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Poly(pyridinium salt)s exhibiting liquid-crystalline and light-emitting properties

James Joseph Cebe
University of Nevada, Las Vegas

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POLY(PYRIDINIUM SALT)S EXHIBITING
LIQUID-CRYSTALLINE AND LIGHT-EMITTING PROPERTIES

by

James Joseph Cebe

Bachelor of Science
University of Nevada, Las Vegas
2000

Bachelor of Science
University of Nevada, Las Vegas
2000

A thesis submitted in partial fulfillment of fulfillment for the

Master of Science Degree in Chemistry
Department of Chemistry
College of Sciences

Graduate College
University of Nevada, Las Vegas
December 2003

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James J. Cebe

Entitled

Poly(pyridinium salt)s Exhibiting Liquid-Crystalline and Light-Emitting Properties

is approved in partial fulfillment of the requirements for the degree of

Master of Science

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ABSTRACT

Poly(pyridinium salt)s Exhibiting Liquid-Crystalline and Light-Emitting Properties

by

James Joseph Cebe

Dr. Pradhip K. Bhowmik, Examination Committee Chair
Assistant Professor of Chemistry
University of Nevada, Las Vegas

The research presented in this thesis is based on the synthesis and characterization of poly(pyridinium salt)s containing tosylate and triflimide counterions that possess both liquid-crystalline properties as well as light emitting properties. Both the solution-state and solid-state emission behavior of these synthesized materials were investigated. They possessed several emission peaks in their spectra ranging from 280 nm to about 550 nm. Some of these polymers were found to form liquid-crystalline properties in common organic solvents such as methanol and dimethylsulfoxide (DMSO), while others were found to exhibit a liquid-crystalline phase upon melting, and are so-called thermotropic liquid crystals. The polymers in solution formed a full-grown lyotropic liquid-crystalline phase at concentrations as low as 5 wt % in methanol and 19 wt % in DMSO. The thermotropic liquid-crystalline polymers containing triflimide counterions had much lower melting transitions than those containing tosylate counterions.
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I would like to thank Dr. Pradip Bhowmik for allowing me to work with him as an undergraduate as well as a graduate student. “You have taught me many things over these years, and not all of it was Chemistry related. You are an exceptional professor and it has been my pleasure to work with you.”

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CHAPTER 1

INTRODUCTION

1.1 Liquid-Crystalline Polymers

In order to talk about liquid-crystalline polymers, it is first necessary to define what constitutes a liquid-crystalline state of matter. This is a state of matter in which liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present. Some polymeric materials are capable of generating such a state of matter through either thermal induction (thermotropic liquid-crystal) or solution induction (lyotropic liquid-crystal). Next, it is important to address what type of materials can form liquid crystals. For any liquid-crystalline phase, the most basic property is its anisotropy, which entails the presence of anisotropic building blocks to obtain the overall anisotropic bulk properties. There are certain geometries that satisfy this requirement, the most common of which are rods (one dimension is much larger than the other two) and discs (one dimension is much smaller than the other two). This discussion, however, will focus primarily on rod-like materials, specifically ionic aromatic polycondensation liquid-crystalline polymers, as this is the scope of the research presented in this thesis.

Main-chain aromatic polymers exhibiting lyotropic liquid-crystalline behavior or thermotropic liquid-crystalline behavior have received increased attention from both industry and academia over the past few decades. Polymers that may form a mesomorphic phase in common organic solvents may find applications in the areas of...
films, coatings, barrier membranes, polymer blends, and composites,\(^2\) while those polymers with lower thermal transition temperatures might lead to easier thermal processability over other polymers. There are several classes of polymers that have been prepared, which exhibit liquid-crystalline behavior. Many of them are neutral polymers, and others are ionic, with either cationic moieties or anionic moieties as part of the polymer chains. One of the more highly studied groups of neutral liquid-crystalline polymers is the main-chain aromatic polycondensation polymers in which polyesters and polyamides are classified. These types of polymers have received increased attention since the development of the thermotropic liquid-crystalline polyester Vectra (Celanese) and the lyotropic liquid-crystalline polyamide Kevlar (Du Pont). The formation of a liquid-crystalline phase allows for the fabrication of ultrahigh-strength and modulus Kevlar fibers from concentrated solution, and the production of the high-strength engineering plastic Vectra by melt processing.\(^2\) The production of these polymers is possible, but the processing conditions are drastic. Kevlar requires the use of concentrated sulfuric acid to prepare a lyotropic liquid-crystalline solution from which its fibers can be made, and polyesters like Vectra require high temperatures for the thermotropic liquid-crystalline phase to form. It would therefore be of interest to develop main-chain aromatic polycondensation polymers that have a lower thermotropic liquid-crystalline transition temperature, or that can form a liquid-crystalline solution in common organic solvents or even water. These more feasibly conditions would help to facilitate the fabrication, processing, and application of these types of polymers. These factors are providing the motivation for the development of these new types of materials.

Incorporating a liquid-crystalline phase into solutions of aromatic polycondensation polymers is complex and dependent on several factors. In general, the polymers should
have a rod-like structure with extended rigid chain character to facilitate the alignment of the macromolecular chain along a particular direction. The polymer's solubility must be sufficiently high to exceed the critical concentration at which the formation of a biphasic solution occurs. A biphasic solution is one in which a liquid-crystalline phase coexists with an isotropic phase. The extent and type of interactions between the polymer chains themselves and those between the chains and solvent molecules can also provide significant influence on the phase behavior of the polymers. Since the solubility and chain rigidity of a polymer are affected by its structure, molecular weight, polymer-polymer and polymer-solvent interactions, and temperature, it seems logical to introduce polar groups onto a polymer chain to increase polymer-solvent and polymer-polymer interactions in hopes of increasing solubility and the prospects of the formation of liquid-crystalline solutions in common organic solvents or even water. Polar substituents may also introduce additional dipolar interactions between polymer chains, which will favor long-range cooperative alignment of the polymer chain.

Over the years, attempts have been made to incorporate these features into many different polyesters and polyanides in an attempt to form liquid crystals in common organic solvents and water. Some of these polymers are shown in Figure 1. Of the materials shown in Figure 1, the only ones that exhibit a lyotropic liquid-crystalline phase are those indicated with the *. These materials formed lyotropic liquid-crystalline solution in aqueous organic solvents (DMSO or DMF and water) as well as pure DMF. In fact the polymer with $X = H$ and $Y = \text{NO}_2$ also showed a lyotropic phase in pure water. Upon heating, these polyesters decompose and did not show any thermotropic liquid-crystalline transitions in the solid state.
The polyamide shown below has also been synthesized, and it also showed a lyotropic phase in aqueous DMSO above 50 wt %.

Another class of polymers that also have the ability to exhibit liquid-crystalline properties is the ionene polymers. These are polymers that contain quaternary nitrogen atoms in the backbone, and examples of this type are shown in Figure 2. One particular type of ionene polymer that has been found to exhibit a thermotropic liquid-crystalline phase are the polymers containing 4,4'-bipyridyl moieties in the polymer backbone. These polyelectrolytes are also known as viologen polymers or polyviologens. Besides their liquid-crystal properties, this class of materials also exhibits a number of interesting properties including electrical conductivity, photochromism, thermochemistry, and photomechanical behavior. Polyviologens are a subset of a larger group of polymers known as poly(pyridinium salt)s, some of which are also shown in Figure 2. These
Figure 2. Polyviologens and Poly(pyridinium salt)s
nitrogen-containing polymers typically consist of π-electron-deficient heterocycles containing imine nitrogen in the aromatic moieties. Harris et al. reported the synthesis of this class of polymers containing BF$_4^{-}$, by a ring-transmutation polymerization and the characterization of their physical properties. Although their glass transition temperature, $T_g$, values cannot be determined, by DSC measurements, they exhibit distinct melting endotherms with a minimum above 380 °C. The thermogravimetric measurements indicated that they started to decompose at about 360 °C prior to their melting transition temperature, $T_m$. Wide-angle X-ray diffraction analysis revealed that the chains were packed in a structure similar to that of a smectic liquid-crystalline glass. Despite the presence of ionic groups in these polymers, they are insoluble in water but soluble to a limited extent in polar aprotic solvents and can be solution cast into tough, flexible films. Additionally, the extent of their solubility in these solvents is insufficient to form lyotropic solutions.$^{15}$ More recently, Huang et al. reported the results of another series of poly(pyridinium salt)s with triflate (CF$_3$SO$_2^{-}$) as a counterion. These polymers were significantly more thermally and thermooxidatively stable than the analogous poly(pyridinium salt)s with BF$_4^{-}$ counterions. They were also soluble in polar aprotic organic solvents including DMSO, DMF, and DMAc from which fingernail creasable films were easily cast.

1.2 Light-Emitting Polymers

Since the discovery of the first light-emitting polymer, poly(p-phenylenevinylene), over a decade ago by Friend and coworkers, the academic and commercial interest in developing polymeric materials for use in light-emitting devices has skyrocketed. Many attempts have been made at producing high quality polymeric materials that show
exceptional light-emitting properties in the solution state and the solid state. Though it is highly desirable to produce materials with good quantum efficiencies as well as good thermal stability, one key feature that is essential for any polymer looking to be used for light emitting device fabrication, is its processability.

Some of the most highly studied and utilized polymeric materials today are the poly(p-phenylene) (PPP) and poly(p-phenylenevinylene) (PPV) materials. These polymers, however, have fundamental drawbacks that make them difficult to process. PPV is an insoluble, intractable, and infusible polymer that requires special precursor polymers for films to be produced using spin coating methods, which yield high-quality thin films. For this reason, several synthetic routes have been employed to produce processable precursor PPV polymers. Like poly(p-phenylenevinylene), PPP is also insoluble and not processable, requiring precursor polymers for it to be made into thin films. This topic has been recently reviewed by Gin and Conticello. An alternative to the precursor routes of preparing usable PPV and PPP polymers is the functionalization approach. This method utilizes PPV and PPP derivatives that have been functionalized by way of adding substituent side groups to the PPV and PPP polymer backbones. These side groups are tailored to produce solution processable polymers of these two types as well as tailoring the photoluminescence emission outputs for optoelectric device applications.

A third class of polymers that have received extensive attention due to their exceptional light-emitting properties, are the polyfluorene based polymers and its derivatives. The polyfluorenes typically have good solubility in common organic solvents and have some of the highest luminescence efficiencies of any polymeric materials produced for these applications. The aforementioned polymers have only
recently been utilized for the incorporation of ionic moieties. Figure 3 shows some of these polymers' ionic derivatives along with some other ionic polymers that are currently being synthesized and studied.

![Chemical structures](image)

Figure 3. Some current ionic polymers.

1.2.1 Ionic Light-Emitting Polymers

The polymers shown in Figure 3 are neither an exhaustive nor extensive representation of the many ionic polymers that are currently being synthesized for light-
emitting device applications. Recently, nitrogen-containing polymers have received unabated attention in the design and synthesis of electroluminescent polymers. They usually include poly(2,5-pyridylene), an analogue of poly(p-phenylene), poly(2,5-pyridyleneyinylene), an analogue to poly(p-phenytleneyinylene), poly(oxadiazole), poly(triazole), poly(triazine), poly(quinoline), poly(quinoxaline), poly(4-vinylpyridine), poly(aniline), poly(pyrole), and polyviologens among others. Unlike the other π-conjugated polymers, all of these polymers contain nitrogen heteroatoms either in the main-chain or in the side chains that provide facile quaternization reaction and protonation of the nitrogen sites. This allows their photoluminescence emission to be tuned essentially at will by adding a charged species to the nitrogen site via manipulation of their electronic structures.

One other class of nitrogen-containing polymers that are of considerable importance is the ionene polymers that contain quaternary nitrogen atoms in the polymer backbone. The polyviologens and poly(pyridinium salt)s that belong to this class of polymers have shown much promise for their use as light-emitting materials. Bhowmik and coworkers have recently reported the solution-state emission properties of a series of polyviologens containing both inorganic and organic counterions that were soluble in water and common organic solvents. Bhowmik et al. has also recently reported several series of poly(pyridinium salt)s that contain bulky organic counterions, which also exhibited light-emitting properties in the solution state and the solid state. Interestingly enough, these series of poly(pyridinium salt)s also exhibited a lyotropic liquid-crystalline phase in both polar protic and polar aprotic solvents. In an attempt to mix the properties of the poly(pyridinium salt)s with those of the PPV polymers, another group of researchers has
synthesized a series of polymers that incorporate stilbene and distyrylbenzene moieties into the pendent groups and main-chain backbone of these poly(pyridinium salt)s.\textsuperscript{50}
ENDNOTES


CHAPTER 2

OBJECTIVE OF THIS RESEARCH

2.1 Liquid-Crystalline Poly(pyridinium salt)s

One of the primary objectives of the research presented in this thesis was to expand on the work done by Harris and Huang by incorporating bulky organic counterions into these same types of poly(pyridinium salt)s in hopes of achieving a liquid-crystalline phase in solution as well as upon heating. The use of bulky organic counterions like tosylate and triflimide offers distinct advantages over inorganic counterions in that they facilitate an increase in solubility in organic solvents. These counterions also have the ability of reducing the Coulombic interactions between cationic centers allowing for reduced melting transition temperatures to facilitate the formation of a thermotropic liquid-crystalline phase.

2.2 Light-Emitting Poly(pyridinium salt)s

With the increased interest in polymeric materials for use in light-emitting device applications, the poly(pyridinium salt)s have a lot to offer in the way of exceptional film forming abilities and increased solubility in organic solvents allowing for ease of processability. These poly(pyridinium salt)s also have good thermal stability upon heating, which is essential for light-emitting device longevity. Pyridine containing polymers have already been shown to exhibit light-emitting properties in their neutral...
state as well as in their quaternary state. Therefore, the second objective of this research is to expand the current inventory of light-emitting polymers by synthesizing a series of polyelectrolytes containing heterocyclic quaternized pyridine rings that have solubility in common organic solvents, possess good film forming abilities, and have light-emitting properties.
CHAPTER 3

EXPERIMENTAL METHODS

3.1 Phenyl Tetraketone Synthesis

The synthesis of the phenyl tetraketone was carried out in a round bottom flask to which a mixture of acetophenone (54.3 g, 0.45 mol) and terephthaldehyde (10.0 g, 0.075 mol) were added in a 6 to 1 mole ratio. The mixture was then stirred in 250 mL of 95% ethanol and heated to 65 °C until completely dissolved. Once the starting materials were dissolved, a solution of potassium hydroxide (10.5 g, 0.19 mol in 10 mL of distilled water) was added dropwise to the reaction mixture with vigorous stirring over a thirty minute time period. A yellow precipitate formed immediately and the heterogeneous reaction mixture was then heated at reflux until it turned pink, which occurred over a 4-5 hour time period. During this time, the p-bischalcone redissolved and reacted with two additional equivalents of acetophenone to form the phenyl tetraketone, which precipitated. The above reaction procedure is shown in Scheme 1.

\[ \text{Acetophenone} + \text{Terephthaldehyde} \rightarrow \text{Phenyl Tetraketone} \]

Scheme 1.

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The reaction mixture was then filtered hot, and the tan solid material was collected by vacuum filtration to afford 41.0 g of crude product. This crude product was then purified by recrystallization from toluene to yield 35.0 g (81% yield) of off-white crystals, which was collected by vacuum filtration and dried in a vacuum oven before the final analysis. This material showed a melting endotherm at $T_{\text{max}}$ at 206.00 °C (mp 205-206 °C) and was determined by Differential Scanning Calorimetry (DSC) at a heating rate of 10 °C/min.

3.2 Bis-pyrylium Monomer Synthesis

The synthesis of 4,4'-((1,4-phenylene)bis(2,6-diphenylpyrylium))ditosylate, $M$, via the cyclodehydration of the phenyl tetraketone, was synthesized by the modification of a procedure by which the corresponding ditetrafluoroborate salt was prepared.$^1$ This reaction is shown in Scheme 2. In a round bottom flask, triphenylmethanol (7.8 g, 0.030 mol) and p-toluenesulfonic acid monohydrate (5.8 g, 0.030 mol) were added to 100 mL of acetic anhydride ($\text{CH}_3\text{CO})_2\text{O}$. These reactants were stirred at room temperature for 3 hours. Once this process was completed, the solid phenyl tetraketone (7.2 g, 0.012 mol) was added to the reaction mixture, and the reaction mixture was heated to 100 °C for 1 hour. The heterogeneous mixture became clear, and upon cooling, yellow crystals appeared and were collected by vacuum filtration. These crystals were carefully washed with acetic anhydride and ethanol respectively. The material was then air dried to give the crude 4,4'-((1,4-phenylene)bis(2,6-diphenylpyrylium))ditosylate, $M$. The crude product was then purified by recrystallization in acetic acid, and dried in a vacuum oven to afford 7.9 g (75% yield) of orange powder. This compound showed several endothermic transitions at 161.00 °C ($T_m$), 195.33 °C, and 304.48 °C ($T_\text{f}$) as determined by DSC at a
heating rate of 10 °C/min. The purity of $M$ was also checked by $^1$H NMR spectroscopy and elemental analysis. $\delta_H$ ($d_6$-DMSO, 400 MHz, ppm): 9.35 (4H, s, aromatic meta to O$^+$), 9.21 (4H, s, 1,4-phenylene), 7.58-8.93 (20H, m, phenyl), 7.46-7.47 (4H, $d$, $J$ = 6.7 Hz, tosylate), 7.09-7.10 (4H, $d$, $J$ = 7.7 Hz, tosylate), 2.27 (6H, s, CH$_3$). The theoretically calculated percent composition for C$_{54}$H$_{42}$O$_8$S$_2$ ($M$) is: C, 73.45; H, 4.79; S, 7.26. The as found results via elemental analysis were: C, 71.25; H, 4.71; S, 7.41.

Scheme 2

3.3 Diaminoanthracene Monomer Synthesis

The reduction of 2,6-diaminoanthraquinone (13.10 g, 55 mmol) was suspended in a 10% sodium hydroxide solution (125 mL) and zinc dust (10 g, 0.15 mol) was added, with magnetic stirring, at room temperature. The mixture was brought to reflux temperature, and 95% ethanol (10 mL) was added to prevent violent foaming. Further portions of zinc dust (2 x 10 g, 2 x 0.15 mol) were added after 30 and 60 minutes had passed. The mixture was then heated under reflux with vigorous stirring for 24 hours. The solid was filtered from the mixture and washed with hot water until the washings became clear. This crude product containing zinc residues was subjected to Soxhlet extraction using acetone.

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Recrystallization of the extract from acetone gave bright yellow crystals in a 40% yield. These crystals were then dried in a vacuum oven before the final analysis. The melting point of this compound was found to be 230 °C (decomposition). This compound was checked by \(^1\)H and \(^{13}\)C NMR and elemental analysis. \(\delta_H (d_6\text{-DMSO}, 200 \text{ MHz, ppm}):\)

- 8.23 (2H, s, H\(_{8,10}\)),
- 8.04 (2H, \(d, J = 8.9 \text{ Hz, H}_4\)),
- 7.33 (2H, \(dd, J = 2.0 \text{ Hz, 8.9 Hz, H}_3\)),
- 7.20 (2H, \(d, J = 1.8 \text{ Hz, H}_1\)),
- 5.63 (4H, s, -N\(_2\)).

\(\delta_C (d_6\text{-DMSO}, 75 \text{ MHz, ppm}):\)

- 144.1,
- 130.7,
- 131.7,
- 128.1,
- 127.5,
- 121.4,
- 121.0,
- 103.8.

The theoretically calculated percent composition for C\(_{14}\)H\(_{22}\)N\(_2\) is: C, 80.74; H, 5.81; N, 13.45. The as found results via elemental analysis were: C, 80.34; H, 6.19; N, 13.42. UV-vis (95 % ethanol): \(\lambda_{max}/\text{nm} = 423, 346, 329, 314, 271 \ (\epsilon = 540, 460, 670, 770, 670, 11,500); \) (after addition of HCl) \(\lambda_{max}/\text{nm} = 374, 354, 337, 252 \ (\epsilon = 670, 750, 560, 20,300).\)

### 3.4 Aliphatic Diamine Preparation

The 1,6-diaminohexane and 1,12-diaminododecane were purchased from Sigma Aldrich and purified by sublimation. Each compound was placed in a sublimation apparatus, which was placed under vacuum while being heated in a hot oil bath. After the sublimation was completed, the compounds were collected and stored for later use. These compounds were checked by \(^1\)H and \(^{13}\)C NMR. The 1,12-diaminododecane was also checked by elemental analysis. The calculated percent composition for C\(_{12}\)H\(_{28}\)N\(_2\) is: C, 71.93; H, 14.09; N, 13.98. The as found results were: C, 72.15; H, 14.04; N, 14.24.

### 3.5 Aromatic Diamine Preparation

Both the 4,4'-oxydianiline (99+ %, sublimed) and 4,4'-diaminobiphenyl (benzidine) were purchased from Aldrich Chemical Company in high purity and used without further
purification. The 9,9-\textit{bis}(4-aminophenyl)fluorene was purchased from TCI in high purity and was further purified by recrystallization in ethanol and chloroform/hexane respectively. After recrystallization, the diamine was collected by vacuum filtration and then dried in a vacuum oven before the final analysis.

3.6 Polymer Synthesis with Tosylate Counterions

The \textit{bis}(pyrylium) salt M was polymerized with the chosen diamines by way of a ring-transmutation polymerization reaction.\textsuperscript{13} In a three-necked flask, a one to one mole ratio of the 4,4'(1,4-phenylene)\textit{bis}(2,6-diphenylpyrylium)ditosylate, M, and a diamine were dissolved in an appropriate amount of dimethyl sulfoxide (DMSO). This reaction procedure is shown in Scheme 3. A small amount of toluene (5-10 mL) was also added to the reaction flask. This was done to distill the water generated from the polymerization medium as a toluene/water azeotrope. The mixture was stirred with a magnetic stirrer until completely dissolved. A thermometer, a Dean Stark with water condenser, and a gas flow valve were added to the three-necked flask. Before the mixture was heated, the reaction vessel was evacuated with nitrogen gas and kept under a continuous flow throughout the reaction. Once evacuated with nitrogen, the reaction vessel was heated to about 80 °C. The solution was allowed to stir for 3-4 hours at which time the temperature was then raised to 145-150 °C and allowed to react for 24-48 hours. The reaction mixture was then allowed to cool to room temperature, while still under the flow of nitrogen gas. Distilled water or ethyl acetate was then used to precipitate the reaction mixture. The polymer was collected by vacuum filtration and washed with several liters of distilled water. A vacuum oven was then used to dry the polymer materials before the final analysis and characterization was performed.

20

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3.7 Polymer Synthesis with Triflimide Counterions

These polymers were prepared by the metathesis reaction of their corresponding tosylate polymer and lithium triflimide in a common organic solvent such as methanol, acetonitrile, or DMSO. A typical procedure is described as follows. Polymer 1-N was prepared by dissolving polymer 1-O in a minimal amount of acetonitrile. Next, a solution of lithium triflimide in 5% excess dissolved in a minimum amount of acetonitrile was added to the polymer 1-O solution. The triflimide solution was filtered as it was added to the polymer solution to remove any insoluble impurities. This new solution was allowed to stir for 2-3 days with gentle warming. After this was done, the new solution was poured into distilled water to precipitate out the polymer material. The polymer material was filtered on a Büchner funnel and washed with distilled water to remove the excess soluble salts of lithium triflimide and lithium tosylate. This polymer material was again
dissolved in a minimal amount of acetonitrile and was subsequently treated with a second portion of a 5% excess lithium triflimide acetonitrile solution. Again, the solution was stirred for 2-3 days and precipitated in distilled water. The final polymer solution was washed extensively with distilled water to remove excess soluble salts and the polymer 1-N was vacuumed dried in an oven before the final analysis and characterization was performed. The theoretically calculated percent composition for \( \text{C}_{56}\text{H}_{36}\text{N}_{4}\text{S}_{4}\text{O}_{9}\text{F}_{12} \) (1-N) is: C, 53.17; H, 2.87; N, 4.43; S, 10.14. The as found results via elemental analysis were: C, 53.15; H, 2.83; N, 4.41; S, 10.22. Scheme 4 shows the synthetic route used to prepare the triflimide polymers, and the corresponding symbols by which they will be referred to in the following text.

![Scheme 4](image)

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3.8 Polymer Characterization

The $^1$H and the $^{13}$C NMR spectra of these polymers were recorded with a Bruker AM 400 FT-NMR spectrometer with three RF channels operating at 400 and 100 MHz, respectively, in $d_6$-DMSO using tetramethylsilane (TMS) as an internal standard. Phase-transition temperatures were measured with a TA Instruments 2100 DSC under a nitrogen flow with both heating and cooling rates of 10 °C/min. The temperature axis of the DSC thermogram was calibrated prior to use with the reference standard of high purity indium and tin. Polymer samples usually weighing 8-10 mg were used for this analysis. The peak maximum of the endotherm was recorded from both the first heating and the second heating cycles, whenever possible. The $T_g$ was taken as the inflection point of this transition during either the first or second heating cycles, whichever was more prominent. The LC textures of these polymers were determined with a polarized light microscope (PLM, Nikon, model Labophot 2) equipped with crossed polarizers and a hot stage. The thermogravametric analysis (TGA) was performed with a TA Instruments 2100 instrument at a heating rate of 20 °C/min under the flow of nitrogen. The absorption spectra of these polymers in methanol, acetonitrile, or DMSO were recorded with a Varian Cary 50 Bio UV-Visible spectrophotometer at ambient temperature. Their photoluminescence spectra in solution and in solvent cast thin films were recorded using a PerkinElmer LS-55 luminescence spectrometer at ambient temperature with a xenon lamp light source. Solvent cast thin films were prepared by placing several drops of the methanol or acetonitrile polymer solutions on a quartz slide and allowing the solvent to evaporate. The films were then dried in a vacuum oven to completely remove any remaining solvent. The FTIR spectra of the polymers were recorded with a Nicolet FTIR analyzer with their neat films on KBr pellets.
ENDNOTES


2. Rabjohns, M. A. Polymer 1997, 38, 3398.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Chemical Structure

The $^1$H and $^{13}$C spectra of polymer 1-O and 6-N recorded in $d_6$-DMSO are shown in Figure 4a and b. Since all of the polymers studied contained either aromatic diamine linkages or aliphatic diamine linkages, these two polymers, one with an aromatic linkage and one with an aliphatic linkage, were chosen as a representative sample to point out the characteristic features this group of polymers possessed. Polymer 1-O was consistent with its proposed structure, and its $^{13}$C spectra only contained aromatic carbon signals between 123 and 162 ppm. The carbonyl resonance at ca. 187 ppm, which was attributable to a vinylogous amide, was not detected suggesting that the ring-transmutation polymerization reaction proceeded to completion. The proton signals for vinylogous amide and amino end groups were also not detected in its $^1$H NMR spectra. The FTIR spectrum of polymer 6-N at room temperature recorded from a KBr pellet contains the following characteristic absorption bands: 3063 (C-H aromatic stretching), 2928, 2856 (C-H aliphatic stretching), 1620 (C=C aromatic ring stretching), 1495 (C-H aliphatic bending), 1351 (C-F stretching), 1193 (H$_2$C-N$^+$), 1134 (S=O asymmetric stretching), 1058 (S=O symmetric stretching), and 778 cm$^{-1}$ (C-H out-of-plane bending). The $^1$H and $^{13}$C NMR spectra of polymer 6-N were also consistent with its proposed structure. The absence of tosylate proton signals suggested that the exchange of
Figure 4a. $^1$H and $^{13}$C spectra of polymer 1-O in $d_6$-DMSO.
Figure 4b. $^1$H and $^{13}$C spectra of polymer 6-N in $d_6$-DMSO.
triflimide anions for tosylate anions in the metathesis reaction was effective under these experimental conditions.

4.2 UV-vis Properties

Due to the highly electron rich π bonds of the 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) moiety in the main chain of all the polymers, their optical properties were examined in both the solution and solid state. All the polymers displayed a broad absorption in their UV-vis spectra with a peak maximum ranging from 324-348 nm respectively. These absorption peak maxima ($\lambda_{\text{max}}$) are characteristic of closely spaced π-π* transitions common to organic rings. A pyridinium salt model compound, 1,2,4,6-tetraphenylpyridinium perchlorate, exhibits a similar absorption spectrum with a $\lambda_{\text{max}}$ = 312 nm in ethanol. Ortho-substituted pyridinium salts contain absorption bands consisting of two electronic transitions that are intramolecular charge transfer complexes of the 2,6- and the 4-substituent with the positively charged nitrogen center.² It was therefore reasonable to conclude that the absorption bands of these polypyridinium salts arose from the same electronic transitions as those in closely related pyridinium salts. The UV-vis spectra of these polymers were essentially independent of the counterion structure as well as the solvent polarity.

4.3 Photoluminescence Spectral Artifacts

It was important to understand all of the features of a typical spectrofluorometer in order to determine the real emission and excitation peaks of a spectrum as opposed to those artifacts that originate as a result of the spectrofluorometer's optics. The optical design of a spectrofluorometer, using two grating monochromators, is shown in Figure 5.
Figure 5. Schematic diagram of the optics designed into a spectrofluorometer.
All peaks of an emission and excitation spectrum are assumed to be real unless otherwise ruled out by other experimental conditions. Figure 6 shows a typical photoluminescence spectrum for one of the polymers studied in solution recorded using a spectrofluorometer. In these spectra, there are several peaks, all of which are not representative of the true emission and excitation spectra for this polymer. The excitation spectrum recorded for this polymer in solution shown in Figure 6 is representative of this material at this concentration, with the exception of the peak marked HW (half-wavelength).

Figure 6. Typical photoluminescence spectrum for one of the polymers studied in solution recorded using a spectrofluorometer.

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The only real emission peaks in this spectra that are representative of the polymer were located at 288, 383, and 530 nm and are denoted by RP (real peak) in Figure 6. The remaining peaks in the emission spectra and the peak marked HW in the excitation spectrum are artifacts of the instrument optics and will be analyzed and discussed next. These artifacts are not limited to the solution state alone; they are also present in solid-state emission and excitation spectra as well.

The most obvious peaks to point out as being artifacts of the instrument were the doubling peaks (denoted by DP in Figure 6) of the excitation wavelengths used to measure the emission curves. These peaks corresponded to the second-order \( n = 2 \) diffraction wavelengths of the excitation wavelengths as defined by the grating equation. The grating equation is given by the following expression

\[
n\lambda = d(\sin \theta_r - \sin \theta_i) \tag{1}\]

where \( n \) is the diffraction order, \( \lambda \) is the photon wavelength, \( \theta_r \) is the reflected photon’s angle measured from the normal to the surface, and \( \theta_i \) is the incident photon’s angle measured from the normal to the surface. Figure 7 shows a schematic diagram of a reflection grating (typical of the kind used in a spectrofluorometer) that illustrates this principle. It is evident from the diagram that the path difference between ray 1 and ray 2 after reflection is

\[
BD - AC = CB \sin \theta_r - CB \sin \theta_i \tag{2}
\]

where \( CB \) is the grating spacing \( d \). Both angles \( \theta_r \) and \( \theta_i \) are taken as positive when they lie on opposite sides of the normal. Since for constructive interference the path difference must be a multiple of the wavelength, the following condition is obtained

\[
n\lambda = d(\sin \theta_r - \sin \theta_i)
\]
Figure 7. Schematic diagram of a reflection grating. A parallel beam of radiation is incident along the rays 1 through 4 at an angle $\theta$, with respect to the normal; the reflected radiation is observed at an angle $\theta_r$. The spacing between the grooves of the grating is $d$.

Thus, the grating equation is derived. It can be shown that the resolution of the grating is given by Equation 3

$$\frac{\lambda}{\Delta\lambda} = nN \quad (3)$$

where $n$ is the diffraction order and $N$ is the total number rulings or blazes. This equation governs the emission patterns recorded by a spectrofluorometer due to the instrument's use of excitation and emission grating monochromators to separate the different wavelengths of light. Thus, for every photon of light with wavelength $\lambda$ incident on a grating, there will be photons of $n\lambda$ ($n = 1, 2, 3, \ldots$) detected at the reflected angle $\theta_r$, with the first order lines usually being the most intense. These peaks were easily noticed in the emission spectra due to their linear dependence on the excitation wavelength.
Correspondingly, the excitation spectra also had an artifactual peak due to this same principle. Peaks of this type occurred at half the wavelength used to measure the excitation spectra and are denoted by an HW in Figure 6. This phenomenon is based on the method in which an excitation spectrum is measured. Excitation spectra are obtained by measuring the luminescence intensity at a fixed wavelength while the excitation wavelength is varied. It is now evident that the half-wavelength peaks in the excitation spectra are a direct result of this method of measurement coupled with the grating equation. Since the excitation spectrum designates the wavelengths of light that produce a specified emission wavelength, \( \lambda' \), it is evident, per the grating equation, that when an excitation wavelength (\( \lambda \) in the grating equation) of \( \lambda'/2 \) is used to excite with, there will be a detectable peak at two times (\( n = 2 \)) the \( \lambda'/2 \) value. Thus, generating an emission peak at \( \lambda' \), the value for which the excitation spectrum was measured. This is the same result stated above for the doubling peaks in the emission spectrum found at twice the excitation wavelengths. These peaks in the excitation spectra were only seen in the solutions with concentrations of less than about \( 5 \times 10^{-4} \) mol/L due the higher concentrated solutions attenuating the transmission of the incident light.

The remaining peak at 576 nm, shown in Figure 6, was not a surprise since this peak was positioned at exactly twice the wavelength of the 288 nm peak and was therefore assigned as the doubling peak of the emission peak centered at 288 nm. Its emission wavelengths followed the emission wavelengths of the higher-energy peak in a linear fashion leading to the suspicion that it was an artifact of the instrument and not a real emission peak. This peak was present in every spectrum that possessed a peak in the range of 265-300 nm (the effective range of maximum emission values observed for this particular peak depending on the solvent and polymer studied). The doubling peak
therefore had a range of maximum emission values of 530-600 nm. In order to substantiate the idea that this peak was indeed a doubling peak of the higher-energy peak at 288 nm, a piece of glass was placed in between the sample holder and the emission photodetector. Since glass absorbs radiation below 350 nm, it attenuated the transmission of this high-energy peak's emission wavelengths, and subsequently no emission peak was produced in the range of 530-600 nm verifying that this peak was indeed a result of the doubling effect.

Clearly an instrument's construction can have a profound effect on the experimental data that it produces. Any scientific instrument used for research purposes must be well understood in order to be used for generating meaningful and reliable data. With these artifacts identified and understood, the photoluminescence properties of these polymers in the solution state and the solid state may be now studied.

4.4 Photoluminescence Properties in Solution

Each of these polymers' fluorescence spectra were recorded in two different solvents with differing dielectric constants (\(\varepsilon\)) to study polarity effects of the maximum emission wavelengths. DMSO, having one of the highest dielectric constants of the common organic solvents (\(\varepsilon = 48.9\)), was the first solvent used in this fluorescence study due to the good solubility of these polymers. This allowed for the comparison of polymer emission spectra based on the polymers' structural differences and not on the differences in solvent. The second solvent used, with a moderate dielectric constant, was either methanol (\(\varepsilon = 31\)), for the tosylate containing polymers, or acetonitrile (\(\varepsilon = 36.7\)), for the triflimide containing polymers. Two different solvents with moderate dielectric constants were used since not all of the polymers exhibit appreciable solubility in both methanol
and acetonitrile. For comparison purposes, it was desirable to use the same solvent for polymers with the same counterion. The photoluminescence properties of these polymers in solution are described in terms of their excitation wavelength dependence as well as their concentration dependence. It was worthwhile to compare these polymers in their respective groups as well as with each other. Polymers with similar spectral data will be grouped together for simplicity of discussion, and specific peaks within these spectra will be assigned to a specific structural moiety when possible. The absorption peak maximum wavelengths ($\lambda_{\text{max}}$) and the emission peak maximum wavelengths ($\lambda_{\text{em}}$) of these polymers in solution are summarized in Table 1.

4.4.1 Polymer 1 (oxydiphenyl linkage)

Both polymer 1-O and 1-N in DMSO have an absorption band at $\lambda_{\text{max}} = 344$ nm in their UV-vis spectra. With a concentration of $1 \times 10^{-3}$ mol/L, these polymers show a single emission peak in their emission spectra centered about 537 nm and a single, narrow excitation peak having a maximum excitation peak wavelength ($\lambda_{\text{ex}}$) near 405 nm. The emission spectra were not well behaved and were very broad. There were several characteristic features (shoulders) present in this emission curve giving it the appearance of a single curve made up of three or more overlapping emission curves. These shoulders were indicative of multiple chromophoric species in the solution. This emission curve overlap accounts for the full width at half-maximum (fwhm = 140-160 nm) value being so large for this peak. Its maximum emission wavelength was highly dependent on the excitation wavelengths used to measure the emission. As the excitation wavelength was increased, the emission curve changed shape, and the $\lambda_{\text{em}}$ value was bathochromically (red) shifted to lower energy in accordance with the excitation wavelength. This red shift
Table 1. Absorption Peak Wavelengths ($\lambda_{\text{max}}$) and Emission Peak Wavelengths ($\lambda_{\text{em}}$) of Poly(pyridinium salt)s in Solution

<table>
<thead>
<tr>
<th>Polymer Number</th>
<th>Polymer Structure</th>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\lambda_{\text{em}}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-O</td>
<td>oxydiphenyl-OTs</td>
<td>DMSO</td>
<td>344</td>
<td>537-530 (a-peaks), 390-366 (b-peaks), 285-299 (y-peaks)</td>
</tr>
<tr>
<td>1-O</td>
<td>oxydiphenyl-OTs</td>
<td>CH$_3$OH</td>
<td>340, 208</td>
<td>524-524 (a-peaks), 386-366 (b-peaks), 285-296 (y-peaks)</td>
</tr>
<tr>
<td>1-N</td>
<td>oxydiphenyl-NTf</td>
<td>DMSO</td>
<td>344</td>
<td>537-530 (a-peaks), 390-366 (b-peaks), 285-299 (y-peaks)</td>
</tr>
<tr>
<td>1-N</td>
<td>oxydiphenyl-NTf</td>
<td>CH$_3$CN</td>
<td>337, 212</td>
<td>529-529 (a-peaks), 386-366 (b-peaks), 285-296 (y-peaks)</td>
</tr>
<tr>
<td>2-O</td>
<td>4,4'-biphenyl-OTs</td>
<td>DMSO</td>
<td>347</td>
<td>532-500 (a-peaks), 390-366 (b-peaks), 292-300 (y-peaks)</td>
</tr>
<tr>
<td>2-O</td>
<td>4,4'-biphenyl-OTs</td>
<td>CH$_3$OH</td>
<td>342, 254, 215</td>
<td>500-500 (a-peaks), 370-362 (b-peaks), 288-296 (y-peaks)</td>
</tr>
<tr>
<td>2-N</td>
<td>4,4'-biphenyl-NTf</td>
<td>DMSO</td>
<td>349</td>
<td>532-500 (a-peaks), 390-366 (b-peaks), 292-300 (y-peaks)</td>
</tr>
<tr>
<td>2-N</td>
<td>4,4'-biphenyl-NTf</td>
<td>CH$_3$CN</td>
<td>341, 253, 205</td>
<td>500-500 (a-peaks), 370-362 (b-peaks), 288-296 (y-peaks)</td>
</tr>
<tr>
<td>3-O</td>
<td>diphenylfluorene-OTs</td>
<td>DMSO</td>
<td>343</td>
<td>550-540 (a-peaks), 390-360 (b-peaks), 287-297 (y-peaks)</td>
</tr>
<tr>
<td>3-O</td>
<td>diphenylfluorene-OTs</td>
<td>CH$_3$OH</td>
<td>339, 208</td>
<td>534-495 (a-peaks), 378-362 (b-peaks), 287-295 (y-peaks)</td>
</tr>
<tr>
<td>3-N</td>
<td>diphenylfluorene-NTf</td>
<td>DMSO</td>
<td>343</td>
<td>550-540 (a-peaks), 390-360 (b-peaks), 287-297 (y-peaks)</td>
</tr>
<tr>
<td>3-N</td>
<td>diphenylfluorene-NTf</td>
<td>CH$_3$CN</td>
<td>337, 205</td>
<td>534-495 (a-peaks), 378-320 (b-peaks), 287-295 (y-peaks)</td>
</tr>
<tr>
<td>4-O</td>
<td>2,6-anthracene-OTs</td>
<td>DMSO</td>
<td>348, 265</td>
<td>390-360 (a-peaks), 285-300 (b-peaks)</td>
</tr>
<tr>
<td>4-O</td>
<td>2,6-anthracene-OTs</td>
<td>CH$_3$OH</td>
<td>345, 260, 203</td>
<td>390-360 (a-peaks), 285-300 (b-peaks)</td>
</tr>
<tr>
<td>4-N</td>
<td>2,6-anthracene-NTf</td>
<td>DMSO</td>
<td>348, 265</td>
<td>390-360 (a-peaks), 285-300 (b-peaks)</td>
</tr>
<tr>
<td>4-N</td>
<td>2,6-anthracene-NTf</td>
<td>CH$_3$CN</td>
<td>344, 263, 205</td>
<td>390-360 (a-peaks), 285-300 (b-peaks)</td>
</tr>
<tr>
<td>5-O</td>
<td>n-hexyl-OTs</td>
<td>DMSO</td>
<td>334</td>
<td>545-530 (a-peaks), 400-365 (b-peaks)</td>
</tr>
<tr>
<td>5-O</td>
<td>n-hexyl-OTs</td>
<td>CH$_3$OH</td>
<td>330, 247, 209</td>
<td>525-442 (a-peaks), 380-362 (b-peaks), 275-286 (y-peaks)</td>
</tr>
<tr>
<td>5-N</td>
<td>n-hexyl-NTf</td>
<td>DMSO</td>
<td>334</td>
<td>545-530 (a-peaks), 400-365 (b-peaks)</td>
</tr>
<tr>
<td>5-N</td>
<td>n-hexyl-NTf</td>
<td>CH$_3$CN</td>
<td>329, 247, 210</td>
<td>525-442 (a-peaks), 380-362 (b-peaks), 275-286 (y-peaks)</td>
</tr>
<tr>
<td>6-O</td>
<td>n-dodecyl-OTs</td>
<td>DMSO</td>
<td>334</td>
<td>545-530 (a-peaks), 400-365 (b-peaks)</td>
</tr>
<tr>
<td>6-O</td>
<td>n-dodecyl-OTs</td>
<td>CH$_3$OH</td>
<td>329, 245, 208</td>
<td>525-442 (a-peaks), 375-362 (b-peaks), 275-286 (y-peaks)</td>
</tr>
<tr>
<td>6-N</td>
<td>n-dodecyl-NTf</td>
<td>DMSO</td>
<td>333</td>
<td>545-530 (a-peaks), 375-362 (b-peaks)</td>
</tr>
<tr>
<td>6-N</td>
<td>n-dodecyl-NTf</td>
<td>CH$_3$CN</td>
<td>324, 247, 204</td>
<td>525-442 (a-peaks), 375-362 (b-peaks), 275-286 (y-peaks)</td>
</tr>
</tbody>
</table>

* The emission peak values are listed as a range due to their concentration dependence. The ranges are shown for decreasing concentrations.

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can be attributed to a strong correlation between excitation energy and the vibronic structure of the emission spectra. A shift in the peaks’ λ_{em} value by as much as 15 nm can be easily seen. When the concentration was decreased to 1 \times 10^{-4} \text{ mol/L}, the emission spectra showed an additional peak that was not present in the 1 \times 10^{-3} \text{ mol/L} spectra.

Figure 8 shows the excitation and emission spectra of these polymers at a concentration of 1 \times 10^{-4} \text{ mol/L}. These spectra showed two peaks centered at approximately λ_{em} = 530 nm (denoted as the α-peak) and 390 nm (denoted as the β-peak) respectively. The peaks centered at 390 nm were well behaved and quite narrow with a full width at half-maximum value of about 30 nm. The characteristic sharpness of this emission peak indicates that the emitting chromophore in these polymers has a well-defined structure and was indicative of a single emitting chromophore. Its position was essentially independent of the excitation wavelength values used for these measurements. However, the peak centered near 530 nm exhibits the same behavior and same characteristics as it did at the higher concentration, though it did have a small hypsochromic (blue) shift to higher energy upon dilution. The excitation spectra of both these polymers consisted of two peaks, one near λ_{ex} = 265 nm, while being monitored at 390 nm and the second one at λ_{ex} = 385 nm, while being monitored at 530 nm. The higher intensity peak in this figure near the 265 nm excitation wavelength is the half-wavelength peak of the 530 nm peak, but the lower intensity peak near 265 nm was a real excitation peak as it showed up when the spectrometer was monitoring for emissions at 390 nm. As the concentration was further diluted from 1 \times 10^{-4} \text{ mol/L} to 1 \times 10^{-5} \text{ mol/L}, a third peak developed (denoted as the γ-peak) at an even higher energy than the β-peak in Figure 8. This new peak was centered near 285 nm. The β-peaks at this concentration exhibited a hypsochromic shift of about 20 nm, and the α-peaks were well behaved as the excitation wavelength...
Figure 8. Excitation and emission spectra of polymers (a) 1-O and (b) 1-N at a concentration of $1 \times 10^{-4}$ mol/L.
increased with the $\lambda_{em}$ remaining constant over a large change in excitation values. This emission curve appeared as a single peak made up from two dominant overlapping emission curves of nearly equal intensity. The two curves that appeared to make up this single curve were centered near 530 nm and 515 nm with the $\lambda_{em}$ for this peak being 530 nm. As the polymer solution was diluted further, to concentrations below $1 \times 10^{-5}$ mol/L, the $\beta$-peaks continued to be hypsochromically shifted to wavelengths approaching 366 nm, while the $\alpha$-peaks remained constant at a peak maximum of about 530 nm. Both peaks remained well behaved as denoted by the emission maxima staying constant over the range of excitation values. In very dilute solutions ($< 1 \times 10^{-6}$ mol/L), the $\alpha$-peak disappeared almost completely, and the $\beta$-peak was reduced to a shoulder of the $\gamma$-peak, which remained present with increased intensity and was well behaved when the excitation wavelengths were increased. Figure 9 shows the emission spectra of polymer 1-N at this low concentration with the $\lambda_{em}$ for the $\gamma$-peak being 299 nm. Notice that this peak is bathochromically shifted compared to its position in the more concentrated solution, which is the opposite effect that dilution had on the $\alpha$-peaks and $\beta$-peaks. The reasons for this will be discussed in Section 4.4.1.1. Due to the complex features these emission spectra can possess, the peaks that arise will be assigned a letter to differentiate them when being discussed in the text. The designation will be consistent throughout and is as follows: a Greek letter "$\alpha$" will be used to identify the lowest energy (longest wavelength) peak, and "$\beta$" for the next lowest energy peak, and so on as needed. The $\alpha$-peak of one spectrum however may not be the same as the $\alpha$-peak of another spectrum. These letter designations are to differentiate the peaks within a single specific spectrum only.
Figure 9. Excitation and emission spectra of polymer 1-N at a concentration $< 1 \times 10^{-6}$ mol/L.
Polymers 1-O and 1-N in methanol and acetonitrile respectively, also had nearly identical emission spectra at all concentrations when compared to one another as they did in DMSO. Polymers 1-O in methanol and 1-N in acetonitrile did not have the same complexity in their emission spectra at high concentrations in these solvents as they did in DMSO. They were both well behaved at all concentrations up to $1 \times 10^{-3}$ mol/L (the maximum practical concentration to study based on the limited absorbance of some of these polymers in these respective solvents). In comparison to these polymers in DMSO, polymer 1-O, in methanol, had an absorption band at $\lambda_{\text{max}} = 208$ and 340 nm, while polymer 1-N, in acetonitrile, had an absorption band at $\lambda_{\text{max}} = 212$ and 337 nm respectively in their UV-vis spectra. Like the DMSO solutions, their emission spectra had a single peak (α-peak) with $\lambda_{\text{em}} = 524$ nm for 1-O and 524 nm for 1-N at a concentration approaching $1 \times 10^{-3}$ mol/L and a second peak (β-peak) at higher-energy that arises and persists as the concentration decreases beyond about $1 \times 10^{-4}$ mol/L. The β-peaks' maximum emission value was near 386 nm. At a concentration of $1 \times 10^{-4}$ mol/L, the maximum emission value for 1-O in methanol was $\lambda_{\text{em}} = 524$ nm with a shoulder of nearly equal intensity at $\lambda_{\text{em}} = 510$ nm, and the maximum emission value for 1-N in acetonitrile $\lambda_{\text{em}} = 529$ nm with a shoulder of nearly equal intensity at $\lambda_{\text{em}} = 514$ nm respectively. They had full width at half-maximum values that were similar to the peaks found in the DMSO solutions. Both sets of peaks were hypsochromically shifted compared to those in the DMSO solutions at the same concentration ($1 \times 10^{-4}$ mol/L). The decrease in solvent polarity, as measured by the change of dielectric constant ($\varepsilon$), of methanol and acetonitrile compared to DMSO, accounts for this shift. A hypsochromic shift is typically observed in $\pi-\pi^*$ transitions as the solvent polarity decreases. Conversely, a bathochromic shift is observed as solvent polarity increases because
attractive polarization forces between the solvent and the absorber tend to lower the energy levels of both the unexcited and excited states. The effect on the excited state is greater, however, and the energy differences thus become smaller with increased solvent polarity. Small bathochromic shifts result from this. The increased blue shift in the methanol solution, as opposed to the acetonitrile solution, was probably not due to the slightly lower dielectric constant that methanol possess, and was most likely a result of the increased solvation of this polymer by the methanol molecules. Methanol's ability to hydrogen bond with the nonbonded electron pairs of the main chain oxygen atom is extensive and thus produces increased solvation of the polymer chain. The maximum emission peak values for both the $\alpha$-peaks and $\beta$-peaks in both solvents were independent of the excitation wavelengths used to measure their emission. As the concentration was decreased to $1 \times 10^{-5}$ mol/L, a higher-energy peak ($\gamma$-peak) developed as in the DMSO solutions, and it was centered near 285 nm. The emission maxima for the $\beta$-peaks underwent a hypsochromic shift like the analogous peaks in the DMSO solutions, and the broader, $\alpha$-peaks' emission maxima were constant like those seen in the DMSO solutions. This phenomenon suggests that the chromophore giving rise to this broad emission peak has a well-defined structure, though it was not necessarily due to a single emissive molecular chromophore. Further dilutions to $1 \times 10^{-6}$ mol/L and beyond resulted in the same effects seen in the DMSO solutions, with the $\alpha$-peaks all but disappearing and the $\beta$-peaks becoming a shoulder of the dominant $\gamma$-peak. The $\gamma$-peaks of the methanol and acetonitrile solutions also underwent a bathochromic shift to longer wavelengths ($\lambda_{em} = 296$ nm) as it did in the DMSO solutions.
4.4.1.1 Molecular Effects on Photoluminescence

To understand the solution-state emission phenomena of hypsochromic and bathochromic shifting due to a solution's concentration, a well-known molecular effect called π-stacking will be examined. As mentioned earlier in Section 4.4.1, a hypsochromic shift is generally observed as the concentration of the polymeric solution is decreased. Likewise, as the polymer concentration increases, a bathochromic shift is observed. A bathochromic shift can be attributed to the formation of polymer aggregates or clusters in solution due to the π-systems stacking on top of each other. This π-stacking phenomenon leads to an effective increased conjugation length (increased delocalization that results in the lowering of the energy of the π\(^*\) orbital giving it less anti-bonding character), which allows the electron being excited to have access to many more closely spaced vibrational energy levels in the π\(^*\) electronic state. These closely spaced vibrational levels lead to a decrease in the energy required to excite one of the π-electrons to the anti-bonding π\(^*\) energy level. This decrease in energy corresponds to a shift in the excitation and emission values to longer wavelengths (lower energy). Conversely, the hypsochromic shift can be attributed to the reduced π-stacking in diluted solutions and the excitable electrons having reduced access to as many closely spaced vibrational energy levels. This effectively decreases the conjugation length (decreases the delocalization) and widens the excitation band gap leading to higher energies required to stimulate emission. Of course, this larger excitation band gap corresponds to higher emissive energies and shorter emissive wavelengths. These effects are not limited to the solution state and are seen in solid emission as well.

With this molecular effect in mind, recall that the β-peaks in all of the solutions were in agreement with the π-stacking model showing bathochromic shifts as the
concentrations were decreased. On the other hand, two peaks show a disagreement with this model, the first being the γ-peaks, which regardless of the solvent, showed a bathochromic shift when the polymer concentration was decreased. This is an apparent contradiction to the π-stacking model just described. The second peaks showing a disagreement with the π-stacking model are the α-peaks of the methanol and acetonitrile solutions, which were constant and showed no energy shifting with an increase or decrease in polymer concentration. This trend of photoemission independent of concentration is inconsistent with the π-stacking model, and an alternative or supplementary explanation must be proposed to account for this discrepancy.

In light of these peaks' behavior, one of two conclusions can be drawn about the π-stacking model described above, either it is an invalid model or it is insufficient by itself for describing the emission effects of these polymers at these concentrations in these solvents. The latter conclusion seems to be more appropriate in this case since the π-stacking effects were evident in the α-peaks of the DMSO solutions for concentrations near $1 \times 10^{-4}$ mol/L and greater. The broadness of this peak along with the shifting emission maximum with increasing and decreasing excitation wavelengths is indicative of π-stacking. To further investigate these emission trends in methanol and acetonitrile, the maximum emission wavelengths for these solutions were plotted as a function of concentration for all the solvents: DMSO, methanol, and acetonitrile. This plot is shown in Figure 10.

For this discussion, it is convenient to define a parameter, $C$, which is the critical concentration at which the solutions' emission spectra became well behaved, and the maximum emission wavelengths remained constant upon further dilutions. When the emission maximum values for these polymers in their respective solvents were plotted
independently as a function of decreasing concentration, the set of curves for the DMSO solutions had a negative slope for concentrations greater than the critical concentration, $C$, and an essentially zero slope at concentrations less than $C$. Both the methanol and acetonitrile solutions had essentially zero slopes for all concentrations studied. A slope that tends toward zero indicates that the emitting chromophore is becoming well defined. This is seen in the DMSO solutions at concentrations less than their critical concentrations of about $1 \times 10^{-5}$ mol/L. However, it is unclear whether this broad $\alpha$-peak is a result of two or more well-defined chromophores with overlapping emission peaks or a well-defined higher-ordered molecular species with a concentration limited emission. These types of curves may have more than one plateau region where the slope is zero or nearly zero connected by another region of positive or negative slope. Figure 11 shows an example of a more complex curve. The plateau region shown in Figure 10 may correspond to the maximum emission wavelength of a unimolecular species (molecular...
Figure 11. Concentration dependent emission curves for complex emitters.
order = 1) or a higher-ordered molecular species (molecular order > 1) that can no longer be reduced by dilution to a lower-ordered molecular species. It is not always possible, through increased dilutions, to determine if a given plateau region in one of these curves belongs to a unimolecular species or a fully reduced higher-ordered molecular species. For these polymers, the α-peaks upon increased dilution (about $1 \times 10^{-8}$ mol/L) were reduced to a broad, flat region (see Figure 9) with minimal intensity that extended from 450-600 nm, approximately, with no discernible peak maxima. The only conclusion that may be drawn from this is that the emitting chromophoric species was in its most reduced state at whatever molecular order it was maintaining. The fact that the DMSO solutions showed a well-behaved constant maximum emission wavelength for the α-peaks at concentrations below its critical concentration, gives some insight into why the methanol and acetonitrile solutions behaved as they did. There appears to be a critical concentration for these polymers in each of these solvents below which the emission maxima remains constant. For the DMSO solutions, it is near $1 \times 10^{-5}$ mol/L and for methanol and acetonitrile it is some value greater than $1 \times 10^{-3}$ mol/L. The data also showed that the emission maxima at the critical concentrations were essentially identical for the DMSO and acetonitrile solutions which were also very close to the emission maxima of the methanol solutions, with the methanol solutions being blue shifted by about 6 nm due to the hydrogen bonding already discussed in Section 4.4.1.

Now that an attempt has been made at rectifying the insufficiencies of the π-stacking model for describing the emission properties of these polymers, the lack of a hypsochromic shift in the α-peaks as the concentration was decreased in the methanol and acetonitrile solutions can be rationalized as such. A molecules maximum solubility in a particular solvent at given temperature can be thought of as the minimum number of
solvent molecules needed to fully solvate that molecule and separate it from its neighboring molecules. Due to the intermolecular attractive forces that exist in polyelectrolytes (based on the work of Ise and coworkers), this minimum number of solvent molecules may not be solvating a single molecule, but rather a set of molecules closely associated with each other giving rise to a solvated higher-ordered molecular species. This set of molecules may exist in solution as a bi-molecular, tri-molecular, or higher-ordered molecular species that is unaffected by increased numbers of solvent molecules. These species maintain their morphology, and likewise their emissive properties, regardless of how dilute the solution becomes. A given solvent undoubtedly interacts differently with a specific molecule than does another solvent as seen by solubility differences in differing solvents. As such, the morphology of these molecular species in one solvent can be significantly different than their morphology in another solvent at the same concentration, even for solvents of similar dielectric constant. A difference in morphology will certainly give rise to a difference in emission wavelengths at equal concentrations. Solvents interacting with these polymers differently at the same concentration are also exemplified in the lyotropic studies where the same polymer in two different solvents achieves a lyotropic liquid-crystalline state at different concentrations, which is a direct result of the solvent/molecule interactions. These studies will be discussed in Section 4.6.

The behavior of the $\gamma$-peaks in these polymers is more complex than those of the $\alpha$-peaks. Their discrepancies with the proposed model will be analyzed based on the structural features of these polymers in conjunction with the proposed $\pi$-stacking model. Upon analyzing the structures of these polymers, it can be seen that there are numerous mono- and di-substituted phenyl rings present. These types of substituted ring structures
have characteristic fluorescence spectra depending on the type of substituent. Table 2 shows the fluorescence wavelengths of benzene and various monosubstituted benzene derivatives.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Wavelength of Fluorescence (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>270-310</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₆H₅CH₃</td>
<td>270-320</td>
</tr>
<tr>
<td>Propylbenzene</td>
<td>C₆H₅C₃H₇</td>
<td>270-320</td>
</tr>
<tr>
<td>Fluorobenzene</td>
<td>C₆H₅F</td>
<td>270-320</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>C₆H₅Cl</td>
<td>275-345</td>
</tr>
<tr>
<td>Bromobenzene</td>
<td>C₆H₅Br</td>
<td>290-380</td>
</tr>
<tr>
<td>Iodobenzene</td>
<td>C₆H₆I</td>
<td>--</td>
</tr>
<tr>
<td>Phenol</td>
<td>C₆H₅OH</td>
<td>285-365</td>
</tr>
<tr>
<td>Phenolate ion</td>
<td>C₆H₅O⁻</td>
<td>310-400</td>
</tr>
<tr>
<td>Anisole</td>
<td>C₆H₅OCH₃</td>
<td>285-345</td>
</tr>
<tr>
<td>Aniline</td>
<td>C₆H₅NH₂</td>
<td>310-405</td>
</tr>
<tr>
<td>Anilinium ion</td>
<td>C₆H₅NH₃⁺</td>
<td>--</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>C₆H₅CO₂H</td>
<td>310-390</td>
</tr>
<tr>
<td>Benzonitrile</td>
<td>C₆H₅CN</td>
<td>280-360</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>C₆H₅NO₂</td>
<td>--</td>
</tr>
</tbody>
</table>

*In ethanol solution.

Here the different substituents' effects on the fluorescence wavelengths can readily be seen. These fluorescence wavelengths show excellent agreement with the γ-peaks data for these polymers. Thus the origins of the peaks in the range of 260-310 nm in all of the polymers' spectra have been assigned to the mono- and di-substituted phenyl rings of the 4,4'- (1,4-phenylene)bis(2,6-diphenylpyridinium) moieties of these polymers. More highly substituted aromatic rings are not being considered as a contributor to this peak as they usually have emission wavelengths that are longer than those measured in the γ-peaks. The shifting in the γ-peaks is complex and is governed by several competing factors. With π-stacking shown to occur in these polymers, the reduction of this effect by
subsequent dilutions, will indeed lead to hypsochromic shifts in this peak. These blue shifts are usually small, however, and are being overshadowed by a more pronounced bathochromic shift in these \( \gamma \)-peaks. In order to explain the origins of these bathochromic shifts, a method used for analyzing the absorbance of a mixture of simple absorbers\(^5\) will be extended to fluorescence emission power for treatment of these more complex emitters.

Since this emission peak has been deemed a result of the many substituted benzene rings in these polymer structures, of which some are monosubstituted, and some are disubstituted, the emission represented by the \( \gamma \)-peaks is a combination of these different species. As was seen in the Table 2 data, the range of emission wavelengths for these substituted rings is very similar to one another even when the substituents were very different in nature. Because the photoabsorption of di-substituted aromatic rings\(^6\) occur at longer wavelengths than monosubstituted aromatic rings, the subsequent photoemissions of the di-substituted rings will generally occur at longer wavelengths as well. With this in mind, if the \( \gamma \)-peaks' emission is now treated as being made up of more than one different fluorescing species (chromophore), the power of this emission peak can be expressed as a linear combination of the emission powers of each of these chromophores. The fluorescence power for a single fluorescing species can be written as follows

\[
F = KP_o (1 - 10^{-\alpha c})
\]  

where \( K \) is the quantum efficiency of the particular fluorescence process, \( \varepsilon \) is the molar absorptivity of the fluorescing species, \( b \) is the path length, \( c \) is the concentration of the fluorescing species, and \( P_o \) is the power of the beam incident upon the solution. Using a Maclaurin series to expand the exponential term gives

50
\[ F = K P_o \left[ 2.303 \varepsilon b c - \frac{(2.303 \varepsilon b c)^2}{2!} + \frac{(2.303 \varepsilon b c)^3}{3!} \right] \] (5)

If \( \varepsilon b c = A < 0.05 \), the higher-order terms are negligible with respect to the first term and can be disregarded. For multiple chromophores contributing to the same peak, the total power can be written as a sum of the individual powers of the contributing species and can be represented mathematically by the following expression

\[ F_r = \sum_{i=1}^{n} F_i \] (6)

Substituting Equation 4 into Equation 5, and neglecting the higher order terms in the Maclaurin series gives

\[ F_r = 2.367^p (A_{\gamma} + \ldots \gamma \text{ term}) \] (7)

As can be seen in Equation 6, each term in the linear expansion has three parameters, \( K \), \( \varepsilon \), and \( c \) that are dependent on the fluorescing species. In fact, for a specific chromophore, the parameters \( K \) and \( \varepsilon \) are essentially constant for solutions with concentrations less than 0.01 mol/L, so the only independent variable in this equation is the concentration.

At this point in the treatment, for simplification purposes, the constraints for the \( \gamma \)-peaks set forth earlier in this section will be applied to Equation 7. If the simplest case, with only two different emitting species \( (n = 2) \) being responsible for the \( \gamma \)-peaks’ emission power, were explored, the total power would be expressed as

\[ F_r = 2.3b P_o \left( K_1 \varepsilon_1 c_1 + K_2 \varepsilon_2 c_2 + \ldots K_n \varepsilon_n c_n \right) \] (8)

The \( n = 1 \) term is arbitrarily chosen to express the power of the monosubstituted contributors, and the \( n = 2 \) term is therefore assigned to the power of the di-substituted contributors. With a simplified expression for the total power of the emitting species giving rise to the \( \gamma \)-peaks emission, it is now possible to investigate this peak’s behavior.
Since at equilibrium, the concentrations of the two emitting species, \( c_1 \) and \( c_2 \), are constant, for a given polymer concentration, a qualitative relationship between \( c_1 \) and \( c_2 \) can be established by examining the structure of these polymers. The number of monosubstituted rings in these polymers is fixed at four, which is always greater than the total number of di-substituted rings, which ranges from one to three for these polymers. This gives a qualitative relationship of the concentration for \( c_1 \) and \( c_2 \), which is

\[
    c_1 > c_2
\]

The \( c_1 \) and \( c_2 \) parameters are related to the polymer concentration, \( \bar{c} \), by the following relationships

\[
    c_1 = 4\bar{c} \quad \text{and} \quad \bar{c} \leq c_2 \leq 3\bar{c}
\]

For high polymer concentrations, the \( \gamma \)-peaks showed a peak maximum that was at shorter wavelengths than they were at low concentrations. When Equation 8 is applied to this data, it means that the power contribution of the first term, the monosubstituted rings, is larger than the power contribution of the second term, for the di-substituted rings, thus \( K_j\varepsilon_1c_1 > K_\varepsilon_2c_2 \) for high polymer concentrations. As previously stated, the \( K \) and \( \varepsilon \) parameters for a given chromophore are constant, and with \( c_1 \) always greater than \( c_2 \), this indicates that \( K_j\varepsilon_1c_1 \) will always be greater than \( K_\varepsilon_2c_2 \) for all polymers concentrations. If this is indeed true, then as the polymer solutions are diluted, the contribution of the monosubstituted rings to the \( \gamma \)-peaks' emission power will always be greater than the contribution of the di-substituted rings, and this equation fails to describe the behavior of the \( \gamma \)-peaks' emission power as a function of polymer concentration.

The shortcomings of Equation 8 to describe the \( \gamma \)-peaks' behavior are not because of its lack of rigor, but because of the assumptions used to extend it to a more complex...
system. The assumption that the $K$ and $\epsilon$ parameters are constant for the emitting species of these polymers is not valid. It has already been shown that $\pi$-stacking can affect the emissive properties of a chromophore by affecting its physical properties in solution, and the extent of the $\pi$-stacking is distinctly dependent on the polymer concentration. These two parameters, therefore, having a direct dependence on the physical properties of the chromophoric species, also have a concentration dependence. If Equation 8 were now rewritten to accommodate these new parameter conditions, it would appear as follows

$$F_r = 2.3bP_0[K_1(\bar{c})\epsilon_1(\bar{c})c_1 + K_2(\bar{c})\epsilon_2(\bar{c})c_2]$$

(9)

where $K(\bar{c})$ and $\epsilon(\bar{c})$ are now represented as some higher order function of the polymer concentration $\bar{c}$. With three independent parameters now governing each of these terms, a set of conditions could certainly exist in which the contribution of the second term, corresponding to the longer wavelength emitters, is greater than the first term, corresponding to the shorter wavelength emitters yielding an emission peak that is shifted to longer wavelengths. The $K$ function is in itself complex and is different for each chromophore. Though it can be observed for some molecules, that an increase in concentration will increase its quantum efficiency, the relationship is certainly not linear, and this observation does not hold true for all molecules, especially large organics.

Since this equation was derived using Beer's Law, the limitations of Beer's Law must also be considered here, particularly deviations of the molar absorptivity $\epsilon$. The molar absorptivity functions in Equation 9 are represented as a higher ordered function of the polymer concentration that can also be corrected to account for changes in the index of refraction of the medium, which are also concentration dependent. When concentration changes cause significant changes in the refractive index $n$ of a solution, departures from
Beers' Law will be observed. This can be corrected by multiplying the $\varepsilon(n)$ function by a correction factor of $n/(n^2 + 2)^2$. In general, this correction is usually small and not significant for concentrations less than 0.01 mol/L. Equation 8 was not successful in describing these polymers because it was based on there being no interactions among the various emitting species. Typically, only solutions with concentrations greater than 0.01 mol/L have an average distance between the molecules responsible for the emission reduced enough so that each molecule effects the charge distribution of its neighbors. These interactions in turn alter the ability of the molecules to absorb a given wavelength of light. Since these interactions depend on the concentration, their occurrence causes deviations from the linear relationship of fluorescence power and concentration. In solutions containing electrolytes, the linearity of this relationship is particularly affected by the close proximity of ions to the absorber. The molar absorptivity of these species is affected by the electrostatic interactions encountered in these types of solutions. While the effect of molecular interactions is usually not significant at concentrations below 0.01 mol/L, an exception must be made for solutions containing large organic ions or molecules. For these types of molecules, deviations from Beers' law can occur even at concentrations below $1 \times 10^{-6}$ mol/L. Since these molecular effects are certainly present in the polymer solutions being studied, the incorporation of concentration dependent $K$ and $\varepsilon$ parameters into Equation 8 is justified. With these effects taken into account, Equation 9 gives a plausible representation of the fluorescence power for the $\gamma$-peaks' emission. It also allows for the contradictory red shifts experienced in these peaks, though it should not be classified as a red shift. The emission represented by the $\gamma$-peaks is most probably blue shifted as a whole, but with the two emissive species contributing to the overall peak emission, the maximum emission wavelength appears to be red
shifting as the longer wavelength emitters contribute more to the γ-peak emission with decreasing concentration.

Now that the important features and characteristics of these polymers' emission spectra have been identified and investigated, the rest of Section 4 will be used to point out specific emission peaks in the remaining polymer materials. They will be compared with other polymers in this series having similar architecture when appropriate. Individual characteristics in the remaining polymer groups that are not consistent with those already discussed will be addressed as they arise.

4.4.2 Polymer 2 (biphenyl linkage)

Both the tosylate and triflimide polymers of this group exhibited the same behavior as the tosylate and triflimide polymers of Polymer 1 in DMSO. They had very similar absorptions in their UV-vis spectra with the $\lambda_{\text{max}}$ for 2-O and 2-N being 347 and 349 nm respectively, which were close to those of the Polymer 1 values in DMSO. For higher concentrations approaching $1 \times 10^{-3}$ mol/L, the emission peak was singular and not well behaved with a shifting maximum emission value (up to 65 nm) as the excitation wavelength was increased analogous to the Polymer 1 materials in DMSO. The emission peak maxima for this α-peak occurred near $\lambda_{\text{em}} = 532$ nm analogous to the Polymer 1 values. When the solutions were diluted to concentrations near $1 \times 10^{-4}$ mol/L, a second less intense emission peak (the β-peak) near $\lambda_{\text{em}} = 390$ nm developed and was sustained throughout further dilutions. The higher-energy β-peaks in these solutions were as narrow and well defined as they were in the previous materials and upon continuous dilution, approached maximum emission values of 365 nm in the most dilute solutions studied. The broad lower-energy peaks of the Polymer 2 solutions also become well behaved at
higher dilutions. Energy shifts in the emission spectra for these polymers were as expected and similar to the Polymer 1 materials in DMSO. The only appreciable difference between the polymer groups' emission spectra could be seen in the broad low-energy peak maxima. A maximum emission peak value near 497 nm was observed in the \( \alpha \)-peaks of the Polymer 2 materials as opposed to 525 nm in the \( \alpha \)-peaks of the Polymer 1 solutions. This peak also had a shoulder, but it was at longer wavelengths for the Polymer 2 materials instead of shorter wavelengths like the Polymer 1 materials. This shoulder appears near \( \lambda_{em} = 520 \) nm and was of near equal intensity as the peak maximum at 500 nm. Further dilutions to about \( 1 \times 10^{-5} \) mol/L also gave rise to a third peak (\( \gamma \)-peak) of higher energy than the \( \beta \)-peaks, and it had a peak maximum near 292 nm. Diluting still again to concentrations below \( 1 \times 10^{-6} \) mol/L showed the \( \gamma \)-peak dominating the emission spectra with both the \( \beta \) and \( \gamma \)-peaks having minimal intensity. It was red shifted as the concentration was decreased and centered near 300 nm as in the Polymer 1 materials.

For the Polymer 2 materials, the UV-vis absorption bands occurred at 215, 254, and 342 nm for polymer 2-O in methanol and 205, 253, and 341 nm for polymer 2-N in acetonitrile respectively. Again, analogous to the Polymer 1 materials in these same solvents, high concentrations gave a single broad emission peak (the \( \alpha \)-peak) that was well behaved for all wavelengths used to excite with. The maximum emission values for both solvents were centered near 500 nm with a shoulder of nearly equal intensity at about 520 nm. These \( \alpha \)-peaks remained constant with dilution like the Polymer 1 materials in methanol and acetonitrile. Upon dilution, a second higher-energy \( \beta \)-peak developed and was centered near 370 nm. Further dilutions hypsochromically shifted the \( \beta \)-peaks as it did in the previous polymer materials, but the broad, low-energy \( \alpha \)-peaks’ maximum emission remained constant, as was the case in the Polymer 1 material in these
same solvents. Notice that the increased hypsochromic shift exhibited by the 1-O polymer in methanol opposed to that of the 1-N polymer in acetonitrile was not carried over here in comparing the 2-O polymer in methanol with the 2-N polymer in acetonitrile. This was as expected due to the Polymer 2 materials not having the ether linkage capable of hydrogen bonding with the methanol solvent like Polymer 1 could. Therefore, the emission spectra of 2-O and 2-N were expected to be very similar with little to no difference in energy shift between the two emission maxima, which was indeed the case as seen in the Table 1 data. This trend can also be noticed in the table for the remaining polymers in methanol and acetonitrile as well since they too did not contain any moieties capable of hydrogen bonding with methanol. Again, increased dilutions showed the presence of the high-energy γ-peaks in these solutions near 288 nm. It persisted and was red shifted as expected with higher dilutions, becoming the dominant emission peak like before.

4.4.3 Polymer 3 (diphenylfluorene linkage)

Of all the polymers studied, the diphenylfluorene based polymers showed the most pronounced variation in emission intensity with successive dilutions. These polymers also did not achieve well-behaved lowest energy peaks (α-peaks) at any concentration, unlike the previous materials. In DMSO, their λmax values in the UV-vis spectra were 443 nm for both polymers, and at 1 × 10⁻³ mol/L, both polymers 3-O and 3-N showed a single broad peak (α-peak) whose maximum emission wavelength shifted with the excitation value by as much as 45 nm. Their maximum emission wavelength at this concentration was centered near 550 nm. This broad peak had several shoulders that contribute to its large full width at half-maximum value of about 150 nm. A single peak in the excitation
spectrum was found and its $\lambda_{ex}$ value was near 390 nm. After a ten-fold decrease in concentration, this peak still had a shifting maximum emission value, but the peaks’ position had been hypsochromically shifted as expected. At this concentration of $1 \times 10^{-4}$ mol/L, a higher-energy peak $\beta$-peak started to develop and appeared near 390 nm, though it only possessed a small percentage of the emission intensity that the broader peak has. Further dilution to a concentration of $1 \times 10^{-5}$ mol/L still failed to bring about a well-behaved $\alpha$-peak in either the 3-O or 3-N polymers, as these peaks were now of low intensity compared to the higher-energy peaks. This concentration gave rise to an increased intensity of the higher-energy $\beta$-peak centered at 390 nm, but shifted its maximum emission wavelength to 378 nm. These $\beta$-peaks were again quite narrow with full width at half-maximum values comparable to those previously mentioned. This concentration also showed the presence of the even higher-energy peak ($\gamma$-peak) centered near 290 nm like the previous polymer materials. It was also well defined and very narrow. For concentrations of $1 \times 10^{-5}$ and lower, the emission intensity of the broad emission $\alpha$-peak was too low to notice any critical concentration at which the emission wavelength could be considered constant. They essentially appeared as a long tail off of the higher-energy $\beta$-peak with no discernible maxima. At $1 \times 10^{-6}$ mol/L the only peaks with a defined peak maximum were the highest-energy $\gamma$-peaks and the $\beta$-peaks. The $\beta$-peaks were now centered near 360 nm, but they appeared as shoulders on the $\gamma$-peaks, which were bathochromically shifted as before.

Polymer 3-O in methanol had its absorption bands at 208 and 339 nm, while polymer 3-N had its absorption bands at 205 and 337 nm respectively. Their excitation spectra showed a singular peak with $\lambda_{ex} = 392$ nm as found in the DMSO solution. A $\lambda_{em}$ value of 534 nm was measured for both solutions at a concentration of $1 \times 10^{-3}$ mol/L. These $\alpha$-
peak emissions were not well behaved as expected with the \( \lambda_{em} \) shifting by as much as 65 nm with increasing excitation wavelength. Both solutions had large fwhm values for these peaks of 150 nm. Concentrations of \( 1 \times 10^{-4} \) mol/L still yielded a broad, low-energy \( \alpha \)-peak that were not well behaved but were expectedly blue shifted in energy. Its maximum emission wavelength was now between 500-524 nm (this maximum is given as a range due to the peak being broad and flat at the top, see Figure 12). As the concentration was diluted to \( 1 \times 10^{-5} \) mol/L, the \( \beta \)-peak was well established and was centered near 378 nm. The \( \gamma \)-peaks were also well established at this concentration and centered near 287 nm. These peaks can also be seen in the emission spectra shown Figure 12. This concentration also showed an \( \alpha \)-peak that retained its broad characteristics, and its \( \lambda_{em} \) was now centered near 495 nm though it was less intense than the higher-energy \( \beta \) and \( \gamma \)-peak. At the lowest concentrations, the \( \alpha \) and \( \beta \)-peaks expectedly disappear leaving only the \( \gamma \)-peak. It was again bathochromically shifted to 295 nm.

4.4.4 Polymer 4 (2,6-anthracene linkage)

The best example of how a single fluorescing moiety, incorporated in a polymer, can influence the photoluminescence emission spectra was found in the Polymer 4 group materials. These polymers possessed only two emission peaks in all the solvents used and at all the concentrations studied. Figure 13 shows one of these polymers' emission spectra at various concentrations. These peaks both possessed high-energy emission wavelengths whose maximum values varied from 360 nm at low concentrations to 390 nm at high concentrations for the \( \alpha \)-peak (lower energy peak) and 300 nm at low concentrations to 285 nm at high concentrations for the \( \beta \)-peaks (higher energy). The \( \beta \)-peaks' emissions correspond to those of the mono- and di-substituted phenyl rings of...
Figure 12. Excitation and emission spectra of (a) 3-O in methanol and (b) 3-N in acetonitrile at a concentration of $1 \times 10^{-4}$ mol/L.
these polymers as discussed earlier. The α-peaks' emissions were believed to be dominated by the emissions of the anthracene moiety in the polymers. Looking at the emission bands in the fluorescence spectrum of pure anthracene at similar concentrations in similar solvents substantiated this belief. The fluorescence spectrum of 1 ppm (1.78 × 10⁻⁴ mol/L) anthracene in ethanol is shown in Figure 14. The typical shifts in wavelengths were encountered when the concentrated solutions were diluted and the peaks were well behaved at all concentrations. In Figure 14, it can be seen that the peak intensity for the 1 × 10⁻⁴ mol/L is less intense than the 1 × 10⁻⁵ mol/L. This is due to the self-quenching of this polymer at that concentration. The emission wavelengths of the α-peaks were blue shifted with increased dilutions, and the emission wavelengths of the β-peaks were red shifted by diluting, as expected. Both the α and β-peaks were relatively narrow with full width at half-maximum values of about 45 nm in the 1 × 10⁻⁴ and 1 × 10⁻⁵ mol/L solutions. At higher concentrations (near 1 × 10⁻³ mol/L), the α-peaks developed a shoulder that tailed off toward longer wavelengths to the end of the visible spectrum. The emission curves of the α-peak for the higher concentration solutions have an inflection point near 435 nm marking the being of this shoulder. For dilute solutions (1 × 10⁻⁵ mol/L or less), this tail was present though it was less prominent. The typical wavelength shifts were present as the solvent’s dielectric constants were changed. Similar to the preceding materials, polymers 4-O and 4-N have UV-vis absorption bands that were close to the others. Their absorption bands were centered at 265 and 348 nm for both DMSO solutions. Polymer 4-O in methanol had absorption bands at 203, 260, and 345 nm, and 4-N in acetonitrile had absorption bands centered at 205, 263, and 344 nm.
Figure 13. Emission spectra for polymer 4-O in methanol at (a) $1 \times 10^{-7}$ mol/L, (b) $1 \times 10^{-5}$ mol/L, (c) $1 \times 10^{-6}$ mol/L.

Figure 14. Fluorescence spectrum for 1 ppm anthracene in alcohol: (a) excitation spectrum; (b) emission spectrum.

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4.4.5 Polymer 5 and 6 (aliphatic linkages)

Due to the aliphatic linked polymers having similar photoluminescence properties, they are grouped together here for discussion. The most pronounced deviation from the emission trends that have been reported thus far came from the Polymer 5 (n-hexyl linked) and Polymer 6 (n-dodecyl linked) group materials. These polymers showed the greatest emission intensity dependence on concentration. These polymers had nearly identical UV-vis absorption maxima in DMSO when compared to all the other polymer groups (as seen in Table 1), but in terms of their emission spectra, these polymers showed significant differences in their DMSO spectra. Even when compared to each other, the DMSO spectra for these groups have notable differences. Their methanol and acetonitrile spectra are also different from their DMSO spectra and will be discussed shortly. Both the Polymer 5 and 6 groups, with both counterions, showed a broad, low-energy α-peak as well as a very low intensity, higher-energy β-peak at a concentration of $1 \times 10^{-3}$ mol/L like the previous polymer groups already discussed (excluding the Polymer 4 anthracene group, which was all together different). The high-energy β-peaks, were centered near 400 nm, and were very low intensity compared to the broader high intensity α-peaks that were centered near 545 nm. At this concentration there were no significant differences between the two polymer groups, but as the concentration was decreased to $1 \times 10^{-4}$ mol/L, there were distinguishable differences in the emission intensity of the two groups. Figure 15 shows some of these two polymer groups’ emission spectra at this concentration. At this concentration, the n-hexyl linked polymers still maintain the broad, low-energy α-peak as the major emitting species, with the higher-energy β-peak having an increased intensity (though still small compared to the broad peak). Both peaks were of course hypsochromically shifted as expected with the reduced concentration. The n-dodecyl
Figure 15. Excitation and emission spectra for (a) 5-0 and (b) 6-0 in DMSO at a concentration of $1 \times 10^{-4}$ mol/L.
linked materials, however, now showed minimal emission intensity from the broad, low-energy $\alpha$-peak as compared to the intensity of the now dominant high-energy $\beta$-peaks. These high-energy $\beta$-peaks in both groups were centered near 380 nm at this concentration. At a further dilution of $1 \times 10^5$ mol/L, the n-hexyl linked materials still showed an emission from the broad $\alpha$-peaks, though they were less than 20% of the emission intensity of the high-energy $\beta$-peak. They had wavelength maxima centered near 530 nm. As for the n-dodecyl linked materials, these broad emission peaks were extinct at this concentration. The $\beta$-peaks' maximum emission values for both polymer groups were centered near 370 nm. One further dilution of these polymer groups to a concentration of $1 \times 10^6$ mol/L yielded the same singular high-energy emission peak centered near 365 nm. The full width at half-maximum values for these high-energy $\beta$-peaks at this concentration were less than 50 nm. The highest energy $\gamma$-peaks, due to the mono- and di-substituted phenyl rings, only appeared in solutions with very high dilutions ($> 1 \times 10^7$ mol/L).

The n-hexyl linked polymers, though more flexible than the aromatic linkages, have reduced polymer chain mobility compared to the n-dodecyl linked polymers. With the fluorescing moieties of the n-hexyl linked polymers in a closer proximity to each other than those in the n-dodecyl linked polymers, there is an increased probability for intramolecular interactions of these fluorescing moieties. The $\pi$-stack in these polymers can be thought of as being comprised of two factors, that from the intermolecular type and that from the intramolecular type. In high concentrations the total amount of $\pi$-stacking is large, and the contributions from the intermolecular and intramolecular parts are not differentiable. When the concentration is decreased, each factors contribution is more distinguishable. If the total probability of $\pi$-stacking at low concentrations is written
as a two component probability function, the total probability, $\Pi_T$, would be given by

$$\Pi_T = \pi_{\text{inter}} \cdot \pi_{\text{intra}}$$

where $\pi_{\text{inter}}$ is the probability of intermolecular stacking and $\pi_{\text{intra}}$ is the probability of intramolecular stacking. It is now possible to examine the prolonged presence of the $\alpha$-peaks in the n-hexyl polymers spectra, as the polymer concentration is decreased, based on this probability function. It will be assumed that the $\pi_{\text{inter}}$ is nearly the same for the two polymer groups, with the n-dodecyl linked polymers having a somewhat smaller probability due to an increased probability of the longer aliphatic chains shrouding the $\pi$-systems during stacking. The $\pi_{\text{intra}}$ parameter is related to the number of structural configurations the aliphatic chains can possess that lead to significant intramolecular $\pi$-system overlap of the chromophores. The n-dodecyl linked polymers can attain a much larger number of structural configurations (at least two orders of magnitude larger) per repeating unit than can the n-hexyl linked polymers. The percentage of these structural configurations that lead to significant intramolecular $\pi$-stacking is therefore much smaller for the n-dodecyl linked polymers than the percentage of those configurations in the n-hexyl linked polymers. This gives the n-hexyl polymers a much large $\pi_{\text{intra}}$ component in the $\Pi_T$ probability function, which corresponds to a higher probability of $\pi$-stacking in this polymer group at lower concentrations.

Emission behavior for these polymers in methanol and acetonitrile differed markedly from the DMSO solutions at the same concentrations. Even when compared to each other, the two polymers produced different emission spectra. At concentrations near $1 \times 10^{-3}$ mol/L, both groups had a single broad peak (\(\alpha\)-peak) centered near 525 nm with a shoulder of near equal intensity near 505 nm. This was similar to the Polymer 1 and 2 methanol and acetonitrile solutions. For the n-hexyl linked materials at a concentration of
I $1 \times 10^{-4}$ mol/L, the single broad emission peak was still present, but its $\lambda_{em}$ shifted to about 450 nm. A shoulder near 380 nm does appear on the emission curve of the broad peak that corresponds to the higher-energy $\beta$-peaks. The $n$-dodecyl polymers had the same broad emission peak centered near 451 nm that Polymer 5 materials had at the same concentration, and all of the $\alpha$-peaks for both groups showed the typical bathochromic shifting with increased excitation wavelength. The maximum emission wavelengths varied by as much as 70 nm when the excitation wavelength was increased. A second higher-energy $\beta$-peak was also present for these $n$-dodecyl linked polymers at this concentration of $1 \times 10^{-4}$ mol/L, but it was of comparable intensity to the broad emission peak instead of just appearing as a shoulder like in the Polymer 5 spectra. This peak was centered near 375 nm, and it had a shoulder peak of its own that corresponded to low intensity versions of the broad $\alpha$-peak just mentioned. Figure 16 shows the emission spectra of these two polymer groups at this concentration. At the next concentration value of $1 \times 10^{-5}$ mol/L, both polymer groups' broad emission $\alpha$-peaks were well behaved and hypsochromically shifted to about 442 nm. As for the higher-energy $\beta$-peaks of these two material groups, those of the Polymer 5 materials increased in intensity only slightly and were still small compared to the $\alpha$-peaks. The $\beta$-peaks of the Polymer 6 materials also increased in intensity but were now comparable in intensity to the $\alpha$-peaks. The emission wavelengths for the $\beta$-peaks of both groups were located near 365 nm at this concentration. Also at this concentration, the higher-energy $\gamma$-peaks had developed in both polymer groups and were centered near 275 nm. When the polymer concentration was reduced to $1 \times 10^{-6}$ mol/L, the intensity of the $\gamma$-peaks in both groups had increased and the peak positions were red shifted, as expected, to 288 nm. The positions of the $\beta$-peaks of both groups were shifted slightly too about 362 nm, and the $\alpha$-peaks of both...
Figure 16. Excitation and emission spectra for (a) 5-O and (b) 6-O in methanol at a concentration of $1 \times 10^{-4} \text{ mol/L}$. 

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groups remained in the same position as they were at the previous concentration. Further dilution showed reduced emission intensity but no change in emission maxima peak positions for the \( \alpha \) and \( \beta \)-peaks, and only a small bathochromic shift (about 2 nm) in the \( \gamma \)-peaks for both groups. These groups of materials, in these solvents, clearly had a critical concentration at which the emission output remained constant for the \( \alpha \) and \( \beta \)-peaks. Also, these materials had the most noticeable solvent dependence of all the polymer materials studied.

4.5 Photoluminescence Properties in the Solid State

Just as the solution-state fluorescence spectra showed a large dependence on the concentration of the polymer solution, the solid-state fluorescence spectra showed a large dependence on the thickness of the polymer films. The solid-state properties of these polymer groups will be discussed in terms this thickness dependence. Due to an inability to measure the actual thickness of these films, they will be discussed in terms of their relative thickness with respect to each other. These films were prepared by dip coating them in a solution of these polymer materials. The solvents used to cast these films were methanol for the tosylate polymers and acetonitrile polymers. These solvents were chosen due to their high volatility, which made casting the films possible. All the films were vacuumed dried before their emission spectra were recorded to remove all traces of the solvents. As was seen in the solution-state data for these polymers, the emission properties of each group were fairly consistent from one counterion to the other. This trend is also extended to the solid state for these polymer groups for films of similar thickness. The solid-state photoemission data summary for these films can be found in Table 3.

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Table 3. Emission Peak Wavelengths ($\lambda_{em}$) of Poly(pyridinium salt)s in the Solid State as Solvent Cast Thin Films

<table>
<thead>
<tr>
<th>Polymer Number</th>
<th>Polymer Structure</th>
<th>Casting Solvent</th>
<th>$\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-O</td>
<td>oxydiphenyl-OTs</td>
<td>CH$_3$OH</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>1-N</td>
<td>oxydiphenyl-NTf</td>
<td>CH$_3$CN</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>2-O</td>
<td>4,4'-biphenyl-OTs</td>
<td>CH$_3$OH</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>2-N</td>
<td>4,4'-biphenyl-NTf</td>
<td>CH$_3$CN</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>3-O</td>
<td>diphenylfluorene-OTs</td>
<td>CH$_3$OH</td>
<td>520 (α-peaks), 390 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>3-N</td>
<td>diphenylfluorene-NTf</td>
<td>CH$_3$CN</td>
<td>520 (α-peaks), 390 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>4-O</td>
<td>2,6-anthracene-OTs</td>
<td>CH$_3$OH</td>
<td>390 (α-peaks), 280 (β-peaks)</td>
</tr>
<tr>
<td>4-N</td>
<td>2,6-anthracene-NTf</td>
<td>CH$_3$CN</td>
<td>389 (α-peaks), 280 (β-peaks)</td>
</tr>
<tr>
<td>5-O</td>
<td>n-hexyl-OTs</td>
<td>CH$_3$OH</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>5-N</td>
<td>n-hexyl-NTf</td>
<td>CH$_3$CN</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>6-O</td>
<td>n-dodecyl-OTs</td>
<td>CH$_3$OH</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
<tr>
<td>6-N</td>
<td>n-dodecyl-NTf</td>
<td>CH$_3$CN</td>
<td>460-480 (α-peaks), 380-400 (β-peaks), 280 (γ-peaks)</td>
</tr>
</tbody>
</table>

*a The casting solvent is the polymer solution solvent used for depositing the polymer onto the quartz slides.

*b The emission peak values listed in bold type are listed as a range due to their concentration dependence. The ranges are shown for decreasing concentrations.

An attempt was made to control the film thickness by depositing a fixed volume of solution to a constant area on a quartz slide. By using solutions with the same concentration ($1 \times 10^{-3}$ mol/L) to prepare the films, the amount of polymer material deposited was essentially constant for these films. Accordingly, by depositing twice the volume of solution, to the same area, the amount of polymer material deposited was doubled, and in theory the thickness was relatively doubled. Due to the assumption that the polymers will deposit evenly over the whole area (theoretically, not practically), this
method can only give films with the similar relative thickness and not films with similar absolute thickness.

4.5.1 Thin Films

Without the presence of solvent molecules to potentially separate these polymer chains from one another, there will undoubtedly be π-stacking occurring within the polymer matrix even in thin films. The thin films of polymer groups 1, 2, 5, and 6, for both counterions, showed basically three peaks in their emission spectra similar to the solution-state spectra. The first (α-peak) was a broad emission peak with a maximum in the range of 460-480 nm, and the second (β-peak) was in the range of 380-400 nm. The formation of a third very low intensity peak (γ-peak) was also seen in some of the films near 280 nm, and is expected to be present in all the films at the appropriate thickness. These peaks are analogous to the peaks seen in the more dilute solution-state spectra of these polymer groups. Based on the similarities of their solution-state spectra, it is no surprise that the solid-state spectra of polymer groups 1, 2, 5, and 6, had nearly identical solid-state spectra. Emission spectra of some films of these groups are shown in Figure 17. The diphenylfluorene polymers had the longest emission wavelengths of any of the groups in the solution-state, and this characteristic was carried over to the solid-state as well. Both of the thin films of polymer group 3, showed three peaks, the first near 520 nm, a second near 390 nm, and a third very low intensity peak at about 280 nm. Just like the solution-state spectra, the polymer 3 materials differed from polymers 1, 2, 5, and 6 only in the position of the lowest energy peak. Polymer 3’s other two higher-energy peaks were essentially the same as these groups. In the solution-state, the anthracene polymers’ spectra were very different from the rest of these groups. This was also the case in the solid-state. Both of the thin films of polymer group 4 showed a λ_{em} near 390
Figure 17. Thin film excitation and emission spectra for (a) 2-O and (b) 6-O cast from methanol solutions.
nm. The solid-state data for the group 4 materials containing the anthracene moieties were virtually identical to the solution-state data. These thin films also appeared to be dominated by the presence of the anthracene moieties in these polymers. They also had a low intensity peak near 281 nm. Figure 18 shows some spectra from the Polymer 3 and 4 groups.

4.5.2 Thick Films

Like the solution-state fluorescence data, increased \( \pi \)-stacking through increased concentration caused the photoemission peaks to shift bathochromically. This effect was also expected to occur in the solid-state emission spectra as the amount of \( \pi \)-stacking was increased by increasing the polymer thickness. Indeed small red shifts were experienced in these polymers’ emission wavelengths when the film thickness was increased. For polymer groups 1, 2, 3, 5, and 6, the intensity of the \( \beta \)-peaks decreased and the \( \gamma \)-peaks disappeared as expected. The same trend was seen in the solution-state data when the concentration was increased. The anthracene materials of polymer group 4 also showed a small red shift when the thickness was increased, and the high-energy peaks near 280 nm showed reduced intensity like the other polymers with this increased thickness.

4.6 Lyotropic Liquid-Crystalline Properties

Besides their photoluminescent properties in solution and the solid state, some of these polymers also exhibit a lyotropic liquid-crystalline phase in common organic solvents. A lyotropic liquid-crystalline phase is a solvent induced phenomenon that some organic molecules may exhibit, in which liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present.\(^8\) Polymers 1-O, 2-O, and 3-O
Figure 18. Thin film excitation and emission spectra for (a) 3-O and (b) 4-N cast from methanol and acetonitrile solutions, respectively.

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exhibited lyotropic properties in DMSO above their critical concentration, C*. They also exhibited lyotropic properties in a polar protic solvent such as methanol.

Similar to nonionic lyotropic liquid-crystalline polymers, polymer 1-0 usually formed an isotropic solution at 20 wt % in methanol. At an intermediate concentration of 30 wt %, it exhibited a biphasic solution in which a liquid-crystalline phase coexisted with an isotropic solution. At relatively high concentrations, 40 wt %, 1-0 formed a fully-grown lyotropic phase. Similarly, it also formed biphasic and lyotropic solutions in DMSO at 20 and 30 wt %, respectively. The C* values were lower in DMSO than those in methanol.

Polymer 2-0 had lower C* values than 1-0 in DMSO due to its more rod-like structure. It formed a biphasic solution at 10 wt % and developed a full-grown lyotropic phase at 19 wt % in DMSO. Additionally, unlike its biphasic solution in DMSO, it formed a biphasic solution in methanol at a very low concentration of 5 wt %, which transformed on standing into two distinct phases. These two phases were easily separable and identified as an anisotropic and an isotropic phase by PLM studies. Their liquid-crystalline textures for each of these biphasic and lyotropic solutions in these solvents showed small and large bâtonnets, different types of polygonal arrays – often referred to as mosaic textures – and individual rounded droplets consisting of characteristic Maltese crosses, all of which were indicative of their lamellar phase. These described textures of polymer 2-0 are shown in Figure 19.

Polymer 3-0 also exhibited lyotropic liquid-crystalline textures above its critical concentration in DMSO and methanol. It developed a birefringent lyotropic liquid-crystalline phase in DMSO at a concentration of 29 wt %. In methanol, it formed a biphasic solution at 10 wt % and developed a full-grown lyotropic phase at 19 wt %. Its
Figure 19. Photomicrograph of (a) polymer 2-O at 31 wt % in DMSO and (b) polymer 3-O at 19 wt % in methanol both taken at room temperature under crossed polars exhibiting a lyotropic solution (magnification 400×).

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liquid-crystalline texture for the lyotropic solutions in these solvents also showed small and large bâtonnets, different types of polygonal arrays – often referred to as mosaic textures – and individual rounded droplets consisting of characteristic Maltese crosses, all of which were indicative of their lamellar phase. Figure 19 contains a photomicrograph showing these textures.

4.7 Thermotropic Liquid-Crystalline Properties

Besides some of these polymers having liquid-crystalline properties in solution, others exhibit liquid-crystalline properties upon melting, which are called thermotropic liquid-crystalline properties. A thermotropic liquid-crystalline phase is a thermally induced phenomenon in which liquid-like order exists at least in one direction of space and in which some degree of anisotropy is present. The polymers that exhibited this type of liquid-crystal behavior were the Polymer 5 group materials and the Polymer 6 tosylate (6-O) material, which contained the long aliphatic linkages. These long carbon chains, along with the incorporation of the tosylate and triflimide counterions, are conducive to lowering the melting transitions of these polymers and allowing for this type of behavior to develop. Poly(pyridinium salt)s with either the tetrafluoroborate (BF$_4$) or triflate (CF$_3$SO$_3$) as the counterion, do not exhibit thermotropic liquid-crystalline properties because of their thermal decomposition prior to melting transitions.$^{9,10}$ The tosylate and triflimide counterions, when incorporated into poly(pyridinium salt)s are conducive to the thermotropic liquid-crystalline properties because they significantly reduce the ionic interactions between the positive and negative charges. These polymers are in excellent agreement with the results of other ionic polymers.$^{11,12}$
Polymer 6-O, with the tosylate counterion, showed a complex crystal-to-liquid-crystal transition, $T_m$, at 116 °C (at a heating rate of 10 °C/min) above which it formed a viscous melt. Upon further heating to higher temperatures, it exhibited an additional liquid-crystal transition at 230 °C that extended up to its thermal decomposition at 254 °C. This decomposition temperature was obtained by thermogravimetric analysis, at a heating rate of 10 °C/min under nitrogen, at which a 5 % weight loss of the polymer occurred. This transition was also verified by polarized light microscopy studies in which a new liquid-crystal texture developed at the expense of the originally complex texture. The $T_m$ of this polymer was reproducible and reversible when it was heated up to 200 °C, which was well below the decomposition temperature, since this transition appeared at each of the heating cycles of the DSC thermograms shown in Figure 20. Figure 21 shows the photomicrograph of polymer 6-O exhibiting its smectic liquid-crystalline phase since it contained small bâtonnets that are the microstructures of this liquid-crystalline phase.\textsuperscript{13,14}

Polymer 6-N, containing the triflimide counterion, also exhibited a $T_m$ at 80 °C (at a heating rate of 10 °C/min), which was lower than that of polymer 6-O. Similar to polymer 6-O, the $T_m$ of this polymer was reproducible and reversible, since it appeared in both of the heating cycles of the DSC thermograms shown in Figure 20. Despite the presence of the main-chain ionic character of these polymers, each of their $T_m$ transitions exhibited a very low degree of supercooling in their cooling cycles. Although its liquid-crystal-to-isotropic transition, $T_i$, was not distinctly detectable in the DSC thermogram because of the broadness of this endotherm, this transition was determined by hot-stage PLM studies to be at about 180 °C at which the complete disappearance of the liquid-crystal texture occurred. These results suggested that the triflimide counterion in this polymer not only decreased the $T_m$ but also the $T_i$. Both of these transitions were well below their
Figure 20. DSC thermograms of polymers 6-O (a) and 6-N (b) obtained at both heating and cooling rates of 10 °C/min.
decomposition temperatures at 316 °C. This decomposition temperature was obtained by thermogravimetric analysis, at a heating rate of 10 °C/min under nitrogen, at which a 5 % weight loss of the polymer occurred. Polymer 6-N had a broad range liquid-crystalline phase of about 100 °C. A photomicrograph of this polymer showing the smectic liquid-crystalline phase containing bâtonnets is shown in Figure 21. The reason for both the low Tm and low Tl of polymer 6-N can be understood by looking at the recently reported crystal structure of 1-benzyl-2-ethyl-3-methyl imidazolium triflimide salt. The negative charge delocalization expected in this organic counterion extends only from the central nitrogen to the neighboring sulfur atoms and not to any great extent onto the four sulfonyl oxygen atoms. The result of this partial delocalization through π-π interactions is that the negative charge is significantly buried within the anion and shielded by four oxygen atoms and two terminal -CF3 groups from Coulombic interactions with neighboring cations. These reduced interactions, therefore, appear to be associated with increased ion mobility and reduced lattice energy in the crystalline states.15,16 Thus it was reasonable to conclude that the reduced ionic interactions between the triflimide anion and the 4,4′-(1,4-phenylene)bis(2,6-diphenylpyridinium) ions in the main chain are similar to those reported for the imidazolium triflimide salt, and therefore provided a unique mechanism for its low Tm and low Tl. The thermal stability of polymer 6-N was also much higher than polymer 6-O. These results are in good agreement with the thermotropic liquid-crystalline properties of viologen polymers containing triflimide anions.11

Polymer 5-O, with the tosylate counterion, also showed a crystal-to-liquid-crystal transition, though it was at a much higher temperature than the 6-O transition. The Tm for this polymer was at 172 °C (at a heating rate of 10 °C/min), and its liquid-crystal phase persisted up to the decomposition temperature. This transition was also verified by
Figure 21 Photomicrographs of (a) polymer 6-O taken at 220 °C and (b) polymer 6-N taken at 110 °C under crossed polarizers exhibiting smectic liquid-crystalline phases (magnification 400×).

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polarized light microscopy studies. The $T_m$ of this polymer was reproducible and reversible when heated to temperature well below its decomposition temperature, since this transition appeared at each of the heating cycles of the DSC thermograms. Polymer 5-O exhibited a smectic liquid-crystalline phase since it contained small bâtonnets that are the microstructures of this liquid-crystalline phase.$^{13,14}$
ENDDNOTES


CHAPTER 5

CONCLUSIONS

5.1 Chemical Structure

The modified polymerization procedure used to prepare the tosylate polymers was found to be successful in synthesizing these types of polymers. It yields polymers of high molecular weight and good purity for polymers of this type. The procedure used to prepare the corresponding triflimide polymers from these precursor tosylate polymers, was also found to be quite effective giving an essentially quantitative exchange of the tosylate anion for the triflimide anion. The elemental analysis results for these triflimide polymers were typically very good, and were usually in error of the calculated percent composition by less than 0.5%. These polymers showed good solubility in common organic solvents and allowed them to be studied by various means such as $^1$H and $^{13}$C NMR and luminescence spectroscopy.

5.2 Photoluminescence Properties

Both the solution-state and solid-state photoluminescence properties of these polymers containing tosylate and triflimide counterions were investigated in terms of their solution concentration dependence and their film thickness. Solutions were made in DMSO, methanol, and acetonitrile. The solution-state behavior of these polymers was complex in all solvents, and for nearly all of these polymers, there were three
fundamental emission bands in their spectra depending on the solution's concentration. The maximum emission wavelengths of these polymers' peaks varied somewhat from one polymer to the next, but can be summarized as a range of wavelengths. For all of the polymers except the anthracene-linked polymers, the emission peak maxima varied from 550-442 nm for the α-peaks (the lowest energy peaks in these spectra), 400-362 nm for the β-peaks (the next lowest energy peaks), and 275-300 nm for the γ-peaks (the highest energy peaks). The anthracene-linked polymers were different that the rest of the polymers as they only contained two emission bands that were concentration dependent. The ranges for these emission bands were 390-360 nm for their α-peaks (the lowest energy peaks) and 285-300 nm for their β-peaks (the highest energy peaks). The expected peak shifts were encountered when the solvent polarity was reduced, and the difference in counterions had no noticeable effect on the emission spectra for any of the polymer groups.

These polymers' solid-state behavior was studied by preparing dip coated quartz slides using a methanol or acetonitrile based solution of these polymers. These emission spectra were also somewhat complex with three emission bands of varying intensity based on film thickness. Again only the anthracene-linked polymer films showed to emission bands. The ranges for the emission bands of the polymers containing three peaks were 520-460 nm for the α-peaks, 380-400 for the β-peaks, and 280 nm for the γ-peaks, depending on the particular polymer and its film thickness. For the anthracene polymers, their peaks were located at 390 nm for the α-peaks and 280 nm for the β-peaks. They showed peak maxima that were essentially independent of film thickness.
5.3 Lyotropic Liquid-Crystal Properties

Polymers 1-O, 2-O, and 3-O exhibited their lyotropic liquid-crystalline behavior in DMSO and methanol at concentrations above their critical concentrations. Polymer 1-O showed increased solubility in methanol and as such its critical concentration was higher for this solvent than for DMSO. It developed a full-grown lyotropic liquid-crystalline phase at 40 wt % and 30 wt % in methanol and DMSO respectively. The rod-like characteristics of polymer 2-O prompted the formation of a biphasic solution in methanol and DMSO at the very low concentrations of 5 wt % and 10 wt %, respectively. The tosylate polymer of polymer group 3 also showed a lyotropic liquid-crystal state at 19 wt % in methanol and 29 wt % in DMSO. It is worth mentioning here that the triflimide polymers of these groups, especially the fluorine linked polymers, showed exceptional solubility in many organic solvents, leading to their non-lyotropic behavior.

5.4 Thermotropic Liquid-Crystal Properties

These aliphatic linked poly(pyridinium salt)s are the first polymers of this type with tosylate and triflimide counterions that exhibit thermotropic liquid-crystalline and light-emitting properties. Thermotropic liquid-crystalline properties were achievable in these types of polyelectrolytes with the introduction of the n-hexyl and n-dodecyl aliphatic linkages, in conjunction with the organic tosylate and triflimide counterion. Their transitions were reproducible and reversible when heating at temperatures well below their decomposition temperatures, and their liquid-crystalline phase exhibited a smectic texture. The longer n-dodecyl linkages showed decreased melting transitions compared to the n-hexyl linked polymers with the same counterion. Using triflimide counterions resulted in a significantly lower melting transition in the polymer 6 materials compared to
the tosylate polymer of the same group. This is believed to be due to reduced Coulombic interactions of this anion with neighboring cations. It was possible for this thermally induced liquid-crystal behavior to develop in both these groups due to the increased thermal stability and the decreased melting transitions they possess.

5.5 Applications of these Polyelectrolytes

The combination of lyotropic liquid-crystalline properties, thermotropic liquid-crystalline properties, the ease of film formation, and photoluminescence makes these polymers interesting for optoelectronic applications such as polymeric light-emitting devices. They are also ideal cationic polyelectrolytes for the buildup of multilayer assemblies with controlled morphologies at a molecular level by the sequential deposition technique with other negatively charged polyelectrolytes.
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