig. 3.3 a, b). Preparations of polymer 3.1 exposed to streptavidin beads produced isolated islands of fluorescence upon co-evaporation under otherwise identical conditions. The isolated islands of PPE-fluorescence are only visible under a DAPI filter, while under a Texas Red filter the sample is non-fluorescent. PPE aggregated onto spheres therefore has a measurable fluorescence in the red, while the PPE itself in the solid state does not show this red-shifted feature. To explain this behaviour we took emission spectra of 3.3 in solution, 3.1 with streptavidin in solution and the complex of 3.3 with streptavidin as a suspension. The change in fluorescence is significant (Figure 3.2) and the aggregation causes a disappearance of the blue shoulder visible for (3.1 + streptavidin) and for uncomplexed 3.3. To get a better idea of the microstructure of this composite, we performed scanning...
electron microscopy of the complex. In Figure 3.4a, the egg crate structure of the composite is visible. The conjugated polymer covers the beads evenly giving testimony to the binding between biotin and streptavidin. In Figure 3.4b, the 3-dimensional arrangement of the polymer covered beads is apparent. The control experiment (3.1 + streptavidin-coated beads) on the other hand (Fig. 3.4c) does not show any defined structure, only
islands of polymer 3.1 are visible in the upper half, while three streptavidin-coated beads are isolated in the lower half of the picture.

Figure 3.4. Scanning electron micrographs of a) complex of 3.3 and streptavidin coated microspheres (18 µm 3 18 µm), b) same as in a) but with lower magnification (53 µm x 53 µm), c) control experiment in which nonbiotinylated polymer 3.2 is co-precipitated with streptavidin-coated microspheres. There are no apparent interactions between polymer (islands on top half) and microspheres (bottom white spots, size 452 µm x 452 µm.). The size of the microspheres is in all cases 5 µm.

3.3 Conclusion

In conclusion we have demonstrated that lightly biotin functionalized PPEs form nanocomposites with streptavidincoated microspheres. This primitive system can be seen as a model for the interaction of cells (emulated by the beads) with functionalized conjugated polymers. This model could play an important role in the simple, colorimetric
or fluorimetric detection of pathogens and toxins by PPE-types. This model also provides solid evidences for the first time that PPEs with suitable probes on side chains can be used as biosensors. The success of this project motivates further investigation of the PPEs sensing capability in Bunz group, and it lead to several qualitative publications latterly.\textsuperscript{14}

3.4 Experimental

Biotinylation of 3.1 to form 3.3:

An oven-dried Schlenk flask with stirbar was cooled under \textsubscript{N}2 gas and charged with biotin (122 mg, 0.500 mmol). Excess (~2 mL) thionyl chloride was added and the reaction was capped with a septum and placed into an ice bath. The reaction was occasionally vented with a needle as it reached ambient temperature over a 2 h period. Excess thionyl chloride was removed by vacuum distillation. The product 3.2 was used without purification. Polymer 3.1 (120 mg, 0.0500 mmol) was dissolved in a freshly distilled mixture of THF/triethylamine (5:1) (~2 mL). This solution was pipetted into the reaction vessel containing 2. The reaction mixture was placed again into an ice bath and allowed to reach ambient temperature over the course of 4 hours. The polymer 3.3 was precipitated into excess methanol, collected over a fritted funnel, re-dissolved in THF and precipitated again into water (110 mg collected).

Characterization of 3.1, 3 and biotin by IR:

Spectra were obtained on a Shimadzu 8400 FTIR with a Pike Technologies Diffuse Reflectance attachment and processed with Shimadzu Hyper-IR v 1.57 software including the Kubelka-Munk function to help resolve the peaks. All samples were
scanned 3000 times. The characteristic bands observed at 3307 and 3358 cm\(^{-1}\) were visible in the expansion in the region of 3500 cm\(^{-1}\) to 3200 cm\(^{-1}\) for polymer 3.3.

![Figure 3.5. IR of Biotin.](image)

![Figure 3.6. IR of Biotin (expansion from 3500 cm\(^{-1}\) to 3200 cm\(^{-1}\)).](image)
Figure 3.7. IR of Polymer 3.1.

Figure 3.8. IR of Polymer 3.1 (expansion from 3500 cm$^{-1}$ to 3200 cm$^{-1}$).
Figure 3.9. IR of Polymer 3.3:

Figure 3.10. IR of Polymer 3.3 (expansion from 3500 cm\(^{-1}\) to 3200 cm\(^{-1}\)).
**Preparation of the polymer solutions for exposure to microspheres:**

Polymer 3.3 (20.0 mg, 5.95 x 10^{-5} mmol) was taken up in a small amount (~1 mL) of THF. Dioctyl sulfosuccinate, sodium salt (100 mg, 0.225 mmol) was dissolved in 100 mL of water. The THF solution was added dropwise to the vigorously stirred surfactant solution. This mixture was then heated at ~50° C for 12 hours, then diluted to a total volume of 1.0 L (Stock A). 10 mL of Stock A was lyophilized, then redissolved in 20 mL of 0.1 M sodium phosphate buffer. 1 mL (containing 10 μg of polymer) of this buffered polymer solution was placed into an Eppendorf tube containing 0.5 mg of streptavidin coated polystyrene microspheres. The Eppendorf tube was capped and placed onto a mechanical wrist shaker for 12 h. The agglutinated composite was found to be immobilized on the side of the capsule as seen in Figure 3.1.

**SEM Images:**

Samples of 3.1 and 3.3 exposed to streptavidin coated beads were prepared for SEM by placing them onto an aluminum sample plate which was covered with a conducting graphitic tape. The samples were placed in a vacuum sputterer and coated with 0.40 nm of gold. Images were obtained digitally on a Hitachi 2500 Delta.
Figure 3.11. Control Sample: Polymer 3.1 + streptavidin coated polystyrene microspheres.

Figure 3.12. Polymer 3.3 combined with streptavidin coated polystyrene spheres.

Figure 3.13. Polymer 3.3 combined with streptavidin coated polystyrene spheres.
**Stoichiometric Calculations:**

Initial calculations used to estimate the approximate percent functionalization of the polymer: Bangs Laboratories states that 1 mg of streptavidin coated polystyrene microspheres (Product Code: CP01N/5622) can bind 0.098 μg of biotin. Thus, the 0.5 mg of beads utilized in this experiment must bind 0.049 μg of biotin. Assuming perfect binding (1:1 streptavidin:biotin) this would mean that 10 μg of polymer (2400 g/mol-repeat) would be ~5% functionalized.

A titration experiment was then performed with free streptavidin to confirm this approximation. A buffered polymer solution of 15 mg/L (Stock B) was prepared for this experiment—the dilutions per flask are listed in the table below. 1 μg of streptavidin was added to each flask. Aldrich streptavidin can bind 14 pg (0.057 pmol) of biotin per μg. Streptavidin may bind up to four biotin molecules, but aggregation can occur if only 2 biotin molecules from separate polymer molecules are bound. To further complicate the matter, interpolymer biotin binding must compete with intrapolymer biotin binding. Thus, the table below shows a range of binding modes (2,3,4). As the spectroscopic changes began with the third dilution (flask 3), the minimum percent functionalization can be found here assuming a binding mode of only 2 biotin molecules per streptavidin.
Table 3.1 Serial dilutions of polymer 3.3 and titration assay with biotin to determine percent loading.

<table>
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<tr>
<th>Flask</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<td>mL stock B</td>
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<td>0.04</td>
<td>0.008</td>
<td>0.00016</td>
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<tr>
<td>μg polymer</td>
<td>15.0</td>
<td>3.0</td>
<td>0.6</td>
<td>0.12</td>
<td>0.024</td>
</tr>
<tr>
<td>pmol of polymer</td>
<td>6.25</td>
<td>1.25</td>
<td>0.250</td>
<td>0.050</td>
<td>0.010</td>
</tr>
<tr>
<td>4:1 biotin:streptavidin</td>
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<td>-</td>
<td>0.057/0.250 = 23%</td>
<td>-</td>
<td>-</td>
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<tr>
<td>3:1 biotin:streptavidin</td>
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<td>-</td>
<td>0.043/0.250 = 17%</td>
<td>-</td>
<td>-</td>
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<tr>
<td>2:1 biotin:streptavidin</td>
<td>-</td>
<td>-</td>
<td>0.029/0.250 = 12%</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3.5. References and Notes


Chapter 4
TEMPO-substituted PPEs: Polystyrene-PPE Garfted Copolymers and Double Grafted Copolymer*26

4.1 Introduction

Synthesis and characterization of novel graft polymers with a poly(paraphenyleneethynylene) (PPE) backbone and polystyrene side chains is reported in this chapter. The first example of a water-soluble double-grafted PPE is showcased.

In PPEs1 phenylene groups are separated by alkyne linkages; PPEs are highly fluorescent, chemically robust and useful in sensory applications.2-4 Their well known thermochromicity,5 solvatochromicity,6 surfactochromicity,7 and fluorescence quenching upon exposure to certain transition metals and viologen-type cations8,9 makes them attractive as they combine signal generation, transduction and amplification handily in one package. Concepts such as molecular wire, amplified quenching and superquenching are connected with the PPE’s photophysical behavior and have attracted significant attention.

The well-defined photophysics of the PPEs inspires the invention of novel macromolecular architectures that exploits their chromicity.5-8 An elegant way of changing PPEs’ architecture is the post-synthetic modification of side chains.2,10 This economic approach introduces molecular diversity at the final stage of the synthetic

scheme, after the polymerization event. In this chapter, we describe the synthesis of a TEMPO-substituted PPE 4.8 as a precursor to grafted\textsuperscript{11} polystyrene-PPEs\textsuperscript{12} 4.10-4.12. The use of the TEMPO-PPE 4.8 is a conceptual progress in the synthesis of useful PPE-architectures. The polymers 4.10-4.12 have properties that differ from those of dialkyl-PPEs\textsuperscript{5-7} as well as from their TEMPO-substituted precursor 4.8. The 4-chloromethyl substituted graft polymer 4.11 is functional but can not be made by a regular Heck-Cassar-Sonogashira-Hagihara\textsuperscript{1} reaction of a suitably grafted diiodoarene, due to the interference of the nucleophilic amines popular as solvent in these coupling reactions. Neither can 4.11 be made by Breens method,\textsuperscript{12} due to the reactivity of benzylic halides under their reaction conditions. The use of the PPE-module 4.8 as a precursor to 4.11 solves this problem.

4.2 Results and Discussion

Syntheses (Schemes 1 and 2): The reduction of 2,5-diiodo-4-methylbenzoic acid 4.1 with the BH\textsubscript{3}-THF complex furnished the benzylic alcohol 4.2 in 87% yield as sole product. The iodo-functionalities in 4.1 are not attacked by this mild reducing agent. Another commonly used reduce agent LiAlH\textsubscript{4} was also tried in this case, but it didn’t work because it attacked the iodo-functionalities. BBr\textsubscript{3} transforms 4.2 smoothly into the benzylic bromide 4.3 (81%). Photochemical reaction of the bromide 4.3 with dimanganese decacarbonyl (4.4) and TEMPO (4.5)\textsuperscript{13} gave rise to the formation of the monomer 4.6 in 40% after chromatography. While the NMR spectra of 4.6 were supportive of its formation, a single crystal X-ray structure analysis was performed to prove its topology.\textsuperscript{14} Figure 4.1 shows two representations of 4.6. The diiodide 4.6 was combined with diyne 4.7 in a Heck-Cassar-Sonogashira-Hagihara coupling.\textsuperscript{1,15} The
polymer 4.8 in formed in excellent yields and a degree of polymerization $P_n = 31$ ($M_n = 18 \times 10^3$; > 60 phenyleneethynylene units) according to gel permeation chromatography (gpc, polystyrene standard); the obtained polydispersity $M_w/M_n = 3.1$ is typical for PPEs produced by these Pd-catalyzed reactions.¹

Figure 4.1 Atomic displacement plot and space filling representations of 4.6. Bond lengths and bond angles are in agreement with expected standard values for C=C, C-C, C-H, C-I, C-N, N-O, and C-O bonds.

The structural integrity of 4.8 was proven by $^1$H NMR, $^{13}$C NMR, UV-vis and fluorescence spectroscopies. Figure 4.2 shows the $^{13}$C NMR spectrum of 4.8. It is gratifying to see that the TEMPO group in 4.6 survives the Pd-catalyzed coupling without any problem. Two set of signals were obtained by extracting the spectral information of bisethylhexyl-PPE (EPPE) and overlaying the peak positions with those of 4.8. The resonances that are virtually identical to those of EPPE are represented in 4.8 by green arrows. Some of the “green” signals are split. Such a split is not visible in EPPE and the split is due to the random orientation of the second, non symmetrically substituted monomer unit that will lead to three dyads in 4.8 (Scheme 4.3). This asymmetry does not lead to a split of the signals attributable to the TEMPO-containing building block (red
Scheme 4.3. Three dyads are encountered in the structural motif of 8 and 10-12.

Figure 4.2. $^{13}$C NMR spectrum of polymer 4.8 in CDCl$_3$. The spectrum is a additive composite of the spectrum of bis(ethylhexyl)-PPE and the spectrum of the TEMPO containing monomer. The green arrows highlight the signals that are attributed to the bis(ethylhexyl) part of the polymer. The interpretation of the signals was performed by overlay of the spectrum of 4.8 with that of bis(ethylhexyl)-PPE. The signal at $\delta = 77$ is due to CDCl$_3$ while the signal at $\delta = 81$ ppm stems from a solvent impurity.

arrows), which is surrounded by the symmetrical bisethylhexylbenzene units. One of the aromatic signals of the TEMPO-carrying units in 4.8 is missing, masked by one of the
“green” peaks. Diagnostic are the resonances at δ = 60 and 76 ppm that represent the signals of the ar-CH₂-O-N-CMe₂-(CH₂)₃-CMe₂ carbons respectively. The alkyne peaks are most heavily split due to the stereochemical dyads. Four signals are expected and three are visible, one however with double intensity. The ¹³C NMR spectrum strongly supports the structure of 4.8.

Controlled radical polymerization is a powerful tool in polymer synthesis. The TEMPO-substituted PPE 4.8 should be an excellent precursor to grafted PPE brushes. Heating 4.8 in the presence of 3 equivalents of styrene (9) in acetic anhydride furnished the polymer 4.10a as an almost colorless but strongly blue emitting solid. In 4.10a the polystyrene side chains are very short and comprise of only 2-3 repeating units. According to NMR spectroscopy, the unmolested TEMPO units are still attached to the polymer. The GPC of the polymer shows Mₙ = 20 x 10³ with an M_w/M_n = 3.5, similar to the gpc of 4.8. In the case of the polymer 4.10b the reaction was carried out in a mixture of neat styrene and acetic anhydride.
Figure 4.3. (a) Full spectrum of 4.11. (b) Magnified section of the same spectrum. The spectra were taken in chloroform-d. The signal at $\delta = 93$ ppm is assigned to the alkyne carbons. The split signal at $\delta = 61$ ppm is due to the Ph-\(\text{C(CH}_2\)H-O-N-units at the active chain ends of the polystyrene substituent.
The weight amount of isolated polymer 4.10b was three times that of the starting material after 3 h at 135°C. As a consequence its molecular weight should approximately have tripled. Comparing the GPC data of 4.8 to that of 4.10b, $M_n$ increased from $18 \times 10^3$ to $56 \times 10^3 \ (M_w/M_n = 3.2)^{5,6,19}$ which is in good agreement with the amount of uptake of styrene. The polymer 4.10b has side chains that are comprised of approx. 12 styrene units per repeat unit according to GPC and mass balance. The excellent agreement between the GPC values and the molecular weight values obtained by mass calculations were surprising. A recent report$^{12b}$ of a similar grafted PPE gave inconsistent molecular weight results when comparing the grafted to the non grafted polymers with the molecular weights of the isolated grafts. The polystyrene PPE grafts 4.10 are conceptually important, modulating the optical properties of the backbone (vide infra). However, polystyrene appendages are non-functional to adapt receptor sites. Accordingly, 4.8 was heated with 4-chloromethylstyrene to 135°C to furnish the poly(4-chloromethylstyrene) functionalized PPE 4.11. According to the increase in weight of the product from 200 mg (4.8) to 760 mg (4.11) (factor of 3.8), the side chains must incorporate on average 7 chloromethylstyrene units. The molecular weight (GPC) increases from $1.8 \times 10^4$ to $1.0 \times 10^5$, giving a factor of 5.6 as the molecular weight increase when going from 4.8 to 4.11. Losses in the workup of 4.11 could account for this discrepancy in the molecular weights. Because this polymer is very soluble, its $^{13}$C NMR spectrum (Figure 4.3) shows prominent signals due to the polystyrene side chains and a set of signals of much lower intensity that corresponds well to the signals seen for polymer 4.8’s in the alkyl region. The alkyne signals of 4.11 are visible at $\delta = 93.6$ and 91.3 ppm, and the Ph-CH(CH$_2$)-O-N- signal, which is displayed in 4.8 at $\delta = 60.4$ ppm is
now split into two signals at $\delta = 61.5$ and 60.6. The split is due to the presence of diastereomers in 4.11. The signal due to the chloromethyl groups is prominently visible at $\delta = 40.7$. PPE 4.11 is a functional polystyrene grafted PPE. Exposure of 4.11 to neat methyloxazoline at 105°C furnished the polymer 4.12. The isolated material weighed 9.36 times as much as the starting material. If we neglect loss during workup, on average every chloromethylstyrene group carries a 20meric polyoxazoline substituent. The overall molecular weight of 4.12, $M_n = 900,000$ amu. Attempts to perform gel permeation chromatography on 4.12 were unsuccessful, because 4.12 never eluted from the column, regardless if THF or chloroform was utilized as elution phase. However, the weight increase for 4.11→4.12 gives a good estimate of 4.12’s molecular weight. The $^{13}$C NMR of 4.12 shows largely signals due to the polyoxazoline side chains. Signals due to the PPE backbone are not visible anymore. The polymers 4.10–4.12 are freely soluble in chloroform and toluene and therefore are not crosslinked. Both the polymer 4.10b as well as 4.11 were investigated by DSC to show a glass transition point at 94 and 106 °C respectively. These values are in good agreement with those of linear polystyrene that shows a glass transition point of 104°C. Polymers 4.8 and 4.12 have more complex DSC traces that are difficult to interpret. They do not show clear melting or glass transition points. To visualize the shape of the PPEs, Figure 4 shows a MM2 representation of an oligomer of 4.10b. During the minimization the main chain adopted a twisted conformation. The shown conformer is a representative conformer but probably not the global minimum.
Figure 4.4. MM2-Representation of an oligomer of 4.10b.


While TEMPO-PPE 4.8 is yellow in appearance in the solid state, the color of the grafted polymers 4.10-4.11 is consecutively lighter. The graft 4.12 displays only a slightly off-white hue, which stems mostly from the polyoxazoline side chain. All of the materials are strongly blue-turquoise emissive in the solid state. To quantify these observations we took UV-vis and emission spectra of 4.8-4.12 in solution and in the solid state. Figures 4.5 and 4.6 show the spectra of 8-11, while Figures 4.7 and 4.8 show the emission spectra of 12.
In solution 4.8, 4.10a,b and 4.11 show spectroscopic properties that are similar to those observed for dialkyl-PPEs (Figure 4.3).\textsuperscript{1,5,7} We attribute the blue shift when going from 4.8 to 4.10 and 4.11 to an increased torsional twist of the benzene units in the PPE main chain with respect to each other. As a consequence, 4.11 has an absorption maximum of only 370 nm. The alternative explanation would be the disruption of the conjugated backbone by the addition of the radical centers to the CC-triple bond of the backbone. Upon crosslinking a red shift of the absorption would be expected. Why? Addition of a radical center to the triple bonds followed by further reaction, would lead to a trisubstituted or tetrasubstituted double bond. Such a reaction would transform parts of the PPEs into PPVs with a considerably smaller band gap. A further radical reaction of the sterically shielded tri- or tetrasubstituted double bonds is not probable with a tetra to hexasubstituted ethane derivative as end product. To exclude the radical addition scenario further, styrene was polymerized by a TEMPO starter in the presence of didodecyl-PPE. After workup the PPE was unchanged in absorption, emission, molecular weight and polydispersity. From these experiments we conclude that the changes in absorption and emission are not due to the production of defect structures, and that dialkyl-PPEs survive the process of radical polymerization unmolested. Attempts to obtain a UV-vis spectrum of 4.12 however failed, due to the tailing background absorption of the polyoxazoline side chains and the dilution of the PPE.
Figure 4.5. UV-vis spectra of **4.8, 4.10** and **4.11** in chloroform.

Figure 4.6. Optical data (emission and absorption) of **4.8, 4.10** and **4.11** in thin films.
Table 1. Optical Data and Molecular Weight Information of 4.8 and 4.10-4.12

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<th>4.10a</th>
<th>4.10b</th>
<th>4.11</th>
<th>4.12</th>
</tr>
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<td></td>
<td>solution</td>
<td>film</td>
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<tr>
<td>Absorption [nm]</td>
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<tr>
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<td>Mol wt. by gpc</td>
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<td>5.6 x 10^4</td>
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<tr>
<td>Mol wt. determined by weight increase</td>
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<td>3.7 x 10^4</td>
<td>6.8 x 10^4</td>
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</table>
Figure 4.7. Emission spectra of 4.12 in different solvents. Top: Solvents in which 4.12 dissolves un-aggregated. Bottom: Highly polar solvents which dissolve 4.12 in an aggregated form.
Figure 4.8. Emission spectra of 4.12 in the solid state.

When going into the solid state, the UV-vis absorption of 4.8 is significantly red shifted as expected for a dialkyl-PPE and $\lambda_{\text{max}}$ is 418 nm. In thin films of didodecyl-PPE $\lambda_{\text{max}}$ is 445 nm. In the case of 4.8, the bulky tetramethylpiperidine substituent perhaps decreases the propensity towards full planarization. In the case of 4.10b and 4.11 the solid state absorption is almost unchanged compared to their solution spectra (Figure 4.6), even though the emission is significantly red shifted. Here, the polystyrene side chains act as “added on” disordered solvent and there is no significant difference in the UV-vis spectra in these materials in the solid state and in solution. This data suggests that in the main chain of 4.10b and 4.11 the phenyl rings are twisted with respect to each other in the thin films. The UV-vis spectra of the PPE 4.10b are mainly determined by the conformation of the side chain and not by the formation of aggregates. The
polystyrene side chains lead to a rotational disorder in the conformation of the main chain by acting as disordered/disordering solvent.

The emission spectra of 4.8 and 4.10-4.11 in chloroform, a good solvent for all of these polymers, are shown in Figures 4.5-4.8. All of the investigated PPEs emit at 428 nm and show a shoulder at 450 nm. It is noteworthy that the shoulder grows when going from 4.8 to 4.10b and then to 4.11. It was ruled out that this spectral change was due to self absorption. The interpretation of the increase of the shoulder at 450 nm is non-trivial and connected to increasing vibronic coupling of ground and excited states. These bands are not a sign of aggregation or excimer formation. In the emission spectrum of 4.12 the shoulder at 450 nm is decreased when compared to that of its precursor 4.11. The quantum yield of emission decreases from 0.78 for 4.8 to 0.11 for 4.12 (in chloroform). There could be two reasons for the decrease: a) the increased vibronic coupling opens up non-radiative vibronically coupled pathways, in corroboration with the increase observed for the shoulder at 450 nm and b) in the case of 4.12, small amounts of absorbing impurities will quench the fluorescence of the main chain by a FRET mechanism. And indeed, we were not able to obtain a satisfactory UV-vis spectrum of 4.12 due to a general background and tailing absorbance observed after the addition of the polyoxazoline chains suggesting that the latter explanation is the correct one. The polymer 4.12 shows an interesting fluorescence behavior. In polar solvents, including water and D$_2$O, the emission of 4.12 shifts to 450 nm, and broadens considerably. The broadening is so severe that both increased vibronic coupling as well as excimer formation via aggregation could play a role, while the emission quantum yield drops from $\Phi = 0.11$ to $\Phi = 0.026$. 
In the solid state the emission of 4.8-11 is centered between 460 – 470 nm. The emission is broad and unstructured, suggesting some excimer formation of twisted chains. Excimer formation of planarized chains\textsuperscript{24a} leads to a strong and broad emission centered around 540 nm. This is in good agreement with the findings emission of twisted PPE chains is blue shifted.\textsuperscript{24b} An additional blue-shifted shoulder is observed at 430-440 nm. Again the interpretation of the data is somewhat ambiguous, the broad emission could either be due to excimers combining twisted chains, or it could be due to a broadening brought about by the increase in the Huang-Rys factors and the increased vibronic coupling.\textsuperscript{22} In the future we will investigate the emissive lifetimes of 4.10-4.12 in solution and in the solid state to gain insight into the operating mechanisms of excimer formation.

4.3 Conclusions

In conclusion we have made the novel TEMPO substituted PPE 4.8 by the Pd-catalyzed reactions of the Heck-Cassar-Sonogashira-Hagihara type, with the TEMPO groups surving the Pd catalysis without problems. We have shown that 4.8 undergoes controlled radical polymerization at elevated temperatures to give the graft copolymers 4.10 and 4.11. The radical reaction proceeds without interference of the triple bonds of the PPE-backbone. The graft copolymers 4.10 and 4.11 show interesting optical properties that are interpreted as a result of the twisted nonplanar conformation of neighboring phenyl groups due to the steric needs of the long side chains. These PPEs therefore should show more of a cylindrical than a lamellar morphology in the solid state according a model proposed by Neher.\textsuperscript{24} The graft polymer 4.11 is attractive because it
has potential to be transformed into novel functionalized polymers. A proof of concept experiment was the synthesis of the doubly grafted water soluble PPE 4.12. In future we will report upon the reaction of 4.8 with other polymerizable groups to give grafted PPEs with unusual sensory and structural properties and explore the physical properties and photophysical traits of these fascinating conjugated grafts in more detail.

4.4 Experimental Materials.

Styrene (99%) and 4-vinylbenzyl chloride (95%) were purchased from Aldrich. Both of these monomers were passed through a basic alumina column to remove the inhibitor and used immediately. All other reagents were used as received.

Characterization

The $^1$H and $^{13}$C NMR were taken on a Varian 300 MHz spectrometer using a broadband probe. UV-VIS measurements were made with a Shimadzu UV-2401PC recording spectrophotometer. Fluorescence data were obtained with a Shimadzu RF-5301PC spectrofluorophotometer. IR data were collected by a Shimadzu FTIR-8400S infrared spectrophotometer. A Headway Research Model PWM32 instrument was used to spin-coat dilute chloroform saturated solution (~10 mg/mL) and filtered of polymer onto quartz slides at 1500 rpm for 30 seconds for thin film experiments. The average thin film thickness is about 50 nm. Fluorescence quantum yields were determined in relation to quinine sulfate ($\approx 10^{-6}$ M in 0.1M H$_2$SO$_4$, $\Phi_F = 0.54$). GPC measurements were conducted in chloroform (25°C) with a Shimadzu SCL-10A VP UV-VIS detector. The molecular weights were determined versus polystyrene standards.
Polymer Viscosity Measurements.

Polymer relative viscosity was measured by Cannon-Fenske Viscometer (Size 25) in DMF at 25°C. DMF efflux time, t₀ = 450 s

Table 4.2. Viscosity Measurements of the Newly Synthesized Polymers

<table>
<thead>
<tr>
<th>sample</th>
<th>efflux time, t (s)</th>
<th>mol wt a</th>
<th>concn (mg/mL)</th>
<th>relative viscosity, η₁ b</th>
<th>specific viscosity, η₆ c</th>
<th>reduced viscosity, η₆ d (mL/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymer 4.11</td>
<td>607</td>
<td>Mₙ = 1.0 × 10⁵</td>
<td>10</td>
<td>1.35</td>
<td>0.35</td>
<td>0.035</td>
</tr>
<tr>
<td>polystyrene standard</td>
<td>574</td>
<td>Mₙ = 6.6 × 10⁴</td>
<td>10</td>
<td>1.28</td>
<td>0.28</td>
<td>0.028</td>
</tr>
<tr>
<td>polystyrene standard</td>
<td>520</td>
<td>Mₙ = 2.8 × 10⁴</td>
<td>10</td>
<td>1.16</td>
<td>0.16</td>
<td>0.016</td>
</tr>
<tr>
<td>polymer 4.12</td>
<td>489</td>
<td>Mₘ (estimated) = 9.0 × 10⁵</td>
<td>2.0</td>
<td>1.09</td>
<td>0.09</td>
<td>0.045</td>
</tr>
<tr>
<td>poly(2-ethyl-2-oxazoline)</td>
<td>467</td>
<td>Mₘ = 5.0 × 10⁴</td>
<td>2.0</td>
<td>1.04</td>
<td>0.04</td>
<td>0.020</td>
</tr>
<tr>
<td>poly(2-ethyl-2-oxazoline)</td>
<td>485</td>
<td>Mₘ = 2.0 × 10⁵</td>
<td>2.0</td>
<td>1.08</td>
<td>0.08</td>
<td>0.040</td>
</tr>
</tbody>
</table>

a PS standard from Showa Denko. Poly(2-ethyl-2-oxazoline) from Aldrich. b Relative viscosity η₁ = t/t₀. c Specific viscosity, η₆ = (t - t₀)/t₀. d Reduced viscosity, η₆ d = η₁/c.

Conclusion:

Viscosity measurements confirmed that polymer 4.11 has a molecular weight higher than 6.6 × 10⁵, and polymer 4.12 has a molecular weight higher than 2.2 × 10⁵.

Synthesis of 4.2: To a nitrogen purged 250 mL round bottom flask was added 4.1 (7.76 g, 20.0 mmol), dry THF (50 mL), and stirred under nitrogen at 0 °C until the acid dissolved. BH₃• THF (1.0 M in THF, 30.0 mL, 30.0 mmol) was added dropwise. The solution was stirred at 0 °C for another 30 min, then warmed to room temperature for 24 h. The solution was quenched with ice water (100 mL), and a white precipitate formed in
the water after the THF was removed. The crude product was dissolved in ether, and purified by column chromatography with eluent ether to obtain the product as a colorless solid (6.50 g, 87%). IR (KBr) cm\(^{-1}\) = 3351, 3206, 2969, 2850, 1701, 1694, 1466, 1437, 1376, 1325, 1294, 1255, 1183, 1136, 1063, 1039, 1002, 984, 896, 880, 862, 688. MP = 186-187°C. \(^1\)H NMR (CDCl\(_3\)) \(\delta = 7.78\) (s, 1H), 7.73 (s, 1H), 4.30 (s, 2H), 2.29 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 143.13, 142.23, 139.87, 138.24, 101.96, 97.31, 68.47, 27.05.\) Anal. Calcd. for C\(_8\)H\(_8\)I\(_2\)O: C 25.69, H 2.16; Found: C 25.53, H 2.16.

**Synthesis of 4.3:** To a nitrogen purged 250 mL round bottom flask, 4.2 (6.50 g, 17.4 mmol) and toluene (50 mL) were added. BBr\(_3\) (5.30 g, 21.2 mmol) was added via syringe. The reaction was stirred at room temperature for 3 h under inert atmosphere. The reaction mixture was poured into ice water, and the organic layer was washed with water (3 x 100 mL) then dried over MgSO\(_4\). The solvent was subsequently removed *in vacuo*. The crude product was purified by crystallization from hexanes to yield a colorless solid (6.12 g, 81%). Mp = 157-158°C. IR (KBr) cm\(^{-1}\) = 3027, 3060, 2958, 2916, 2847, 1574, 1465, 1434, 1419, 1371, 1340, 1260, 1220, 1208, 1190, 1002, 894, 888, 870, 794, 788, 759, 709, 627. \(^1\)H NMR (CDCl\(_3\)) \(\delta = 7.84\) (s, 1H), 7.73 (s, 1H), 4.42 (s, 2H), 2.32 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\)) \(\delta = 141.21, 141.13, 140.82, 140.26, 100.58, 99.83, 37.91, 27.80.\) Anal. Calcd. for C\(_8\)H\(_7\)BrI\(_2\): C 21.99, H 1.62. Found: C 21.85, H 1.64.

**Synthesis of 4.6:** To a 100 mL Schlenk tube, 4.3 (2.18 g, 5.00 mmol), 4.5 (1.24 g, 7.94 mmol), 4.4 (0.390 g, 1.00 mmol) and toluene (20 mL) were added. The tube was degassed, then filled with nitrogen. The flask was irradiated by a broadband sunlight
lamp for 24 h. The reaction mixture was filtered and purified by column chromatography (hexanes) to obtain 4.6 as a colorless solid (1.03 g, 40%). Mp = 126-128°C. IR (KBr) cm⁻¹ = 2962, 2959, 2903, 2842, 1444, 1373, 1352, 1335, 1260, 1256, 1243, 1183, 1132, 1129, 1041, 1036, 1025, 926, 876. ¹H NMR (CDCl₃) δ = 7.87 (s, 1H), 7.62 (s, 1H), 4.72 (s, 2H), 2.38 (s, 3H), 1.60-1.20 (m, 6H), 1.20-1.10 (d, 12H). ¹³C NMR (CDCl₃) δ = 142.10, 140.45, 139.48, 138.38, 101.16, 96.55, 81.38, 60.41, 40.07, 33.36, 27.62, 20.85, 17.48. Anal. Calcd. for C₁₇H₂₅I₂NO: C 39.79, H 4.91, N 2.73. Found: C 40.06, H 5.04, N 2.69.

Synthesis of polymer 4.8: A 50 mL Schlenk flask was charged with 4.6 (513 mg, 1.00 mmol), 4.7 (351 mg, 1.00 mol), THF (5 mL), piperidine (1.50 mL), (PPh₃)₂PdCl₂ (2 mg, 2.8 μmol) and CuI (1 mg, 5.3 μmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at room temperature for 24 h. The reaction mixture was filtered over silica on a fritted funnel with hexane. After hexane evaporated, the crude product was dissolved in chloroform (10 mL), and added into from methanol (300 mL) dropwisely. A bright yellow solid (603 mg, 94%) was obtained. IR (KBr) cm⁻¹ = 2949, 2924, 2920, 2915, 2907, 2891, 2870, 2853, 1501, 1464, 1456, 1447, 1378, 1373, 1359, 893. ¹H NMR (CDCl₃): 7.68 (bs, 1H), 7.42-7.20 (bm, 3H), 5.10 (bs, 2H), 2.93-2.61 (bs, 4H), 2.47 (bs, 3H), 1.90-1.05 (m, 36H), 1.00-0.75 (bd, 12H). ¹³C-NMR (CDCl₃): δ = 141.29, 138.60, 137.64, 133.65, 133.08, 123.43, 121.57, 94.50, 93.32, 92.29, 76.51, 60.39, 40.67, 40.12, 38.82, 33.42, 32.78, 26.05, 23.47, 20.81, 17.54, 14.53, 11.39. GPC (vs. polystyrene standards in chloroform): Mₙ = 18 x 10³, Pₙ = 18, Mₘ/Mₙ = 3.1. Quantum yield (in chloroform): 0.78.
**Synthesis of 4.10a:** An oven-dried 50 mL Schlenk flask was charged with **4.8** (200 mg, 0.329 mmol counted by the TEMPO functional group), **4.9** (208 mg, 2.00 mmol), xylene (3 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed by three freeze-pump-thaw cycles and refilled with nitrogen. The reaction was allowed to stir at 135 °C for 8 h. The solution was precipitated from methanol (200 mL). A light yellow solid was obtained (242 mg, 51% with respect to utilized styrene). GPC (vs. polystyrene standards in chloroform): \(M_n = 20 \times 10^3\), \(M_w/M_n = 3.5\). IR (KBr) \(\text{cm}^{-1} = 3080, 3059, 3025, 2917, 2907, 2897, 2846, 1945, 1900, 1780, 1701, 1600, 1492, 1451, 1373, 1359, 1180, 1027, 905, 892, 758, 698\). \(^1\)H NMR (CDCl\(_3\)): \(\delta = 7.83-6.75\) (m, 28H), 5.10-5.00 (bs, 2H), 3.03-2.00 (m, 14H), 2.00-0.20 (m, 54H). \(^{13}\)C NMR (CDCl\(_3\)): \(\delta = 145.82, 143.29, 141.27, 138.61, 137.59, 133.57, 132.99, 130.99, 128.181, 123.38, 121.54, 94.52, 93.81, 92.24, 60.37, 40.68, 38.87, 33.49, 32.85, 30.10, 29.22, 26.52, 23.51, 20.80, 17.55, 14.55, 11.27\). Quantum yield (in Chloroform): 0.62.

**Synthesis of 4.10b:** An oven-dried 50 mL Schlenk flask was charged with **4.8** (200 mg, 0.329 mmol counted by the TEMPO functional group), styrene (5 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at 135 °C for 3 h during which the reaction mixture solidified. Chloroform (20 mL) was added into the flask to dissolve the solid, then the solution was precipitated from methanol (200 mL). A very lightly yellow polymer was obtained (631 mg, 13% with respect to used styrene). IR (KBr) \(\text{cm}^{-1} = 3081, 3057, 3024, 3000, 2921, 2912, 2896, 2849, 1600, 1492, 1451, 1374, 1360, 1180, 1066, 1027, 906, 747, 697\). \(^1\)H NMR (CDCl\(_3\)): 7.45 (bm), 7.42-6.30 (bm), 2.40-1.0 (bm), 1.00-0.85 (bs).
Synthesis of 4.11: An oven-dried 50 mL Schlenk flask was charged with 4.8 (200 mg, 0.329 mmol counted by the TEMPO functional group), 4-vinylbenzyl chloride (5 mL), and acetic anhydride (20 mg, 0.196 mmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at 135 °C for 3 h during which the reaction mixture solidified. Chloroform (20 mL) was added into the flask to dissolve the solid, then the solution was precipitated from methanol (200 mL). A lightly yellowish polymer was obtained (760 mg, 14% with respect to used styrene). IR (KBr) cm⁻¹ = 638, 665, 672, 708, 744, 798, 814, 821, 832, 911, 946, 965, 1018, 1108, 1182, 1213, 1240, 1265, 1315, 1352, 1421, 1443, 1507, 1610, 1909, 2848, 2923, 2988, 3015, 3025, 3050, 3087. 

¹H NMR (CDCl₃): 7.60-6.90 (bs), 6.90-6.20 (bs), 4.90-4.20(bs), 2.40-0.50 (bm). ¹³C-NMR (CDCl₃): δ = 145.1 (ps), 145.0 (ps), 134.8 (ps), 128.7(ps), 128.1(ps), 93.6 (alkyne), 91.3(alkyne), 61.5, 60.6, (both CH-O-N), 46.7 (ps), 44.1(ps), 43.1(ps), 42.3 (ps), 40.7 (ps), 33.6, 32.8, 29.2, 26.0, 23.5, 21.6, 14.6, 11.3 (ethylhexyl signals and signals due to the TMP group). GPC (vs. polystyrene standards in chloroform): Mₙ = 10 x 10⁴, Mₘ/Mₙ = 3.1. Quantum yield (chloroform): 0.36.

Synthesis of 4.12: To a 50 mL nitrogen purged round bottom flask, 4.11 (100 mg), and 2-methyl-2-oxazoline (3.57 g, 42.0 mmol) were added. The flask was heated to 105 °C. The reaction was stopped after 12 h when the mixture was solidified. The solid was dissolved in chloroform (10 mL), then the solution was precipitated from ether (200 mL).
A slightly off-white polymer was obtained (931 mg, 25% with respect to utilized 2-methyl-2-oxazoline). IR: 672, 763, 777, 885, 969, 1026, 1115, 1244, 1300, 1361, 1411, 1422, 1488, 1635, 1652, 1732, 1771, 2913, 3241. $^1$H NMR (CDCl$_3$) $\delta$ 3.60-3.15(bs), 2.40-2.20 (bs), 2.20-1.80 (bm). GPC: unable to determine. $M_n = 90 \times 10^4$ (estimated by weight). Quantum yield (in chloroform): 0.11.

4.4 References


14. Crystal data: for 6: C17H25I2NO, triclinic, M = 513.18 g cm⁻³, space group = P-1. T = 150(2) K, Mo-Kα, a = 8.0000(5), b = 11.5696(7), c = 11.8431(7) Å, α = 62.9210(10), β = 76.8720(10), γ = 76.0130(10)°, Z = 2, D = 1.816 g cm⁻³, μ = 3.351 mm⁻¹, 7588 measured reflections, 3298 independent reflections, R (Rw) = 0.0225.


19. A bimodal distribution was observed in 10b with the second considerably smaller peak showing an Mₙ of 1.7 x 10⁶. We attribute the second peak to aggregation of 10b.


5.1 Introduction

In 1995 Swager examined fluorescent “molecular wires” – poly( paraphenyleneethynylene) (PPE) derivatives – in sensory applications.\(^1\) He chose a donor-substituted PPE containing a cyclophane cavity, which Stoddard had shown to form strong complex with paraquat,\(^2\) embedded into the conjugated backbone, and paraquat served as the analyte model. The system was chosen because high Stern-Volmer constants\(^3\) (up to \(10^5\)) resulted. Swager’s PPE combines receptor, transducer and actuator in one molecule. Developing that concept further, Yang and Swager\(^4\) reported ipticene-containing PPEs as sensors of dinitrotoluene (DNT) by fluorescence quenching. DNT, which is the major constituent of vapor exuded by land mines,\(^4\) interacts with the nanoporous PPE films and quenches its emission. From both studies, the interaction of PPEs with electron deficient aromatics is well documented. To our knowledge however, there are no reports of fluorescence quenching of PPEs with electron rich arenes except for Swager’s newly investigation on the PPE with a [2.2.2] bicyclic ring system.\(^26\)

5.2 Results and Discussion

We are interested in the synthesis, chromogenic properties, and structuring of PPEs\(^5\)\textsuperscript{-9} with particular emphasis on the preparation of water soluble polymers. Several concepts have been used to confer water solublity to PPEs: sugar decoration,\(^10\) the addition of sulfonate\(^11\) or amino\(^12\) side groups, as well as the use of polyamine mini-
dendrimers\textsuperscript{13} as substituents. Charged water soluble conjugated polymers play an important role as bio-actuators as shown by Bazan,\textsuperscript{14} Wudl,\textsuperscript{15} Schanze,\textsuperscript{16} Leclerq\textsuperscript{17} and Whitten.\textsuperscript{18} We intend to improve water solubility of PPEs, by adding water soluble polymeric side chains,\textsuperscript{14} as demonstrated for 5.3, 5.7 and 5.9 in Scheme 5.1, 5.2 and 5.3.

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {\text{COOH}}; \node (b) at (1.5,0) {\text{CH\textsubscript{2}OH}}; \node (c) at (3,0) {\text{O}}; \node (d) at (4.5,0) {\text{O}}; \node (e) at (6,0) {\text{O}}; \node (f) at (7.5,0) {\text{O}}; \node (g) at (9,0) {\text{COOH}}; \node (h) at (0,-1) {\text{BH\textsubscript{3}}-\text{THF}}; \node (i) at (1.5,-1) {\text{BH\textsubscript{3}}-\text{THF}}; \node (j) at (3,-1) {\text{Sn(OCT)}\textsubscript{2}, 120\textdegree C}; \node (k) at (4.5,-1) {\text{Sn(OCT)}\textsubscript{2}, 120\textdegree C}; \node (l) at (6,-1) {\text{Sn(OCT)}\textsubscript{2}, 120\textdegree C}; \node (m) at (7.5,-1) {\text{Sn(OCT)}\textsubscript{2}, 120\textdegree C}; \node (n) at (9,-1) {\text{Sn(OCT)}\textsubscript{2}, 120\textdegree C}; \node (o) at (0,-2) {\text{5.1 87\%}}; \node (p) at (1.5,-2) {\text{5.2 96\%}}; \node (q) at (3,-2) {\text{5.3 69\%}}; \node (r) at (4.5,-2) {\text{5.1 87\%}}; \node (s) at (6,-2) {\text{5.2 96\%}}; \node (t) at (7.5,-2) {\text{5.3 69\%}}; \node (u) at (9,-2) {\text{5.1 87\%}}; \node (v) at (10.5,-2) {\text{5.2 96\%}}; \node (w) at (12,-2) {\text{5.3 69\%}}; \node (x) at (0,-3) {, triethylamine, Cul,}; \node (y) at (1.5,-3) {, triethylamine, Cul,}; \node (z) at (3,-3) {, triethylamine, Cul,}; \node (aa) at (4.5,-3) {, triethylamine, Cul,}; \node (ab) at (6,-3) {, triethylamine, Cul,}; \node (ac) at (7.5,-3) {, triethylamine, Cul,}; \node (ad) at (9,-3) {, triethylamine, Cul,}; \node (ae) at (10.5,-3) {, triethylamine, Cul,}; \node (af) at (12,-3) {, triethylamine, Cul,}; \node (ag) at (0,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (ah) at (1.5,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (ai) at (3,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (aj) at (4.5,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (ak) at (6,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (al) at (7.5,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (am) at (9,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (an) at (10.5,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \node (ao) at (12,-4) {Pd(Ph\textsubscript{3})\textsubscript{2}Cl\textsubscript{2}, THF}; \end{tikzpicture}
\end{center}

Scheme 5.1. Synthesis of polymer 5.3

Reduction of 2,5-diiodo-4-methylbenzoic acid\textsuperscript{1} (Scheme 5.1) with the BH\textsubscript{3}-THF complex furnishes alcohol 5.1 (87\%). Tin(II)bis(ethylhexanoate)\textsuperscript{15} catalyzes the reaction of 5.1 with 3,6-dimethyl[1,4]dioxane-2,5-dione to furnish the macromonomer 5.2 (96\%) with a degree of polymerization (P\textsubscript{n}) = 25 (M\textsubscript{n} = 1.8 x 10\textsuperscript{3}) and a polydispersity M\textsubscript{w}/M\textsubscript{n} = 1.24 according to gel permeation chromatography (GPC, CHCl\textsubscript{3} vs. polystyrene standards). Macromonomer 5.2 was dissolved in a mixture of triethylamine and THF, reacting with (Ph\textsubscript{3})\textsubscript{2}PdCl\textsubscript{2}, Cul and acetylene gas at RT for 24 h led to the smooth
isolation of polymer 5.3 (69%) after aqueous workup and precipitation from ethyl ether. While 5.3 ($M_n = 49 \times 10^3$, $P_n = 27$, $M_w/M_n = 3.7$) is well soluble in DMSO and DMF, it is insoluble in pure water, suggesting that the polyester side chains are not sufficiently hydrophilic to allow for water solubility.

![Scheme 5.2. Synthesis of polymer 5.7]

Polyoxazolines\textsuperscript{16} are water soluble and easily prepared from benzylic halides; 5.7 should be more water soluble than 5.3. Starting from 5.4, tosylation in pyridine furnishes 5.5 (69%) which was reacted with 2-methyloxazoline\textsuperscript{16} to give the macromonomer 5.6 (100%) with a $P_n$ of 10 and a $M_w/M_n = 1.15$ according to GPC. Monomer 5.6 is freely soluble in water and in polar organic solvents. Reaction of 5.6 with acetylene gas under standard Pd/Cu-catalyzed reaction conditions\textsuperscript{7} furnished the polymer 5.7 (54%, $M_n = 23 \times 10^3$, $P_n = 27$, $M_w/M_n = 3.7$). Polymer 5.7, showed good solubility in chloroform, DMF, DMSO, and water.
Scheme 5.3. Synthesis of cationic polymer 5.9

Polymer 5.9 (100%) was synthesized from chloromethyl styrene grafted PPE\textsuperscript{22} and triethylamine. This cationic polymer only dissolved in DMF and water. It shows better water solubility than 5.7. The absorption and emission spectra of 5.9 (Figure 5.11 in experimental section) in water indicate that this polymer is less aggregated than 5.7. This is also proven by its higher quantum yield (0.19) in water. Preliminary investigations of detecting DNAs were carried out. As a cationic conjugated polymer, 5.9 was quenched by DNA. Similar to other cationic conjugated polymers, the interaction between polymer 5.9 and DNA is nonspecific.

Spectral properties of the new polymers 5.3 and 5.7 were studied in different solvents. Broad, almost structureless absorption bands centered around 390 nm were noted for 5.3 or 5.7 in different solvents. Weak solvatochromic responses were present for all polymers’ absorption. In chloroform, a structured narrow emission band with a maximum around 420 nm was observed for 5.3, 5.7 (Figure 5.8 and 5.9 in experimental section), identical to that observed for didodecyl-PPE. The fluorescence quantum yield decreased from unity for the didodecyl-PPE down to 0.66 (Table 5.2) for 5.7, probably
due to self-quenching by the polyamido- and piperidine-containing side-chains. In other solvents, the emission spectra of 5.7 (Figure 5.1) demonstrated bimodal behavior. In addition to an emission at 420 nm, a broad band with a maximum at 487-510 nm was observed. This red-shifted excimer emission was probably caused by aggregation, and the fluorescence quantum yields obtained in solvents in which significant aggregation occurred was much lower than those obtained from the solvents with dominating single chain emission.

Figure 5.1. Normalized emission spectra of the polyoxazoline grafted PPE 5.7 in different solvents.

It is interesting to note that neither polarity nor proticity seemed to play a role. While at the current stage we are unable to explain this selective solvent effect on aggregation and solvatochromism of 5.7, it is probably due to the selective interaction and subtle interplay of the solvent with both the hydrophilic side chain as well as the rigid PPE backbone.
Table 5.1. Fluorescence quantum yields $\Phi_F$ and Stern-Volmer constants ($K_{sv}$, M$^{-1}$) of 5.3, 5.7, and didodecyl-PPE in chloroform

<table>
<thead>
<tr>
<th>Polymer</th>
<th>1,2-Phenylenediamine</th>
<th>4-Fluoro-nitrobenzene</th>
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<tr>
<td>Polyoxazoline PPE 5.7</td>
<td>73</td>
<td>176</td>
</tr>
<tr>
<td>Polylactide PPE 5.3</td>
<td>40</td>
<td>106</td>
</tr>
<tr>
<td>DidodecylPPE</td>
<td>8</td>
<td>105</td>
</tr>
</tbody>
</table>

We studied the quenching of fluorescence of polymers 5.3 and 5.7 not only with traditional electron-deficient aromatic compounds, but also with strong electron donors, such as ortho-phenylenediamine. When small amounts of the latter were added to solutions of 5.3, 5.7, or didodecyl-PPE in chloroform, no bathochromic shift of the emission was observed. Instead the fluorescence of the polymers was quenched efficiently. The Stern-Volmer plots were linear, suggesting that either only static or only dynamic quenching occurs. PPE 5.7 shows a $K_{sv}$ of 73, while PPE 5.3 as well as the model didodecyl-PPE shows a smaller $K_{sv}$ of 40 and 8 respectively when exposed to ortho-phenylenediamine. As a comparison, we have checked the quenching of 5.3, 5.7, and didodecyl-PPE by 4-fluoronitrobenzene. In this case, the Stern-Volmer constant is somewhat higher, and all three polymers are quenched with similar efficiency. Static quenching is observed when the quencher and the fluorophore form a ground state complex, while dynamic quenching occurs if the excited state of the fluorophore reacts with the quencher. A simple way to discern static quenching from dynamic quenching is
to determine the change of fluorescence lifetime upon addition of quencher. The lifetimes of 5.3, 5.7 and didodecyl-PPE in chlorofom were short (0.3 – 0.8 ns) and no lifetime changes were observed upon addition of quenchers to their solutions. Similarly to results of Swager et al.1,4 we suggest that the fluorescence quenching of 5.3, 5.7, and didodecyl-PPE is static in nature regardless of the chemical structure of quencher.

Table 5.2 Quantum yield measurements

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chloroform</th>
<th>DMF</th>
<th>Water</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polylactide PPE 5.3</td>
<td>0.87</td>
<td>0.59</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>Polyoxazolibe PPE 5.7</td>
<td>0.66</td>
<td>0.28</td>
<td>0.13</td>
<td>0.21</td>
</tr>
<tr>
<td>Cationic PPE 5.9</td>
<td>N.A.</td>
<td>0.21</td>
<td>0.19</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The cationic polystyrene grafted PPE 5.9 forms micro or nanospheres depending on different synthetic approaches. If polymer 5.9 was obtained by reacting 5.8 and triethylamine in THF/water, the product has a nanosphere structure. If DMF was used instead of THF/water, then the product exhibited a microsphere structure. These controlled size fluorescent spheres might be useful in bio-applications such as DNA detection and immobilization.
Bunz reported that adding methanol into didodecyl PPE/chloroform diluted solutions would cause aggregation and planarization of PPE chains\textsuperscript{23} (Figure 5.3). In
chloroform solutions, didodecyl PPEs display absorption peaks at 390 nm. Upon aggregation, there appears a red shifted shoulder or additional peak centered at 440 nm. The same trend is echoed in the emission spectra. In a good solvent, there is an emission peaks at 425 nm while in poor solvents or the solid state this shifts to a maximum at 450 nm with a second peak or shoulder at 480 nm.

However, it is not discussed that in the emission spectra, the peak at 430 nm actually had a blue shift with increasing methanol content. It is difficult to explain the blue shift by aggregation or planarization of PPE chains.

A similar phenomenon was observed when water was added to dilute DMF solutions of 5.3 and 5.7 (Figure 5.4). DMF is a good solvent for the side chains of 5.3 and 5.7, and it is a better solvent than water for the PPE main chains. In dilute DMF solution, chains of 5.3 and 5.7 are separated. Upon the addition of water, which is a poor solvent for main chain of PPEs, “aggregation induced” absorption bands form in polymer 5.3 (445 nm, Figure 5.4 b) and polymer 5.7 (440 nm, Figure 5.4 a). In their emission spectra, the aggregation and planarization of the PPE chains cause the rise of the band at 460 nm and formation of a new band at 500 nm (Figure 5.4 d and e). Blue shifts are observed at a higher energy band (420 nm). At this point, it is not clear why the blue shift at a higher energy band and a red shift at a lower energy band occur at same time.

Two assumptions were proposed, however, there is not enough evidence to prove either one. The first assumption is that when water is added into DMF, the dielectric constant of the solvent mixture is changed, which causes blue shifts at a higher energy band. On the other hand, the aggregation and planarization of PPE molecules causes the red shift on the lower energy bands.
Figure 5.4. Changes in absorption and emission spectra (normalized) upon adding water to polymer DMF solutions. (a) Absorption spectra of polymer 5.7; (b) absorption spectra of polymer 5.3; (c) absorption spectra of polymer 5.9; (d) emission spectra of polymer 5.7; (e) emission spectra of polymer 5.3; (f) emission spectra of polymer 5.9.
The second assumption is shown in Figure 5.5 in which a simplified energy diagram model is used. When polymers are dissolved in a good solvent, electrons are excited to S2 from the ground state S0, they quickly relax to S1, and the emission obtained is from S1 to S0. In a good solvent, S1 and S2 are very close, so the transition is fast. When water is added to DMF, the polymers become planar, and S1 and S2 become very different. The polar solvents stabilized the S2 state, and the electrons relaxation to the S1 takes longer time. This is evidenced by lifetime measurements (Table 5.3). In more polar solvents, the excited states have a longer lifetime of emission. Therefore, it is possible to have emission from the S2. This explains the blue shift in the higher energy band. At the same time, the aggregation and planarization of PPE
molecules causes the energy gap between S1 and S0 to become smaller. This causes the red shift at the higher energy band. It also has excitation directly from S0 to S1, which could explain the new red absorption peak.

Table 5.3. Life Time Measurements

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solvent</th>
<th>Lifetime, τ (ps) @ 420 nm</th>
<th>Lifetime, τ (ps) @ 460 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polylactide PPE 5.3</td>
<td>Chloroform</td>
<td>423</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>455</td>
<td>479</td>
</tr>
<tr>
<td></td>
<td>DMF/Water=80: 20</td>
<td>688</td>
<td>808</td>
</tr>
<tr>
<td>Polyoxazoline PPE 5.7</td>
<td>Chloroform</td>
<td>388</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>DMF</td>
<td>667</td>
<td>766</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>859</td>
<td>909</td>
</tr>
<tr>
<td>Cationic PPE 5.9</td>
<td>DMF</td>
<td>537</td>
<td>590</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>618</td>
<td>1084</td>
</tr>
</tbody>
</table>

Polymer 5.9 does not aggregate or planarize the same way as polymer 5.3 or 5.7. The cationic sidechains are too bulky and they also have charge repulsion to prevent aggregation. This keeps the backbone twisted even in pure water.
5.3 Conclusion

We have made novel PPE-grafted polymers 5.3 and 5.7 utilizing the acetylene gas method.7 PPE 5.7 is freely water soluble and shows attractive chroomic properties in emission. Polymer 5.3 and 5.7 displays static fluorescence quenching not only with electron-poor, but also with electron-rich donor-substituted arenes. Cationic PPE 5.9 is the best water soluble polymer among those three, and it has potential bioapplications such as DNA detection and immobilization.

5.4 Experimental

Compound 5.1: To a nitrogen purged flask were added 2,5-diiodo-4-methyl-benzoic acid (7.76 g, 20.0 mmol), and dry THF (50 mL). This mixture was stirred under nitrogen at 0°C until acid dissolved. BH₃·THF (1.0 M in THF) (30.0 mL, 30.0 mmol) was added slowly. The solution was stirred at 0°C for another 30 min, and then increased to room temperature for another 24 h. The excess BH₃ was quenched by ice water (100 mL). A colorless solid was precipitated out in the water after removal of THF. The crude product was redissolved in ether, and further purified by a short flush column. The product was obtained as a colorless solid (6.50 g, 87%). IR (KBr) cm⁻¹ = 3351, 3206, 2969, 2850, 1701, 1694, 1466, 1437, 1376, 1325, 1294, 1255, 1183, 1136, 1063, 1039, 1002, 984, 896, 880, 862, 688. MP = 186-187°C. ¹H NMR (CDCl₃) δ = 7.78 (s, 1H), 7.73(s, 1H), 4.30 (s, 2H), 2.29 (s, 2H) ¹³C NMR (CDCl₃) δ = 143.13, 142.23, 139.87, 138.24, 101.96, 97.31, 68.47, 27.05. Anal. Calcd. for C₈H₇I₂O: C 25.69, H 2.16; Found: 25.53, 2.16.

Macromonomer 5.2: An oven-dried Schlenk flask cooled under nitrogen was charged with 5.1 (1.87 g, 5.00 mmol), 3,6-dimethyl-1,4-dioxane-2,5-dione (7.20 g, 50.0 mmol), and tin(II)-2-ethylhexanoate (127 mg, 313 μmol). The flask was heated to 120°C while
stirring. The reaction was stopped after 12 h. The light yellow solid product was diluted with chloroform (10 mL), and then precipitated into acidified methanol (300 mL). The diiodo-polyester macromonomer, 5.2, was obtained as a colorless solid. Yield: 8.76 g, 96%.

GPC (vs. polystyrene standards in chloroform): $M_n = 1790$, $M_w/M_n = 1.24$. IR, cm$^{-1}$: 3489, 2986, 2940, 2878, 2613, 2378, 2047, 1750, 1733, 1447, 1378, 1352, 1258, 1211, 1203, 1176, 1079, 1020, 1009, 859, 605. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta =$ 7.70-7.60 (bd, 2H), 5.30-4.98 (b, 21H), 4.20-4.40 (b, 1H), 2.30 (s, 3H), 1.70-1.30 (m, 60H), $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta =$ 169.71, 169.51, 169.47, 169.240, 144.058, 140.07, 139.57, 136.83, 100.89, 98.05, 72.71, 69.94, 69.45, 69.27, 66.96, 27.61, 20.87, 17.25, 17.11, 17.04, 16.54, 16.16. Anal. Calcd. for C$_{68}$H$_{88}$I$_2$O$_4$: C 44.99, H 4.89; Found: 45.67, 5.12.

**Polymer 5.3:** The diiodo polyester macromonomer 5.2 (2.56 g, 1.40 mmol) was combined with piperidine (1.5 mL), THF (1.5 mL), (PPh$_3$)$_2$PdCl$_2$ (2 mg, 3 μmol, 0.2 mol%) and CuI (1 mg, 5 μmol, 0.4 mol%) in a Schlenk flask (volume: 37 mL). Acetylene gas (34 mL, 1.40 mmol) was added through the side arm with a balloon. The reaction was allowed to stir at room temperature for 24 h. The resulting polymer was filtered over a cotton plug using dichloromethane as a solvent before precipitating from ether. The polymer was collected over a fritted funnel, redissolved in dichloromethane and precipitated from hexane again. A bright yellow polymer was obtained (1.56 g, 69% yield). GPC (vs. polystyrene standard in chloroform): $M_n = 48 \times 10^3$, $M_w/M_n = 3.7$. Repeat = 1600 g/mol, $P_n = 30$. IR, cm$^{-1}$: 3478, 2987, 2156, 1739, 1734, 1652, 1502, 1456, 1379, 1305, 1202, 1188, 1184, 1173, 968, 859, 771, 749, 680. $^1$H NMR (300 MHz, CDCl$_3$): $\delta =$ 7.40-7.25 (bd, 2H), 5.30-4.98 (b, 21H), 4.20-4.40 (b, 1H), 2.30 (bs, 3H), 1.70-1.30 (m, 60H), $^{13}$C NMR (400M Hz, CDCl$_3$): $\delta =$ 174.98, 170.64, 169.48, 169.29,
169.02, 140.42, 138.54, 135.01, 123.85, 123.18, 93.45, 92.73, 69.28, 69.05, 68.87, 66.58, 64.95, 29.56, 27.57, 20.88, 19.93, 16.61, 16.53.

Figure 5.6. $^1$H NMR of polymer 5.3 (top); $^{13}$C NMR of polymer 5.3 (bottom)

**Compound 5.5:** An oven-dried Schlenk flask cooled under nitrogen was charged with 2,5-diiodo-4-methylphenethylalcohol (2.00 g, 5.03 mmol), p-toluenesulfonyl chloride (1.07 g, 5.53 mmol), pyridine (1.0 mL), and chloroform (30 mL). The reaction was kept at room temperature for 12 h. The reaction mixture was washed with water (50 ml) twice.
A colorless solid, 5.5, was collected after the solvent was removed in vacuo. This crude product was further purified by recrystallization in methanol. Yield 1.93 g, 69%. IR (KBr), cm⁻¹: 2971, 2915, 2733, 2523, 2445, 2401, 2304, 2267, 1923, 1811, 1736, 1677, 1594, 1469, 1429, 1354, 1299, 1175, 1094, 1040, 992, 905, 871, 809, 775, 663, 554,494, 432. ¹H NMR (CDCl₃, 300 MHz): δ = 7.67 (d, 2H), 7.55 (s, 1H), 7.50 (s, 1H), 7.26 (d, 2H), 4.20 (t, Hz, 2H), 4.05 (t, J₃H,H = 6.8 Hz, 38H), 2.42 (s, 3H), 2.32 (s, 3H). ¹³C NMR (CDCl₃, 300 MHz): δ = 144.79, 142.37, 140.16, 139.99, 138.05, 132.93, 129.94, 128.01, 101.06, 99.89, 68.91, 39.11, 27.36, 22.07.  Mp = 97-98°C.  Elemental analysis: Calc. C: 35.44, H: 2.97.  Found. C: 35.44, H: 3.01.

**Macromonomer 5.6:** To a nitrogen purged flask, toluene-4-sulfonic acid 2-(2,5-diiodo-4-methyl-phenyl)-ethyl ester (0.770 g, 1.40 mmol), and 2-methyl-2-oxazoline (1.19 g, 14.0 mmol) were added. The flask was heated while stirring to 105°C. The reaction mixture solidified after 1 h. The excess monomer was removed by high vacuum at 100°C. IR, cm⁻¹: 3024, 1740, 1730, 1640, 1616, 1610, 1574, 1438, 1414, 1410, 1357, 1169, 1117, 1034, 1029, 1009, 973, 711, 609, 572. ¹H NMR (CDCl₃) δ = 7.69-7.60 (b, 2H), 7.59-7.56 (b, 2H), 7.19-7.15 (b, 2H), 3.77-3.70 (b, 2H), 3.60-3.30 (b, 40H), 2.38-2.32 (b, 6H), 2.22-1.98 (b, 30H). ¹³C NMR (CDCl₃) δ = 170.68, 169.75, 144.84, 142.30, 139.70, 138.16, 129.93, 128.89, 127.89, 125.81, 101.02, 99.86, 68.97, 47.81, 47.12, 45.47, 43.99, 38.98, 27.32, 22.02, 21.54. GPC (vs. polystyrene standard in chloroform): Mn = 1320, Mw/Mn = 1.15.  Elemental analysis: Calc. C: 48.48, H: 6.97.  Found. C: 49.35, H: 7.04.

**Polymer 5.7:** The diiodo polyoxazoline macromonomer 5.6 (1.85 g, 1.40 mmol) was combined with piperidine (1.5 mL), methanol (1.5 mL), (PPh₃)₂PdCl₂ (2 mg, 3 μmol, 0.2 mol%) and CuI (1 mg, 5 μmol, 0.4 mol %) in a Schlenk flask (volume: 37 mL).
Acetylene gas (34 mL, 1.40 mmol) was added through the side arm with a balloon. The reaction was allowed to stir at room temperature for 24 h. The resulting polymer was filtered over a cotton plug using dichloromethane as a solvent before precipitating from THF. The polymer was collected over a fritted funnel, redissolved in dichloromethane and precipitated in ether again. A yellow polymer, 5.7, was obtained (0.832 g, 54 % yield). GPC (vs. polystyrene standard in chloroform): $M_n = 23 \times 10^3$. Repeat = 1100 g/mol, $P_n = 23$, $M_w/M_n = 3.7$. IR, cm$^{-1}$: 3566, 3337, 3268, 2967, 2863, 1669, 1630, 1611, 1606, 1549, 1505, 608.98, 1490, 1473, 1456, 1147, 1046, 1037, 983, 975, 964, 864, 781, 636, 620. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.41 (bs), 4.36 (bs), 4.04 (bt), 3.62 (bs), 2.94 (bs), 2.28 (bt), 1.62 (bm), 1.36 (bm). $^{13}$C NMR (400MHz, CDCl$_3$): $\delta$ = 173.69, 173.50, 13.83, 136.73, 133.40, 132.84, 123.85, 123.18, 93.18, 92.54, 65.15, 64.09, 63.05, 62.55, 34.06, 32.27, 28.29, 25.47, 25.25, 24.52, 20.29. Elemental analysis: Calc. C: 61.91, H: 9.18. Found. C: 64.01, H: 8.56.
Polymer 5.9 Method 1: To a 50 mL nitrogen purged round bottomed flask, 5.8 (0.100 g, 0.041 mmol), triethylamine (1.01 g, 10.0 mmol), and DMF (5 mL) were added. The flask was heated to 100°C overnight. The excess triethylamine and DMF was removed by high vacuum at 100°C. A light green polymer, 5.9 was obtained (112 mg, 100%).

Method 2: To a 50mL nitrogen purged round bottomed flask, 5.8 (0.100 g, 0.041 mmol), triethylamine (1.01 g, 10.0 mmol), and THF (5 mL) were added. After 1 h stirring, a light green solid started to precipitate. Water (10 mL) was added, and the solid redissolved. Reaction was allowed to stir at 60°C for 24 h. The excess triethylamine was removed by vacuum at 100°C. A light green polymer, 5.9, was obtained (112 mg, 100%). Quantum yield: 0.19 in water. $^1$H NMR (CDCl$_3$) $\delta = 7.30-6.90$ (b), 6.80-6.30 (b), 4.40-4.00 (bs), 3.20-2.55 (bm), 1.60-0.40 (bm).
Optical Properties

Figure 5.8. Normalized absorption and emission spectra for polymer 5.3
Figure 5.9. Normalized absorption and emission spectra for polymer 5.7

Figure 5.10. Normalized emission spectra for polymer 5.7 in piperidine/chloroform. 5.7 in piperidine (100%), titrated by chloroform, blue shift observed.
Figure 5.11. Normalized absorption and emission spectra of polymer 5.9

Stern-Volmer Plot

Sample preparation: 5.7 (8.0 mg) dissolved in acetonitrile (95 mL) and dichloromethane (5 mL), dodecylPPE (0.2 mg) dissolved in dichloromethane (100 mL).
Figure 5.12. Stern-volmer plot of polyoxazoline PPE 5.7 vs 1,2-phenylenediamine
Figure 5.13. Stern-volmer plot of polyoxazoline PPE 5.7 vs 1-fluoro-4-nitrobenzene. [The last data([Q]=0.056286M) is off the line. It is not included.]
Figure 5.14. Stern-volmer plot of didodecylPPE vs 1,2-phenylenediamine
Figure 5.15. Stern-volmer plot of didodecylPPE vs 1-fluoro-4-nitrobenzene
Figure 5.16. Stern-volmer plot of polylactide PPE 5.3 vs 1,2-phenylenediamine
Figure 5.17. Stern-volmer plot of polylactide PPE 5.3 vs 1-fluoro-4-nitrobenzene
DSC

Figure 5.18. DSC of polylactide PPE 5.3

Figure 5.19. DSC of diiodo polylactide macromonomer 5.2
Figure 5.20. DSC of polyoxazoline PPE 5.7

Figure 5.21. DSC of diiodo polyoxazoline macromonomer 5.6
5.5 References and notes


Chapter 6
Nanoscale Phase Separated Grafted PPEs: a Precursor Towards Nanoporous Conjugated Materials

6.1 Introduction

Block copolymers with rod-coil structures undergo self-assembly during nanophase separation. An example is Hillmyer’s polystyrene (PS) and polylactide (PLA) block copolymers.\textsuperscript{1} Thick nanoporous polymeric films (0.5 mm) were made from these polymers by cleaving the polylactide (Figure 6.1). Such materials are useful as catalyst carriers,\textsuperscript{2} sensors,\textsuperscript{3} in separations,\textsuperscript{4} as drug delivery platforms,\textsuperscript{5} and as templates for the synthesis of nanoobjects.\textsuperscript{6}

![Nanoporous material prepared from PS/PLA block copolymer.](image)

Figure 6.1. Nanoporous material prepared from PS/PLA block copolymer.\textsuperscript{*}

A mechanism of nanoporous structures was proposed by Hillmyer (Figure 1.2).

\textsuperscript{*} Adapted from ref 1a
Figure 6.2. Preparation of nanoporous materials from polystyrene (PS) and polylactide (PLA) block copolymer. a.) PS/PLA block copolymer; b.) selfassembly of copolymer; c.) alignment of monolith; d.) cleavage of PLA.

Wooley prepared a poly(acrylic acid-\textit{b}-methyl acrylate-\textit{b}-styrene) triblock copolymer in THF/water and observed the formation of a single-layered ringlike nanostructure upon addition of 2,2'-(ethylenedioxy)diethylamine (EDDA) (Figure 6.3)\textsuperscript{16d}.

Figure 6.3. A.) TEM image of ringlike structure. B.) Cartoon schematic of ringlike structure. [PS (red), PMA (brown), PA (yellow), and EDDA (blue)].\textsuperscript{9}

\textsuperscript{*} Adapted from ref 1a.
\textsuperscript{#} Adapted from ref 17.
Several PPE-containing AB and ABA block copolymers have been synthesized. Although fibrous aggregation and self-assembly has been observed, the morphologies of these materials are quite different from those nanocircles prepared by polystyrene-\textit{b}-polylactide block copolymers and PAA-PMA-PS triblock copolymer which were reported by Hillmyer and wooley.

![Image of self-assembled nanostructures of nanotubes from PPE-\textit{b}-PDMS block copolymer]

Figure 6.4. Self-assembled nanostructures of nanotubes from PPE-\textit{b}-PDMS block copolymer. The dimension of the picture is 5 x 5 microns.

6.2 Results and Discussion

Synthesis of partly grafted PPEs

Since Wang et al. reported the first grafted PPE—polycaprolactone grafted PPE in 2003, several other grafted PPEs such as polystyrene grafted PPEs have also been
However, all of reported grafted polymers have large macromolecular side chains. In most cases, the PPE main chain weight percentages are less than 10%, therefore their morphologies are dominated by side chains. To achieve nanoscale phase separation with grafted PPEs, the side chain content must be reduced. We adapted the results from Hillmyer’s reports\(^1\) in which the ratio of rigid polymer (rod) to flexible polymer (coil) is about 60:40 by weight. In our case, the designed flexible side chain weight percentage is about 40% of total grafted PPEs. To force phase separation, the flexible side chains have to reach a certain length. Taking these factors into account, partially grafted PPEs are an excellent approach for the development of self-assembled co-polymers.

Scheme 6.1. Synthesis of polymer 6.5.

Two methods were developed to synthesize grafted PPEs. In the first method, macromonomer 6.3 was made by reacting 6.1 with ε-caprolactone catalyzed by Sn(O–C=OCHEtBu)₂ at 100°C for 12 h (Scheme 6.1). After drying at 60°C in vacuo overnight, diiodo monomer 6.4 (nine equivalents) was added. The mixture was dissolved in THF and piperidine. Addition of a trace amount of (Ph₃P)₂PdCl₂ (0.2 mol%), Cul, and a measured quantity of acetylene gas furnished a deep-yellow, flaky material, 6.5, after precipitation from acidified methanol. The polydispersity index (PDI) of 6.5 was 5.6 and the $M_n$ is $46 \times 10^3$. In the second attempt, 6.1 (10%), 6.4 (40%), and 2,5-bis(ethylhexyl)-1,4-diethynyl benzene (50%) were dissolved in THF and piperidine. (Scheme 6.2) (Ph₃P)₂PdCl₂ (0.2 mol%) was added after oxygen was removed. Reaction was stopped after 24 h. Polymer 6.6 was obtained as bright yellow solid after precipitation from methanol. The GPC measured a $M_n = 13 \times 10^3$, and PDI = 3.1. Polymer 6.6 was dried under vacuum at 60°C for 48 h to remove water and methanol. Precursor 6.6 and xylene
were added into an oven-dried pressure tube. Then the reaction mixture was heated up to 115°C under a nitrogen flow for 30 min to remove trace amounts of water. The pressure tube was sealed after lactide and tin(II)-2-ethylhexanoate were added. The reaction was allowed to stir at 130°C for 24 h. A green solid was precipitated from acidified methanol. From GPC result, polymer 6.7 has a $M_n = 26 \times 10^3$, and PDI = 2.9.

The first scheme is good for controlling the length of macromolecular side chains, however, the final grafted PPE will have a greater PDI. The second scheme yields a grafted PPE with relatively lower PDI, however, the length of side chains may not be controlled as well as in first scheme.

Fabrications of honeycomb microporous structured polymer films

Microporous polymer films with pore sizes on the micro/nanometer scale have received increasing interest in the past a few years for opto-electronic applications, and biomaterials. Many methods have been developed to fabricate such microporous materials. Srinivasarao’s et al. developed a simple and robust method that can be used for fabrication of conjugated polymer PV cells which have a honeycomb nanostructure. In this method, polymer sample was dissolved in carbon disulfide at a concentration of 0.1-5% (weight). The polymer solution was cast onto a glass substrate, and carbon disulfide was evaporated by a moisture rich airflow. Within a few seconds, the solvent evaporated, and left behind an ordered array of holes on the solid polymer surface.
The mechanism of bubble array formation has been proposed (Figure 6.5). The bubble array is prepared by placing a drop of polymer solution onto the substrate at low temperature. Moisture rich air blows across the surface, and causes the solvent to evaporate. Evaporation brings the surface temperature close to 0°C (shown in A). The cold solution surface causes the nucleation and growth of moisture (shown in B and C). Water droplets sink into the solution, and new ordered arrays generates (shown in D and F). After the solvent evaporation is completed, the film returns to room temperature, water droplets start to evaporate, and a honeycomb structured polymer film remains (shown in G).  

Figure 6.5. A model for the formation of the honeycomb structured polymer film

10a
Polymer 6.5 surprisingly formed bubble arrays with an average diameter around 200 nm (Figure 6.6). The regular size of PPE bubbles is about 1-10 μm⁹, and they are all made from hydrophobic polymers. Polymer 6.5 is the first polymer with hydrophilic side chains that can produce breath figures, and its bubble size is significantly smaller than those of the hydrophobic polymers. A possible explanation for the smaller size is that the hydrophilic polycaprolactone side chain can enter the templating water droplet, reducing the diameter of the resulting pore. On the other hand, every repeat unit of the polycaprolactone side chains has five methylene groups, which are hydrophobic, they are able to provide enough surface tension so that the water droplets do not coalesce (Figure 6.7).
Honeycomb microstructures cannot be made from polymer 6.7 due to lack of bubble formation. The polylactide is much more hydrophilic than polycaprolactone, therefore, there is not enough surface tension to hold the water droplets apart.

**Nanoscale phase separation**

A thin film prepared from a solution of 6.5 in chloroform (0.1 wt%) dropcast on a silicon wafer at 26°C shows nanoscale phase separation. The film was investigated by AFM at different setpoints. The setpoint measures the force of the AFM tip tapping the sample surface. A decreased setpoint indicates an increased tapping strength. By adjusting the tapping strength, the structure of the polymer film underneath the surface can be investigated. In Figure 6.8 (p.116) and 6.9 (p.117), at very light tapping force, the AFM scan gave (a) and (d), which revealed the height and phase morphology of the thin film surface. As the setpoint decreased down to 1.65 V, there was no significant change on both height and phase images, as indicated in (b) and (e). As the setpoint was set to...
1.32 V, which is about 0.7 \( V_0 \) (\( V_0 \) is the setpoint where the AFM tip starts to interact with the sample), a dramatic change in both height and phase images was observed. With the strong tapping force, doughnut-like circles were observed. The holes in the doughnuts in the height image (c) corresponded to the bright area in the phase (f) (doughnut structures can be seen clearly on enlarged graphs of Figure 6.8). The areas inside and between doughnuts collapse upon strong tapping force. This part of the “doughnuts” must be softer than its backbone. One explanation is that inner part consists of soft polyester side groups and the rigid PPE forms doughnut backbone. The phase separation observed in (f) also supports this. The detailed explanation about (c) and (f) is in Figure 6.10 (p.118).

Figure 6.8. AFM tapping mode images of 6.5 with a scan size of 3.0 \( \mu \text{m} \) under different tapping strength. (a),(b),(c) Height images with decreasing setpoints, (d),(e),(f) phase images corresponding to (a)-(c). The top inserts in each of the images represent a two dimensional Fourier transform (2-D FT), which indicates the isotropic distribution.
Setpoint = 1.69 V  setpoint = 1.36 V  setpoint = 1.23 V

Figure 6.9. Enlarged images of Figure 6.8 (polymer 6.5)

From the power spectrum density (PSD) spectrum (PSD is one dimensional profile of two dimensional Fourier transform spectrum) in Figure 6.10, two characteristic domain sizes, 33 (± 5) nm and 98 (± 10) nm, were observed. The dimension of 98 nm was related to worm-like structures, while the feature ascribed to 33 nm corresponded to the average diameter of all the circles in 3 x 3 μm² scan area, as indicated by the height profiles in Figure 6.10. Also, some short rods can be found among doughnuts. The average diameter of the circles, 33.1 nm, gave a circumference of the circles as 103 nm, which is twice the average length of fully stretched molecules of 6.5.
Figure 6.10. AFM tapping mode image of 6.5 with a scan size of 3.0 μm. (a) Height image, (b) phase image. The top inserts in each of the images represent a 2-D FT, which indicates the isotropic distribution. A circle, which corresponds to a characteristic distance of 33.1 nm, can be observed from the 2-D FT of (a). The characteristic distance of 33.1 nm can also be extracted from the inserted power spectrum density (PSD) of 2-D FT on the bottom in (a). The two peaks in the PSD spectrum indicates two characteristic domain sizes, 33.1 nm and 98.5 nm roughly, corresponding to the doughnuts and worm-like structures separately.
Figure 6.11. Cartoon demonstrating the size of polymer 6.5

Referring to Figure 6.12, the height image gave detailed structure information of the doughnuts and nearby short rods. The height profile in (c) shows that the diameter of one specific doughnut-like structure is about 28 nm. Some of the doughnuts were connected to each other, and some partly overlapped. If the doughnuts consist of PPE backbones, overlap via π-π stacking between PPE backbones could be one of the
explanations. Other structures were also found in height images, such as rods, and half
circles, which filled the spaces between doughnuts. Due to the rigidity of the backbone,
short PPEs do not bend. The phase profile (d) gave a width of 14 nm of the area between
doughnut backbones. This distance was close to the dimension of a fully stretched
polyester side chain. Therefore, the doughnut-structure consists of only one or few
molecules of 6.5.

Considering the rigidity of the PPE backbone, these doughnut structures were not
stable and disappeared by annealing the film at 140 °C (Figure 6.13).

Figure 6.13. AFM tapping mode images of 6.5 with a scan size of 3.0 um under different
tapping strength. (a),(b),(c) height images with decreasing setpoints, (d),(e),(f) phase
images corresponding to (a)-(c). The top inserts in height images are PSD spectrum and
the inserts in phase images are 2-D FT.
The thin film of polymer 6.5 was annealed at 90°C, which was above \( T_g \) of polyester side chain (85°C) but lower than the \( T_g \) of the PPE backbone (130°C). There was no significant change observed by AFM. However, once annealed at 140°C for 8 h, the morphology of thin film changed (Figure 6.13).

As shown in Figure 6.14, after annealing at 140°C, the phase image (f) shows a different pattern. In height images, the “doughnuts” disappeared at strong tapping force. The phase image shows the appearance of the worm-like morphology. Locally, those worms are parallel to each other. In the whole image, those worms were distributed isotropically, which was indicated in the FT (Fourier Transform) of the height image (not shown here). Further analysis in Figure 6.14 indicates that the worm size is consistent with the fully stretched grafted PPE molecules.

![Image](image_url)

**Figure 6.14.** The zoomed-in images of 6.5 from Figure 6.8 (c) and (f) reveal detailed structure information. The images have a scan size of 1000 nm. Here (b) phase image, (c) the phase profile corresponding to the line in (b).

The profile in Figure 6.14 (c) indicates the width of the worm is 14.4 nm, which is somewhat smaller than a single fully stretched PPE molecule (around 17 nm based on the
calculation\textsuperscript{15}). The length of the worms here is not as clear as the width. A rough estimate of the length gives an average value of 55 nm, which is about the average length of fully stretched PPE 6.5 molecules. The number of “worms” decreased significant compared to that of doughnuts at room temperature, which indicates that one “worm” forms from several doughnuts. Thus the worms here are probably small lamellar crystallines consisting of several PPE molecules.

Figure 6.15. Cartoon demonstrating the formation of doughnut and worm like structures of 6.5.
From the information obtained, we can deduce that the doughnut structure of polycaprolactone-grafted PPE is not stable upon thermal treatment. The competition between rigidity of PPE main chains and interaction between soft side chains determine the conformation of PPE molecules and thus the morphology of the PPE thin films.

In order to obtain nanoporous materials from thin films of polymer 6.5, the polyester side chains had to be cleaved. The drop cast thin films made from 0.1 wt% polymer 6.5 chloroform solution was put into 1-5 wt% KOH methanol/water (50:50) solution for 12-72 h. The results were discouraging; the films peeled off silicon substrate and deformed. Therefore, they were not suitable to further study.

To solve the problem, polymer 6.7 was targeted because it is easier to degrade. Polylactide polymers are well known as degradable plastic. It was expected to be more vulnerable to basic conditions than polycaprolactone. AFM images show that 6.7 forms a fingerprint structure (Figure 6.12). The phase image (b) shows worm-like structures forming a fingerprint. The distance between separate features is about 31 nm, as indicated in the phase profile in Figure 6.16. This distance was somewhat larger than the length of fully stretched side groups (2 x 14 nm = 28 nm) of 6.7. The worm length observed in Figure 6.16 was between 100-200 nm, which is much larger than that of a fully stretched PPE molecule (28 nm based on the calculation). Therefore, this worm-like structure consists of more than one molecule. A possible assembly of the worm was that the crystallization of polyester side chains cause PPE molecules to form lamellar structures. Bending of the main backbone was not observed at this point. Efforts are currently under way to produce the doughnut-like morphologies using polymer 6.7.
Figure 6.16. AFM image of polylactide grafted PPE 6.7. Sample preparation: 0.1wt% 6.7 in chloroform, drop cast onto oxidized silicon, dried in air at room temperature for 5 h.
The cleavage of polylactide side chains was studied under the same condition as that of polymer 6.5. A thin film prepared from polymer 6.7 (0.1 wt% in chloroform) delaminated in the KOH solution. When the polymer concentration was increased from 0.1 wt% to 1.0 wt%, the resulting film was able to keep its shape for 24 h in KOH solution. The SEM images show that polylactide side chains were partially cleaved (Figure 6.18). From proton NMR data we found that however only about 10% polylactide side chains were removed. More efficient methods to cleave a higher percentage of the side chains are still under investigation.
6.3 Conclusion

This project was motivated by Hillmyer and Wooley’s work. However, the obtained results were unexpected. The formation of doughnut-like nanostructures of polymer 6.5 is totally different from their systems. One “doughnut” consists of only one or two PPE chains, which is significantly less than in any reported self-assembling system. This new mechanism of self-assembly is an interesting case of morphological control on a single molecular level. We have demonstrated that a macromolecule can preferentially form toroids or linear aggregates depending on temperature control.

More work should be done to investigate how to control the size of doughnut, e.g., the effect of length of main chain and side chain, the ration of main chain vs side chain.
chain, the role of solvent, etc. In order to prepare nanoporous materials, more efficient method of cleaving side chains should be developed.

6.4 Experimental

Macromonomer 6.3: An oven-dried Schlenk flask cooled under nitrogen was charged with 2,5-diiodo-4-methylphenethylalcohol (54 mg, 0.14 mmol), ε-caprolactone (228 mg, 2.80 mmol), and tin(II)-2-ethylhexanoate (1 mg, 3.2 μmol). The flask was heated while stirring to 100°C. The reaction was stopped after 12 h. The reaction mixture was dried under vacuum at 60°C overnight. The diiodo-polyester macromonener, 6.3, was obtained as a colorless solid (Yield: 281 mg, 100%). GPC (vs. polystyrene standards in chloroform): $M_n = 2400$, $M_w/M_n = 1.1$. IR (KBr, cm$^{-1}$): ν 2941, 2893, 2866, 1722, 1683, 1652, 1506, 1471, 1456, 1394, 1294, 1244, 1190, 1107, 1045, 962, 933, 877, 840, 731, 709. $^1$H NMR (CDCl$_3$, 400 MHz): δ = 7.67 (s, 1H), 7.63 (s, 1H), 4.24 (t, 2H), 4.05 (t, 38H), 3.64 (t, 2H), 2.98 (t, 2H), 2.30 (t, 40H), 1.68-1.60 (m, 80H), 1.41-1.33 (m, 40H).

$^{13}$C NMR (CDCl$_3$, 400 MHz): δ = 173.73, 173.54, 173.29, 141.91, 139.91, 139.87, 139.82, 100.76, 100.03, 64.54, 64.14, 63.95, 63.10, 62.62, 38.64, 34.23, 34.12, 33.95, 33.82, 33.34, 28.53, 28.35, 28.18, 26.96, 25.93, 25.53, 25.31, 24.98, 34.69, 24.58, 24.39.


Polymer 6.5: 6.3 (281 mg, 0.140 mmol) was combined with 6.4 (685 mg, 1.26 mmol), piperidine (1.5 mL), THF (1.5 mL), (PPh$_3$)$_2$PdCl$_2$ (2 mg, 2.8 μmol, 0.2 mol%) and CuI (1 mg, 5.3 μmol, 0.4 mol%) in a Schlenk flask (37 mL). Acetylene gas (34 mL, 1.40 mmol) was added through the purged side arm with a balloon. The reaction was allowed to stir at room temperature for 24 h. The reaction mixture was extracted by dichloromethane (50 mL) and washed with ammonium hydroxide (10%, 50 x 2 mL), and HCl (10%, 50 mL).
The organic layer was dried over MgSO\textsubscript{4} and concentrated under reduced pressure. The remaining mixture (10mL) was precipitated from acidified methanol. The polymer was collected over a fritted funnel, re-dissolved in dichloromethane and precipitated from acidified methanol again. A green polymer, 6.5, was obtained (0.591 g, 89 % yield).

GPC (vs. polystyrene standard in chloroform): $M_n = 4.6 \times 10^4$, $P_n = 75$, $M_w/M_n = 5.6$. $^1$H NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 7.41$ (bs), 4.04 (bt), 3.62 (bt), 3.49 (s), 2.76 (bs), 2.32-2.28 (bt), 1.62-1.40 (bm), 1.36-0.90 (bm). $^{13}$C NMR (400 MHz, CDCl\textsubscript{3}): $\delta = 173.69, 141.01, 133.35, 123.85, 123.18, 93.46, 92.54, 65.15, 64.09, 63.05, 62.55, 40.28, 38.56, 34.06, 32.27, 28.80, 28.29, 25.47, 23.10, 25.25, 24.52, 20.29, 14.10, 10.83. Elem. Anal. Cal. C: 77.73%, H: 10.04. Found: C: 78.94%, H: 10.98%

Polymer 6.6: An oven-dried Schlenk flask cooled under nitrogen was charged with 6.1 (195 mg, 0.500 mmol), 6.4 (1.09 g, 2.00mmol), bisethylhexyl-diethynyl-benzene (0.875 g, 2.50 mmol), THF (5 mL), piperidine (1.50 mL), (PPh\textsubscript{3})\textsubscript{2}PdCl\textsubscript{2} (2 mg, 2.8 µmol) and CuI (1 mg, 5.3 µmol). The flask was degassed and filled with nitrogen. The reaction was allowed to stir at room temperature for 24 h. The reaction mixture was filtered over silica on a fritted funnel with hexane. After hexane evaporated, the crude product was dissolved in chloroform (10 mL), and added into from methanol (300 mL) dropwisely. A bright yellow solid, 6.6, (1.342 g, 85%) was obtained. GPC (vs. polystyrene standards in chloroform): $M_n = 1.3 \times 10^4$, $M_w/M_n = 3.1$. $^1$H NMR (CDCl\textsubscript{3}): $\delta = 7.46$ (bs), 7.42-7.20 (bm), 4.00 (bt), 2.93-2.61 (bm), 2.53 (bs), 1.90-1.05 (m), 1.40-0.90 (bm), 0.85-0.75 (bd). $^{13}$C-NMR (CDCl\textsubscript{3}): $\delta = 141.29, 133.25, 123.07, 93.38, 62.83, 40.28, 38.58, 32.48, 28.80, 25.60, 23.10, 14.10, 10.83. Elem. Anal. Cal. C: 88.55%, H: 10.93. Found: C: 87.52%, H: 11.03%
DSC data of 6.5

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Figure 6.19. DSC data of 6.5. Two peaks observed: 85°C (Tg of polycaprolactone) and 130°C (Tg of PPE main chains).

**Polymer 6.7: 6.6** (0.600 g) was added to xylene (5 mL) in a pressure tube at 125°C under nitrogen flow. After 30 min, lactide (0.400 g, 2.78 mmol), tin(II)-2-ethylhexanoate (13 mg, 31 μmol) was added, and the pressure tube was sealed. The reaction was heated while stirring to 125°C for 24 h. The reaction mixture was precipitated from acidified methanol (100 mL). Polymer 6.7 was obtained as a green solid (0.853 g, 85%). GPC
(vs. polystyrene standards in chloroform): \( M_n = 2.6 \times 10^4, M_w/M_n = 2.9 \). \(^1\)H NMR (CDCl\(_3\), 400 MHz): \( \delta = 7.42\text{-}7.20 \) (bm), 5.35\text{-}4.90 (bm), 2.93\text{-}2.61 (bm), 1.90\text{-}1.05 (m), 1.60\text{-}1.40 (bm), 1.40\text{-}0.90 (bm), 0.85\text{-}0.75 (bd). \(^{13}\)C NMR (CDCl\(_3\), 400 MHz): \( \delta = 169.48, 141.01, 133.82, 124.05, 93.40, 69.05, 40.28, 38.56, 32, 47, 28.80, 25, 60, 23.10, 20.47, 16.61, 14.10, 10.90 \). Elem. Anal. Cal. C: 71.47%, H: 8.57. Found: C: 74.42%, H: 9.24%.

**DSC data of 6.7:**

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Figure 6.20. DSC data of **6.7**. Two peaks observed: 68°C (Tg of polylactide); 132°C (Tg of PPE main chains)
6.5 References and notes


15. Calculation of polymer 6.5: a) Side chain: one repeat unit of polycaprolactone is about 0.84 nm, 20 repeat unit is close to 17 nm. b) Main chain: one PPE repeat unit is 0.7 nm, 75 repeat units is close to 54 nm.


Chapter 7
Allyloxy PPEs: Precursor to a Highly Fluorescent Photocrosslinked Conjugated Polymer

7.1 Introduction

A variety of poly(phenyleneethynylene)s (PPEs) have been synthesized and studied. However, to our knowledge, there is no report of thermal or photocrosslinkable PPEs. Photocrosslinkable conjugated polymers are of great interest, because they can be easily microstructured utilizing photolithography. Potential applications include but are not restricted to flexible light emitting diodes, photovoltaic cells, transistors, sensory laminates and potentially waveguides. In a recent contribution, Zojer et al. have tuned the electroluminescence color in light emitting devices by utilizing a thiol-addtion through the double bonds of PPVs or through photoaddition of hydrazine gas to a PPV derivative, while Kido et al. have shown that photobleaching of dye molecules in a polyvinylcarbazole matrix can be utilized to photopattern fluorescent materials. While exposure to photons often leads to bleaching, fluorescence enhancements are much less common. In this chapter, we will present a case here, where negative photolithography of polymer 7.5 leads to a) a crosslinked and insoluble structure, and b) the crosslinked material is one decade more fluorescent than its precursor 7.5.
Allyl monomers are not good candidates for radical homopolymerization because of the process of hydrogen abstraction from the allylic methylene group, leading to stable radicals. Therefore, the chain transfer rate is higher than propagation rate which explains why radical homopolymerization of allyl monomers has a low rate and gives low molecular weight products.\textsuperscript{18} However, in our case, allyl side chains are attached to PPE macromolecules, which have molecular weights of 7000-10000, so even very small amounts of allyl side chains dimerize, that will make the resulting PPE insoluble.

\begin{center}
\begin{tikzpicture}
\node (A) at (0,0) {R-O-CH\textsubscript{2}CH=CH\textsubscript{2}};\node (B) at (1.5,0) {\text{stable radical}};\node (C) at (1.5,-0.5) {R'H};\node (D) at (3.5,0) {R'O-CH-CH=CH\textsubscript{2}};
\draw (A) to [bend right] node[above] {R'} (B);
\draw (A) to (C);
\draw (B) to (D);
\end{tikzpicture}
\end{center}

Scheme 7.1. Formation of stable allyloxy radical

The second goal of this project is motivated by the potential application of polymer 7.5 as a precursor for two photon microfabrication (TPM). By TPM technology, three dimensional microstructures can be prepared. Such structures can be used as photonic crystals (PC), a dielectric material which has periodicity on the optical wavelength range. The applications of PC include localization of light, low threshold lasers, and faster fiber optics in the telecommunications wavelength.\textsuperscript{16}
2.2 Results and Discussion

![Scheme 7.2.Synthesis of the diallyloxy-PPE 7.5.](image)

Starting from 2,5-diiodohydroquinone 7.1, reaction with 3-bromopropene in the presence of potassium carbonate in acetone at room temperature furnishes 1,4-bisallyloxy-2,5-diiodobenzene 7.2 in almost quantitative yield. Pd-catalyzed coupling of 7.2 with the diyne 3 forms the PPE 7.4 that is isolated as greenish material after precipitation into methanol. Upon examination of the PPE 7.4 we found that part of the allyl groups were cleaved off the backbone, due to the presence of the Pd-catalyst. Such types of Pd(0) catalyzed deallylation reactions have been reported and are not that unusual, but in this case the partial deallylation was undesired. The structural integrity of the obtained PPE is not compromised by this deallylation reaction. To obtain a structurally uniform material we decided to fully allylate 7.4 by exposure towards an
excess amount of 3-bromopropene in the presence of potassium carbonate in DMF. The isolated and now fully allylated PPE 7.5 did not display defects according to its NMR spectra. It is greenish-yellow in appearance. In solution the allyloxy PPE 7.5 displays a fluorescence quantum yield of 0.45 in chloroform.

Fluorescence increasing upon UV irradiation

Figure 7.1 shows the absorption and emission spectra of 7.5 in solution and in thin films. In solution, 7.5 has an absorption maximum at 413 nm and an emission maximum at 449 nm, while in the solid state both values are red shifted to 441 and 471 nm respectively. Both spectra are in consistent with published values.12

Figure 7.1. Normalized absorption and emission spectra of 7.5 in chloroform and in the solid state.
Carbon-carbon double bonds can perform photochemical [2+2] cycloadditions into cyclobutanes, therefore, we reasoned that a films of polymer 7.5 should be photo-patternable. A fused silica mask displaying the US Airforce test pattern on was placed over a thin spin-cast film of 7.5 (thickness: 40-60 nm) and irradiated for 23 min under nitrogen with a 100 W high pressure Hg vapor-lamp (365 nm). After irradiation, the un-exposed areas could be washed away by THF. Features with a line width of ~3 μm and sharp edges were formed by photopatterning and development of 7.5 (Figure 7.2). Interestingly, the fluorescence of the photocrosslinked areas of 7.5 in thin films were significantly enhanced relative to that of the unexposed areas. Exposure of a film through a transmission mask with the letter GT (without development) resulted in a strongly fluorescent pattern with good contrast relative to the unexposed area (Figure 7.2).

Figure 7.2. Photopatterning structures with allyloxy-PPE 7.5.
Figure 7.3. (a) Uv-vis spectrum of a thin film of 7.5 after different times of irradiation. (b) Emission spectrum of the same sample. Inset: Comparison of the Uv-vis spectra of 7.5 at 0 min and 23 min of irradiation.
To further investigate photochemical crosslinking process, we irradiated thin spin-cast films of different optical densities (0.061, 0.032, 0.024, 0.009). In Figures 7.3 and 7.4 a series of irradiation experiments are displayed. Optically thicker films show larger fluorescence enhancements, and when the film thickness is < 0.024 in absorption, the enhancement factors are small. In thick films the fluorescence increase exceeds a factor of 10, but the shape of the emission does not change much, as is clear from Figure 7.3. In absorption, there is a blue-shift and a decrease in absorptivity recorded. In the inset of Figure 7.3 a normalized comparison of the film of 7.5 before and after 23 min of irradiation under nitrogen is shown. These experiments were repeated several times to exclude artifacts and to verify reproducibility of the fluorescence enhancements. We obtained a large increase in fluorescence intensity upon irradiation in every experiment.

![Figure 7.4. Emission intensities versus irradiation time for thin films of 7.5 with different optical densities.](image)

To obtain information about the structural changes in the polymer we performed Raman and IR spectroscopies on the pristine and the irradiated samples. In both cases
only the peaks around 1549 cm\(^{-1}\), attributed to the vibrations of the double bond in the allylic groups of 7.5, changed to a significant extent while all of the other peaks, particularly the peak attributed to the C-C triple bonds at 2197 cm\(^{-1}\) remained unchanged. Solid-state \(^{13}\)C NMR spectroscopy on 7.5 before and after crosslinking was not able to detect any change.

Figure 7.5. Top: Raman spectra of 7.5 before and after crosslinking. Inset shows the detail region at 1549 cm\(^{-1}\). Bottom: IR spectra of 7.5 before and after photo crosslinking.
From the data presented, two questions arise: What is the structure of the crosslinked polymer and why does it show a significant change in emission and absorption?

From the experimental results we conclude that only a small amount of allyl groups crosslinking, and that is sufficient to induce full insolubility to this PPE. That is a reasonable assumption, because PPE 7.5 is not overly soluble to begin with. If two or three allyl groups in each chain photodimerize, a polymer of ultrahigh molecular weigh results. If the chemical structure of the photocrosslinked polymer is so similar to that of pristine 7.5 why do the optical properties change significantly? It is known that both absorption and emission of PPEs are dependent upon the conformation of the main chain.14,15 Particularly in the solid state this can lead to dramatic changes in emission lifetimes and the position of the emission maximum. From the Uv-vis spectra we conclude that the crosslinking induces a twist of the backbone, while in the emission we see a slight red shift, suggesting, that the chromophoric backbone is not disturbed. We suggest here that the UV-irradiation has “burned out” any non-emissive defect structures in 7.5 and has disturbed the planar packing of the PPE 7.5 to give a material with the described and desirable optical properties.

**Two-photon microfabrication (TPM)**

Polymer 7.5 was found be photocrosslinked by UV light, which is a basic requirement of TPM. A simplified scheme of two photon polymerization was shown in the Figure 7.6.9 Surprisingly, polymer 7.5 can undergo two-photon polymerization without an initiator.
Figure 7.6. Energy diagram for two photon polymerization. Valence electrons of an initiator are excited from the ground (S0) to the first excited (S1) single state by simultaneously absorbing two photons. The excited electrons then relax by transition to the triplet state (T1) via intersystem crossing, where the initiator can undergo bond cleavages, producing radicals for photopolymerization or relax to ground state by fluorescence or phosphorescence emission.

By TPM, polymers can form elaborate 3D structures, useful for photonic crystals (PCs). PCs have periodicity in optical wavelength. The applications of PCs include localization of light, low threshold lasers, etc. For polymers used for PC applications, high refractive index is desirable. The refractive index of 7.5 was found to be 1.69. Although it still does not reach the critical refractive index 1.9 (for woodpile structures to achieve full 3D band gaps), it is much higher than other polymers such as PMMA (around 1.3) used in TPM. 3D woodpile (Figure 7.7 and 7.8) structures have been successfully made from polymer 7.5.
Bubble arrays

Similar as azide crosslinkable PPE, \(^\text{17}\) allyloxy PPE forms bubble arrays, which can be used to make picoliter beakers. The thermal crosslinking reaction of \textbf{7.5} does not
involve the C-C triple bonds on the PPE’s main chain, so after crosslinking, the bubble arrays are still fluorescent.

Figure 7.9. Picoliter beaker made from polymer 7.5 by thermal crosslink at 200°C.

From previous experiments we know only a small part of allyloxy side chains undergo crosslinking reaction, and most of the unreacted unsaturated C-C double bonds are left. This allows us to crosslink the bubble arrays first, and then modify the array by a solid state reaction.

7.3 Conclusion
We have shown that suitably allyloxy-substituted PPEs are photo-crosslinkable; the formed materials are chloroform insoluble yet highly fluorescent. This processing scheme should allow the use of specific PPEs for photo-patterned emissive structures that may be useful for LED applications as waveguides and as fluorescent “chemical noses”. Preliminary experiments show that potential of device fabrication, two-photon crosslinking and construction of three-dimensional structures utilizing this approach.
7.4 Experimental

**Compound 7.2:** To a nitrogen purged flask were added 1 (7.34 g, 20.0 mmol), acetone (250 mL), potassium carbonate (13.8 g, 0.100 mol), and allyl bromide (7.26 g, 60.0 mmol). The reaction was allowed to stir at 26°C for 3 d. The reaction mixture was poured into water and extracted with methylene chloride (2 x 100 mL). The organic layer was washed by water (2 x 200 mL), and then dried over MgSO₄. The solvent was subsequently removed *in vacuo*. A light brown color solid **7.2** was obtained (8.39 g, 95%). IR (KBr) cm⁻¹ = 736, 813, 860, 929, 1097, 1265, 1352, 1444, 1485, 1544, 1647, 1865, 2742, 2823, 3072. ¹H NMR (CDCl₃) δ = 7.19 (s, 2H), 5.85-6.15 (m, 2H), 5.51-5.45 (d, 2H), 5.32-5.29 (d, 2H), 4.51-4.49 (d, 4H). ¹³C NMR (CDCl₃) δ = 152.2, 132.1, 123.0, 117.6, 86.0, 70.6. Elemental analysis: Calc. C: 32.61, H: 2.74. Found. C: 32.55, H: 2.83.

**Polymer 7.4:** An oven-dried Schlenk flask cooled under nitrogen was charged with **7.2** (0.553 g, 1.25 mmol), **7.3** (0.439 g, 1.25 mmol), piperidine (1.5 mL), THF (1.5 mL), (PPh₃)₂PdCl₂ (2 mg, 2.8 μmol, 0.2 mol%) and CuI (1 mg, 5 μmol, 0.4 mol%). The reaction stirred at room temperature for 16 h. dichloromethane (100 mL) was added into reaction mixture, then washed with 10% ammonia hydroxide (2 x 300 mL) and 10% HCl (300 mL). The organic layer was concentrated to 20 mL under reduced pressure at room temperature, and filtered over cotton before precipitating into methanol (300 mL). Polymer **7.4** (0.337 g, 55%) was obtained as a deep green solid. GPC (vs. polystyrene standards in chloroform): Mₙ = 8,230, Mₘ/Mₙ = 2.54. IR (KBr) cm⁻¹: 727, 983, 1024, 1267, 1303, 1350, 1359, 1415, 1440, 1460, 1485, 1502, 1544, 1598, 1647, 2198, 2586, 2729, 2856, 2954, 3016, 3529. ¹H NMR (CDCl₃, 300 MHz): δ = 7.37 (bs, 2H), 7.13 (bs,
0.7H), 7.04 (bs, 0.8H), 6.94 (bs, 0.5H), 6.12 - 6.07 (m, 1.4H), 5.53 - 5.47 (d, 1.4H), 5.33 - 5.30 (d, 1.4H), 4.65 - 4.63 (bd, 2.8H), 2.80 - 2.60 (bm, 4H), 1.82 - 1.70 (bm, 2H), 1.42 - 1.20 (bm, 16H), 0.98 - 0.75 (bm, 12H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ = 153.4, 150.6, 141.8, 141.4, 133.9, 124.1, 123.3, 122.6, 119.1, 117.7, 115.3, 110.4, 97.3, 94.6, 90.8, 87.9, 70.4, 41.2, 38.6, 32.8, 29.2, 25.9, 23.5, 15.0, 11.2.

**Polymer 7.5:** Polymer 7.4 (0.337 g, 0.700 mmol) combined with potassium carbonate (0.191 g, 1.40 mmol), allyl bromide (0.168 g, 1.40 mmol), and DMF (40 mL) in a round bottomed flask. The reaction was allowed to stir at room temperature for 4 d. The reaction mixture was added into dichloromethane (100 mL), washed with water (2 x 300 mL). The organic layer was concentrated to 20 mL under reduced pressure at room temperature, and then filtered over cotton before precipitating into methanol (300 mL). A green polymer, 7.5, was obtained (0.387 g, 96% yield). GPC (vs. polystyrene standard in chloroform): $M_n$ = 8,420, $M_w/M_n$ = 2.51. IR(KBr) cm$^{-1}$: 727, 773, 827, 898, 921, 995, 1024, 1101, 1155, 1207, 1217, 1274, 1359, 1379, 1415, 1456, 1487, 1508, 1539, 1587, 1647, 1847, 2200, 2817, 2858, 2910, 3016. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ = 7.37 (s, 2H), 7.02 (s, 2H), 6.12 - 6.00 (m, 2H), 5.53 - 5.47 (d, 2H), 5.32 - 5.29 (d, 2H), 4.63 (bd, 4H), 2.80 - 2.60 (bm, 4H), 1.82 - 1.70 (bm, 2H), 1.42 - 1.20 (bm, 16H), 0.98 - 0.75 (bm, 12H). $^{13}$C NMR (CDCl$_3$, 300 MHz): $\delta$ = 152.9, 141.1, 132.9, 122.6, 119.1, 117.7, 116.9, 94.6, 90.8, 70.0, 41.2, 38.1, 32.3, 28.6, 25.4, 23.5, 13.9, 10.7. Elem. Anal. Cal. C: 82.28%, H: 8.83%. Found: C: 79.77%, H: 8.72%

**Preparation of films**
The thick films of 7.5 for TPM were made by drop casting and evaporation of a concentrated solution of 7.5 on allyloxyundecyltrimethoxysilane (AUTMS)-treated cover slips. Saturated solutions of 7.5 in THF or toluene were prepared and films were prepared on cover slips (22 x 22 x ~ 0.120 mm, Fisher Scientific). Irradiation and washing demonstrated that 7.5 can polymerize without using a photoinitiator during the TPM process. Therefore, we did not dope any photoinitiator into films of 7.5 for the TPM.

The thin films for fluorescence experiments were made by spin-coating (6000 rpm, 40 seconds) of polymer 7.5 solutions on quartz (pre-cleaned by concentrated H₂SO₄) (solvent: toluene, spectroscopically grade) with different concentrations to achieve different absorbances ranging from 0.1 to 0.009 (absorption peak value). The solutions were filtrated by the 100 nm-pore size PTFE filter before the spin-coating.

**Absorption and emission experiments**

The absorption and emission spectra were taken by UV-2401 PC UV-vis Recording spectrophotometer, Shimadzu and RF-5301 PC Spectrofluorophotometer, Shimadzu. The emission spectra were done with a 90°-offset geometry (the sample holder tilted a little bit away from the right angle and no reflected light can be detected by the emission detector). The UV lamp is Entela certified Blak-Ray Long Wave UV Lamp (Model B 100AP, MDSK, 100 W, 365 nm) and the fluence of the lamp is 11.65 mW/cm² at 365 nm. The exposure was done in air and in argon.

**TPM experiments**

Thick films were made as described above. The TPM experiments were performed by using a femto-second laser (wavelength of 730nm) with different powers.
The optical polarized microscope and SEM imagine taken

The structures were first viewed by a transmission microscope (Micropublisher 3.3, Nikon). SEMs were done with the LEO 1530 thermally-assisted field emission scanning electron microscope (SEM) in the MSE department.

**IR spectra measurements under microscope**

The IR spectra were measured under microscope using our DigiLab IR microscope using cover slip and gold mirror as the references for the transmission and reflection measurement respectively.

**UV patterning**

![Microscope images](image)

Figure 7.10 Microscope images of polymer 7.5 after UV exposure

**UV bleaching Experiments**
Figure 7.11. Emission change of 7.5 upon the UV irradiation. (Film UV absorption max = 0.061)

Figure 7.12. Emission change of 7.5 upon the UV irradiation. (Film UV absorption max = 0.032)
Figure 7.13. Emission change of 7.5 upon the UV irradiation. (Film UV absorption max = 0.024)

Figure 7.14. Emission change of 7.5 upon the UV irradiation. (Film UV absorption max = 0.009)
Figure 7.15. Emission change of 7.5 upon the UV irradiation. (Film UV absorption max = 1.087)

7.5 References


