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14. ABSTRACT
In materials strategy, the Department of the Navy is the first to consider the development of novel anti-corrosion inhibitors. Thus we proposed to develop novel corrosion inhibitors based on polymer metallocomplex composite materials. These new materials can cut off the electron transfer path via the polymer metallocomplexes. Bipyridine-based polymerizable ligand monomers were synthesized starting from 4,5-diazafluoren-9-one (1). The copolymers of the polymerizable methacrylate-type monomer with styrene, methyl methacrylate, and butyl methacrylate have strong blue-light-emitting properties. Amphiphilic tris(2,2'-bipyridine)ruthenium-cored star polymers of polystyrene and poly(N-isopropylacrylamide) were found to self-assemble into core-shell micelles in which the ruthenium ions are located on the interface between core and shell. The amphiphilic star-shaped metallopolymer with longer PNIPAM blocks formed micro-sized aggregates at high concentration. To prepare ligand-endfunctionalized polymers, we also synthesized ligand-functionalized initiators. We also synthesized the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; nanoporous silicate host materials of up to 30 nm pore diameter, using poly(alkylene oxide) copolymers, which when removed will yield a mesoporous material; and investigated the zeolite Y/Nanporous composite materials as hosts for corrosion inhibitors.

15. SUBJECT TERMS
RAFT POLYMERIZATION; GALVANIC CORROSION; 2,2'-BIPYRIDINE; 2,2'6'2"-TERPYRIDINE; POLYSTYRENE; POLY(N-ISOPROPYLACRYLAMIDE); RUTHENIUM; METALLOPOLYMER; MICELLE; SELF ASSEMBLY; ZEOLITE

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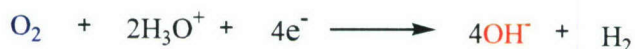
TABLE OF CONTENT

Title	Page
Background	3
Objectives	4
Approach	4
Accomplishments	5
References	17
Publications	19
Patent Applications	20
Presentations	20
Number of Students	23
Major Instruments Purchased	23

BACKGROUND:

Improved performance and weight reduction are becoming increasingly important on naval ships, vehicles and aircrafts. Substantial weight reduction can be achieved by replacing metal with advanced composite materials such as carbon/bismaleide/metal (carbon/BMI/metal) and carbon/polyimide/metal (carbon/PI/metal) composites. However, most of these advanced composite materials with high thermal stability and high durability are reinforced by carbon fibers. The use of carbon fibers in advanced composite materials gives rise to a serious galvanic corrosion problem. Carbon fibers exhibit relatively high conductivity compared with other nonmetals. When coupled with an electrolyte, e.g. H₂O, this semi-metallic behavior allows electrochemical reactions to occur at the surface of the composite. Many structural metals oxidize and corrode due to passage of current. This galvanically-induced corrosion could, of course, lead to catastrophic consequences. In addition, corrosion can induce degradation of the composite matrix resin. All matrix resins degrade, but saponifiable resins such as bismaleimides (BMIs), polyimides (PIs), cyanate/triazines are especially susceptible.^[1] Thus, the utility of carbon/BMI/metal and carbon/PI/metal composites is limited despite their desirable properties such as high specific strength and stiffness, coupled with directional tailorability and design versatility enabling reductions in number of parts and fasteners.

Galvanically-induced corrosion stems primarily from the formation of nucleophilic hydroxide (OH⁻) and/or per-hydroxide (OOH⁻) by the reduction of oxygen in the presence of water via electrochemical ways as shown below.



Other mechanisms have also been proposed. No matter which mechanism, all the electrode reactions involve the generation of electrons with the formation of OH⁻ and/or OOH⁻. It is established that as the active component of the couple (metal) corrodes in the presence of an electrolyte (H₂O), the corresponding cathodic reactions occur at the graphite fiber surface causing degradation of the composite system.^[2-8] Detailed studies into the reaction of OH⁻/OOH⁻ ions with thermoplastic polyimides and BMIs show that the OH⁻/OOH⁻ ions open the imide rings to form water-soluble carboxyl functional hydrolysis products. To prevent this kind of corrosion, White *et al.*^[9] reported that protection schemes which consisted of coatings on the composite and the metal, sealant on the fraying surface and around the fastener, and fiberglass barrier ply, reduced the corrosion found in unprotected couples. However, they cautioned that the protection schemes were only effective if all surfaces were coated and if the sealant layers were not porous. Wolf *et al.*^[10] showed that under specific exposure conditions, hydrolysis rates could be significantly reduced through annealing of the polymer prior to exposure. However, this does not address in-service exposure to moisture. Furthermore, heat drying enhances corrosion.

Various groups have attempted to develop methods based on chemical structural modification to prevent galvanically-induced composite corrosion.^[9, 10-12] These approaches although meritorious are also to some extent self-defeating in that, they compromise on the desired properties of the

composites, such as high dimensional strength. In order to prevent galvanically induced corrosion, a more desirable effective approach will be to avoid the occurrence of electrochemical reactions under marine environments.

On the other hand, polymer metallocomplexes of the general formula $[M(\text{bipy})_2\text{P}]$, $M = \text{Os}^{\text{II}}$, Ru^{II} have motivated substantial interest in part due to their potentials as conducting polymers and their use as multielectron redox materials.^[24-28] Polypyridyl and polyphenanthrolyl complexes of ruthenium that contain aromatic groups undergo electrochemically induced oxidative reactions.^[29] The resulting systems are stable electrochemically on carbon electrodes. Stabilization involves several contributing resonance structures.^[30] The processes are reversible under appropriate conditions, e.g., exposure to ultraviolet irradiation. 2,2-Bipyridine and 2,2':6',2''-terpyridine are specially important ligands (Figure 2) for the fabrication of polymer metallocomplex due to their high binding affinity for transition metal ions.^[31] Their metal complexes exhibit effective ability to scavenge electrons.

However, no report exists on the use of polymer metallocomplexes to prevent galvanically-induced corrosion. By combining the outstanding properties of both polymers and ligand metal complexes, we proposed to prepare polymer metallocomplex composite materials to be used as galvanically induced corrosion inhibitors.

OBJECTIVES:

In order to meet the challenges of the 21st century, the United States Department of the Navy The Navy will increasingly rely on new high performance materials to improve process efficiencies, enhance product quality, lower energy consumption, and reduce equipment downtime. In materials strategy, the Department of the Navy is the first to consider the development of novel anti-corrosion inhibitors. In the light of the above-mentioned galvanically induced corrosion mechanism, we proposed to develop novel corrosion inhibitors based on polymer metallocomplex composite materials. These new materials can cut off the electron transfer path via the polymer metallocomplexes. Thus this can avoid the formation of electrochemical cells during galvanically induced corrosion.

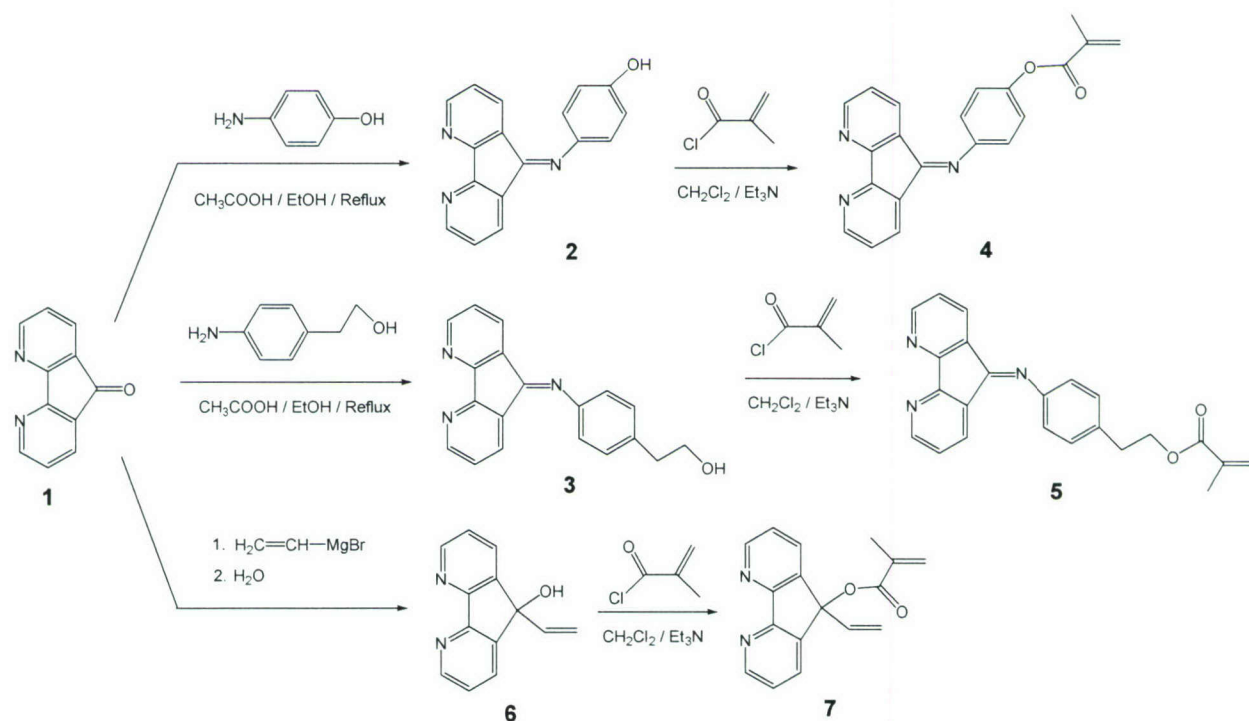
APPROACH:

Metal-containing polymers are attracting significant interest as these materials may combine the processability and mechanical properties of polymers with the unique optoelectronic properties of metal complexes. Therefore, a number of different synthetic approaches have been explored to prepare a variety of polymeric metal complexes. Specifically, these can be divided into four main types. First, conventional free radical polymerization, in which ligand or metal complex-functionalized monomers are copolymerized with other comonomers or homopolymerized. Second, condensation polymerization/coupling reaction by which bipyridine-backed polymers are generally produced. Third, end-group functionalization in which terpyridine or bipyridine mono- or di-functionalized oligomers first prepared by general chemical reactions, and then further interacted with metal ions to form supramolecular metallopolymers. Fourth, living or controlled polymerization in which bipyridine or terpyridine-functionalized initiators with or without metal ions are used for atom transfer radical polymerization (ATRP) or ring-opening polymerization (ROP). Living polymerizations allow for exquisite control over molecular weight and architecture in organic polymers. However, both ATRP and ROP are successful only for a limited number of monomers and suffer from a number of disadvantages

such as high reaction temperature and expensive reagents that are sometimes difficult to remove. Therefore, we employed RAFT polymerization technique to prepare polymeric metallocomplexes with well-defined structures. RAFT polymerization technique is not versatile and can lead to colored polymers with long time consumption. So, conventional free radical polymerization still possesses great potential from an industrial stand-point. Here, we also employed conventional free radical polymerization technique to prepare metal-containing polymers via ligand-functionalized monomers and initiators two ways.

ACCOMPLISHMENTS:

Metal-Containing Random Copolymers

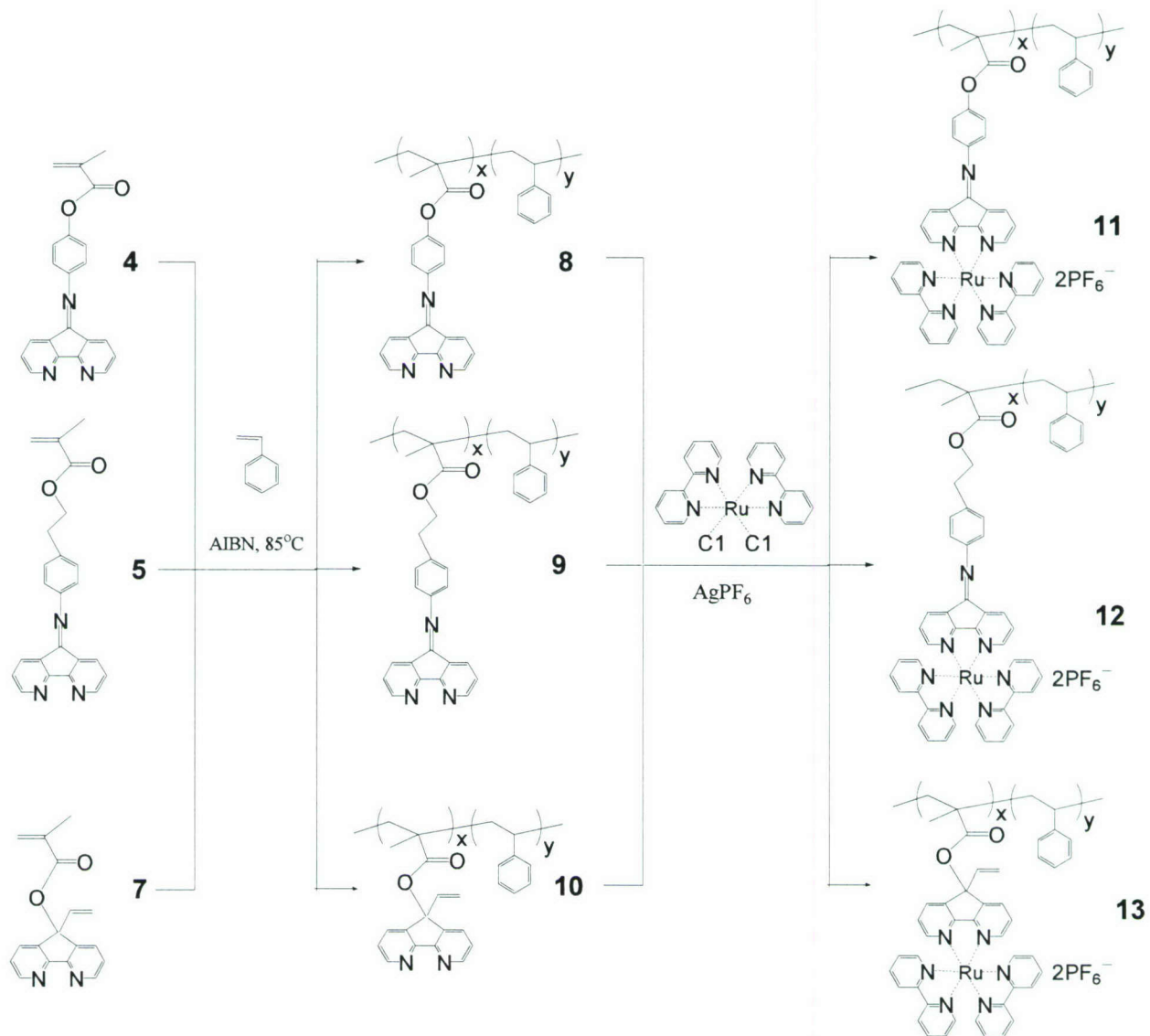


Scheme 1. Synthetic Route of Ligand-functionalized Monomers

It has been shown that the concept of copolymerization of different functional monomers is a simple way of incorporating two different materials functions into a polymer chain. So, conventional random copolymerization was used to prepare polymeric metal complexes due to its advantages of simplicity and ease of use. For this purpose, three bipyridine-based polymerizable ligand monomers were first synthesized starting from 4,5-diazafluorene-9-one (1). The commercially available ligand compound 1 in the presence of catalytic acetic acid condensed with 4-aminophenol and 4-aminophenylethyl alcohol to produce two intermediate 2 and 3, respectively (Scheme 1). The two intermediate 3 and 4 were further reacted with methacryloyl chloride respectively with catalytic triethylamine to give two polymerizable ligand monomers 4 and 5, respectively (Scheme 1).

In addition, 1 reacted with vinylmagnesium bromide which further hydrolyzed to produce 9-hydroxyl-9-vinyl-4,5-diazafluorene (6) (Scheme 1). The monomer 6 was further converted into

the monomer **7** by methacrylation with methacryloyl chloride with catalytic triethylamine (Scheme 1).



Scheme 2

Styrene was first randomly copolymerized with three bipyridine –functionalized methylacrylate monomers to produce three copolymers (**8-10**) with bipyridine functionality on side chains respectively (Scheme 2). The molar content of bipyridine units in copolymers are in good agreement with the original composition of the monomer mixture: thus, the two monomers were built into the final random copolymers according to the original monomer feeds.

To graft the ruthenium complex, the $\text{Ru}(\text{bpy})_2(\text{MeOH})_2^{2+} \cdot 2\text{PF}_6^-$ intermediate was first obtained by refluxing $\text{Ru}(\text{bpy})_2\text{Cl}_2$ with AgPF_6 in methanol overnight, and then refluxed with the three copolymers with bipyridine units on side chains in dimethoxyethane (DME) for 72 h respectively (Scheme 2) to produce three copolymeric ruthenium complexes (**11-13**). The UV-vis spectra of the two metallopolymers **11** and **12** show characteristic MLCT (metal-to-ligand charge transfer) absorption band of tris(bipyridyl)Ru(II) unit at $\lambda = 457$ nm. Their fluorescence spectra both show an emission at ca.365 nm as they were excited at 270 and 330 nm respectively. Meanwhile, the

schiff-base results in a shift of emission at from 620 nm to 365 nm for standard tris(bipyridyl)Ru(II) units. However, the ruthenium macromolecular complex **13** showed absorption band at 450 nm and emission band at 325 nm of tris(bipyridyl)Ru(II) units in its respective UV-vis and fluorescence spectra.

Very interestingly, the monomer **6** is able to emit blue light. However it is quite difficult to be (co)polymerized. So it has to be converted to a methacrylate-type monomer **7**. The new methacrylate-type monomer **7** lost the intrinsic fluorescent property of the precursor monomer. Surprisingly, the copolymers of the polymerizable methacrylate-type monomer **7** with styrene, methyl methacrylate, and butyl methacrylate have strong blue-light-emitting properties.

Metallopolymers with Well-defined Structures

Although conventional radical copolymerization is quite simple, it has involved the construction of systems with broad molecular weight distributions and lack of control over polymer architecture. Moreover, the properties of the final metallopolymers depend mainly on several variable components: the metal complex, its ligand set, as well as molecular weight and architecture of the polymer itself. Thus, living polymerization is a powerful tool for synthesis of metal-containing polymers with well-defined binding sites and architecture.

Among living polymerization techniques, RAFT polymerization seems the most promising for ligand-functionalization of polymers due to its applicability to a wide variety of monomers and metal-free polymerization environment. The key to successful operation of RAFT polymerization lies on the use of a highly efficient chain transfer agent called the RAFT agent, which is typically a thiocarbonylthio compound. In general, the vast majority of RAFT-prepared (co)polymer chains bear CTA fragment groups at both ends (Figure 1).

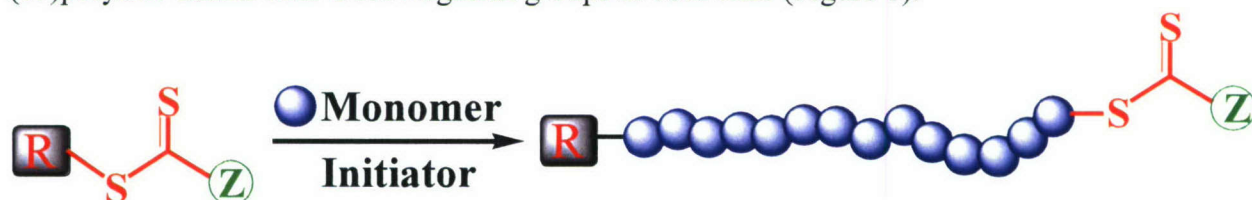
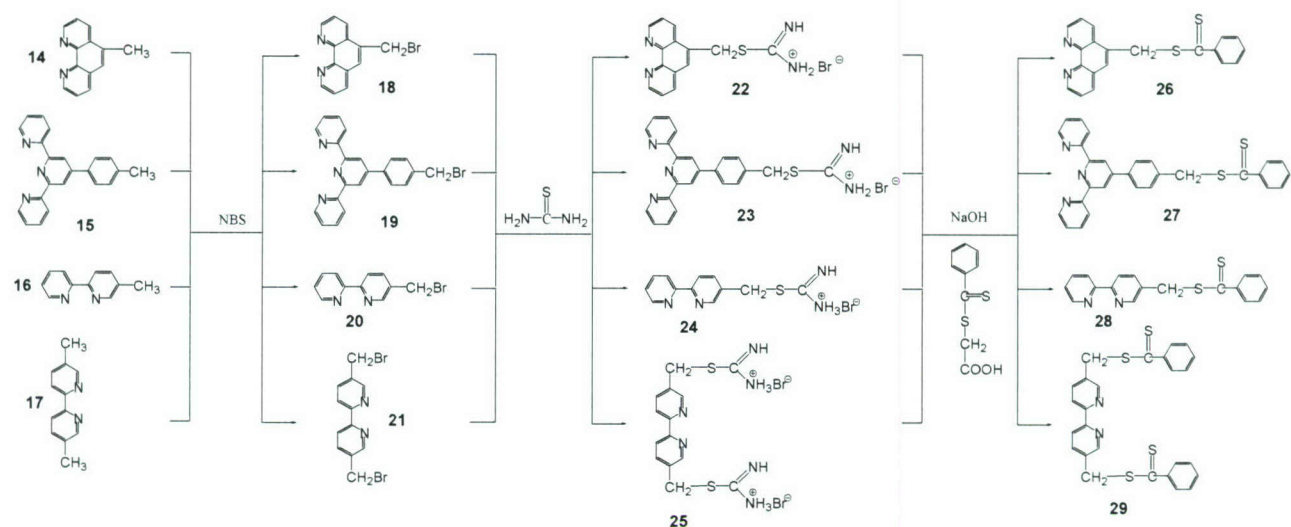


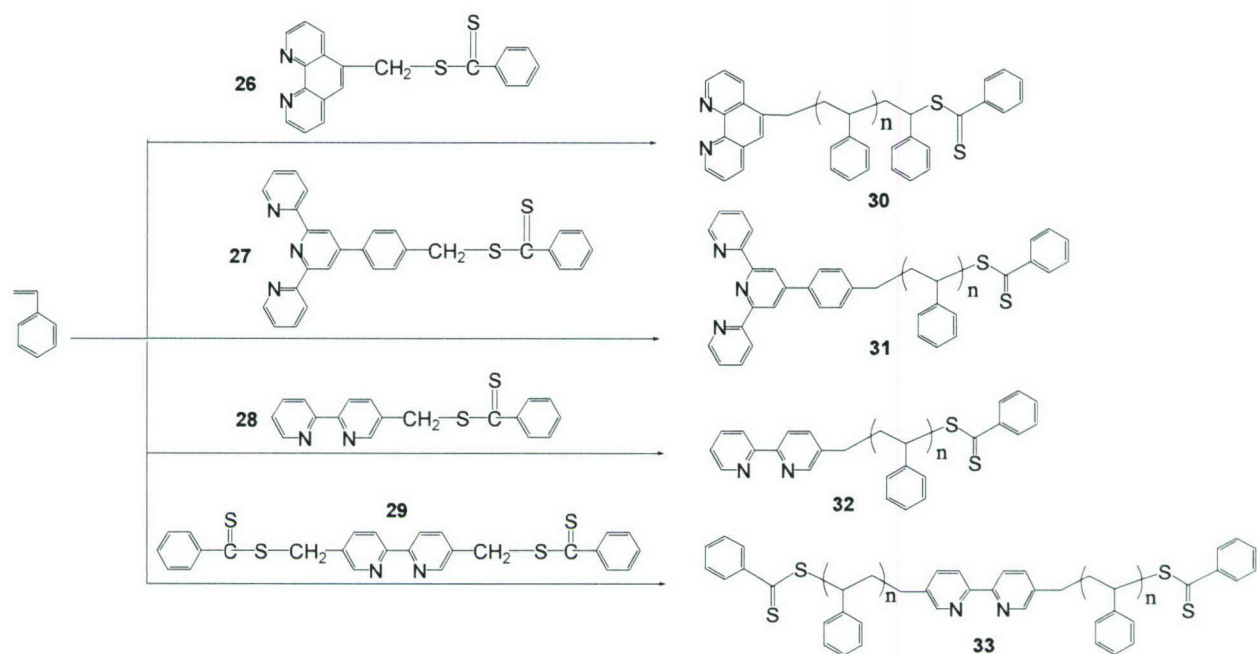
Figure 1

2, 2'-Bipyridine, 1,10-phenanthroline and 2,2',6',2''-terpyridine are of particular interest for introducing metal-binding sites into polymers. Therefore, we designed and synthesized four ligand-functionalized RAFT agents (Scheme 3). Bipyridine and terpyridine compounds (**14-17**) with active methyl groups were first bromomethylated to give compounds (**18-21**), then reacted with thiourea to give isothiurea hydrobromide salts (**22-25**). The salts further hydrolyzed into thiols in the presence of a base. The thiols reacted *in-situ* with the commercially available carboxymethyl dithiobenzoate catalyzed by a base to give bipyridine- and terpyridine-functionalized RAFT agents (**26-29**).

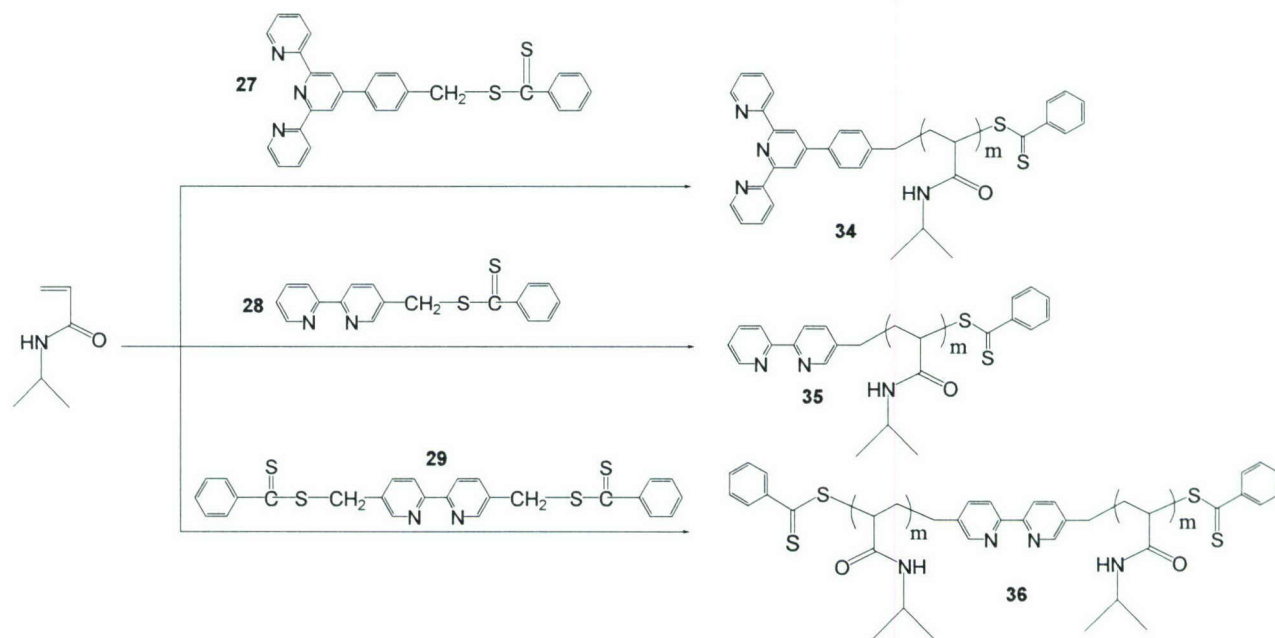


Scheme 3. Synthetic Route of Ligand-Functionalized RAFT Agents.

In order to examine the effectiveness of the novel dithioesters as RAFT agents, a series of RAFT polymerizations with two different monomers – styrene and N-isopropylacrylamide were carried out (Scheme 4 and 5) to produce bipyridine or terpyridine end (or center)-functionalized polystyrene polymers (**30-33**) and poly(N-isopropylacrylamide) polymers (**34-37**) with controlled molecular weights. To each dithioester, the first-order kinetic plot is linear no matter which monomer was used. Furthermore, the molecular weights determined by SEC and NMR increased linearly with conversion. The polydispersities of these RAFT-prepared polymers are generally low, ranging from 1.01 to 1.27. All these results indicate that the new bipyridine and terpyridine-functionalized dithioesters are quite efficient RAFT agents. The good agreement of the NMR-determined number-average molecular weight with theoretical values indicates almost all polymer chains were functionalized either at the chain center by bipyridine group or at one chain end by bipyridine or terpyridine groups derived from the RAFT agents used for polymerization.



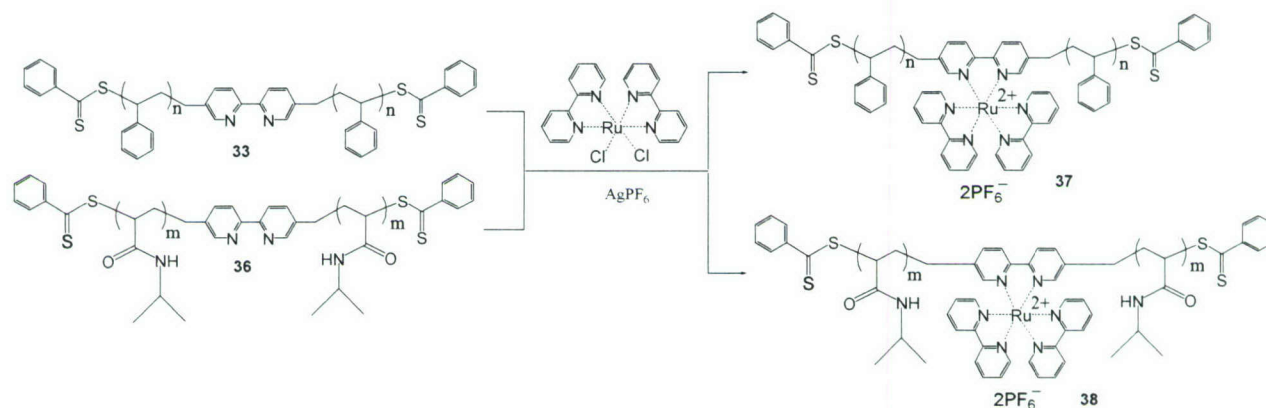
Scheme 4. RAFT Polymerization of Styrene with Different Ligand-Functionalized RAFT Agents



Scheme 5. RAFT Polymerization of N-isopropylacrylamide with Different Ligand-Functionalized RAFT Agents

The bipyridine-centered polymers **33** and **36** were further reacted with bis(bipyridine)ruthenium ion to produce metallopolymers **37** and **38** (Scheme 6). The purified complexes were characterized by UV-vis spectroscopy and fluorescence technique. Obviously, their UV-vis spectra exhibited a new absorption band at 453 nm attributed to characteristic MLCT (metal-to-ligand charge transfer) absorption band of tris(bipyridyl)Ru(II) unit as compared with the

corresponding precursor polymers **33** and **36**. Moreover the fluorescence spectra of these complexes are different from that of their corresponding precursors. The emission spectrum of the complexes show only the well-known $[\text{Ru}(\text{bpy})_3]^{2+}$ band with $\lambda_{\text{max}} = 625 \text{ nm}$ for polystyrene, 605 nm for poly(N-isopropylacrylamide). The metalopolymers were also characterized by DSC. The glass transition temperatures of all polymer complexes are higher than their corresponding precursor polymers due to the effect of the hexacoordinated tris(bipyridyl) Ru(II) complex incorporated into the center of the polymer chain.



Scheme 6. Schematic Representation for Preparation of Tris(2,2'-bipyridine)ruthenium(II)-Centered Metalopolymers

Terpyridine is a well-known tridentate chelating ligand, which forms octahedral complexes with a large variety of transition-metal ions such as Fe^{2+} , Zn^{2+} , and Ru^{2+} . Figure 2 represents a three-dimensional model showing the octahedral geometry of the complex.

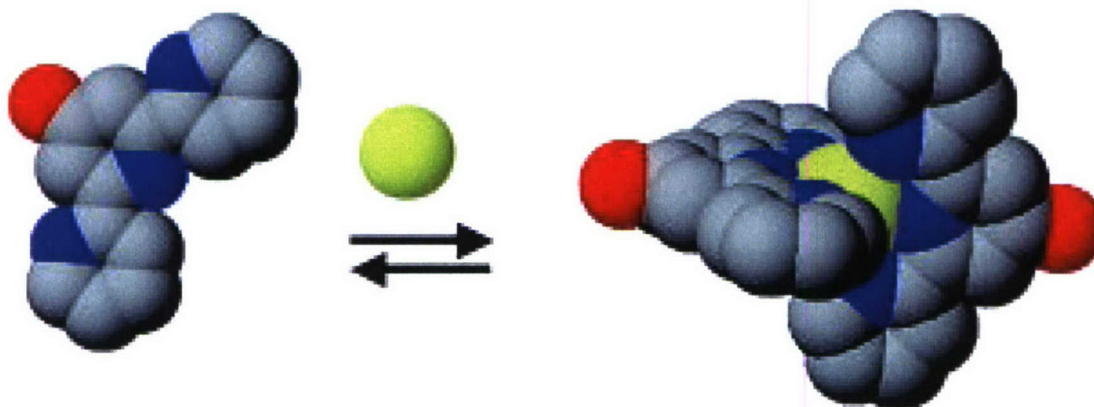
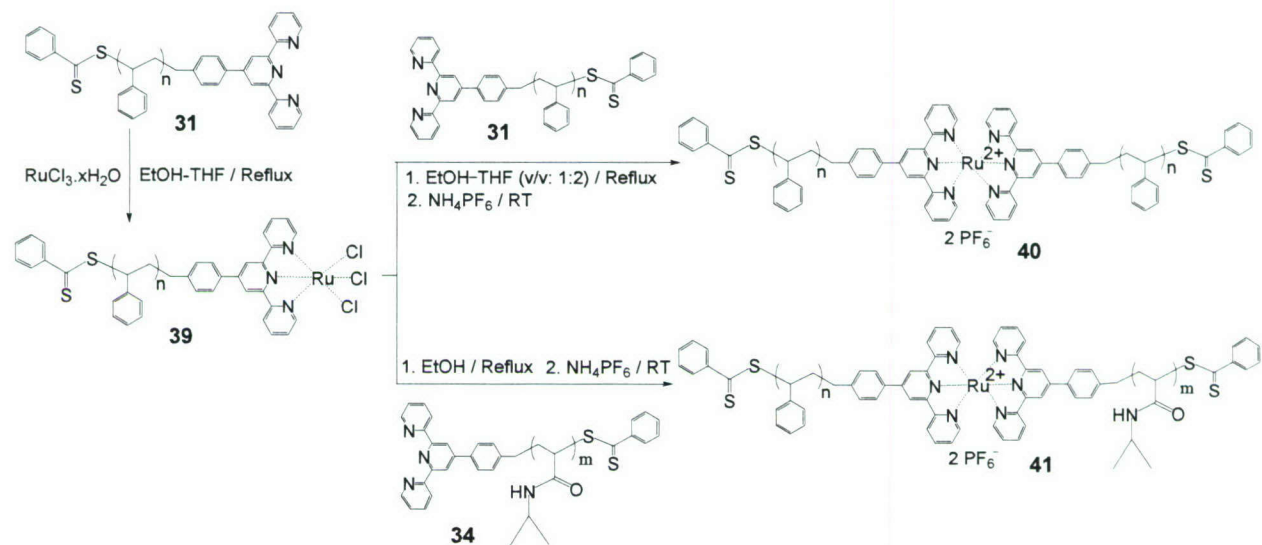


Figure 2

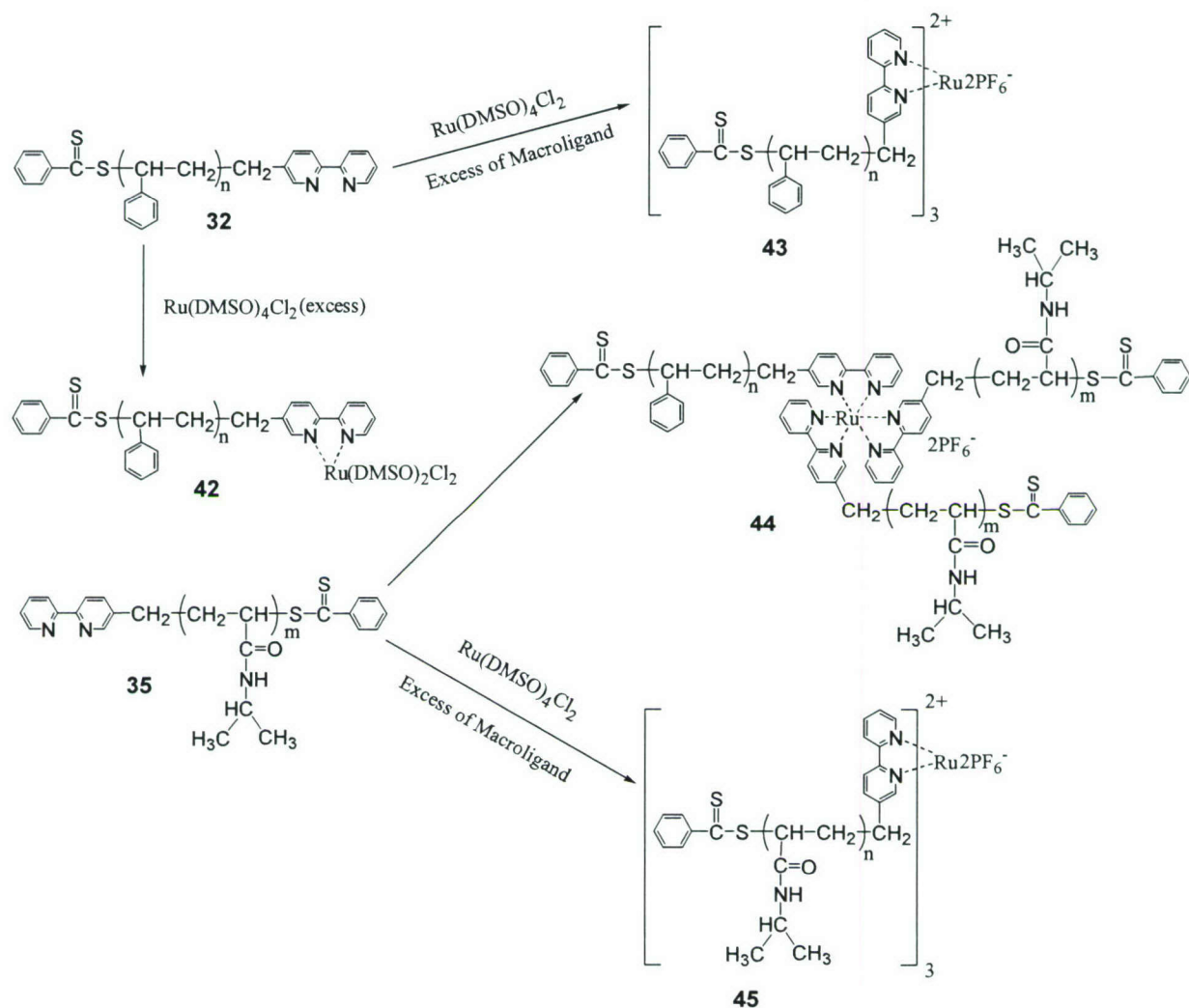
The terpyridine end-functionalized polystyrene polymer **31** was treated with an excess of $\text{Ru}(\text{III})\text{Cl}_3 \cdot x\text{H}_2\text{O}$ to give an intermediate monocomplex $\text{PS-Ru}^{\text{III}}\text{Cl}_3$ (**39**). The monocomplex was then further treated with a slight excess of terpyridine end-functionalized polystyrene and poly(N-isopropylacrylamide) polymers **34**, respectively, to form dimeric polystyrene ruthenium complex **40** and thermosensitive amphiphilic metalopolymer **41**. Similarly, the UV-vis spectra of

the purified metallopolymers clearly revealed the typical metal-ligand charge-transfer (MLCT) band of the bis(terpyridine) ruthenium(II) complex at $\lambda = 493$ nm. The glass transition temperatures of the metallopolymers are higher than that of their corresponding precursor polymers. These results indicate the formation of bis(terpyridine)ruthenium complex at the conjunction of two blocks.



Scheme 7

The RAFT-prepared bipyridine end-functionalized polymers **32** and **35** were used as macroligands for the preparation of ruthenium-cored star-shaped metallopolymers. As shown in Scheme 8, two types of ruthenium-cored star-shaped polymers were prepared. One is homogenous $\text{Ru}(\text{bpy})_3^{2+}$ -cored star-shaped metallopolymers, the other one is amphiphilic $\text{Ru}(\text{bpy})_3^{2+}$ -cored star-shaped metallopolymers. For the preparation of homogenous star-shaped polystyrene metallopolymers **43**, $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was reacted with more than 3 equivalents of the polystyrene macroligands **32**. Dehalogenating with AgPF_6 resulted in the formation of the targeted metallopolymers. The polystyrene precursors of low molecular weight are soluble in diethyl ether, thus uncomplexed polystyrene macroligand precursor can be removed from the two crude ruthenium-cored star-shaped polystyrene metallopolymers by washing with diethyl ether. The unreacted $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ were removed by washing with water. As a result, a pure polystyrene star-shaped metallopolymer was obtained. For the preparation of homogenous star-shaped poly(N-isopropylacrylamide) metallopolymers **45**, $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ was similarly reacted with more than 3 equivalents of the poly(N-isopropylacrylamide) macroligands **35** in methanol at 90 °C under argon for 3 days. Dehalogenating with AgPF_6 resulted in the formation of the targeted metallopolymers. To remove unreacted $\text{Ru}(\text{DMSO})_4\text{Cl}_2$, the crude poly(N-isopropylacrylamide) metallopolymers were dialyzed against deionized water. To further remove the uncomplexed poly(N-isopropylacrylamide) **35**, the following typical procedure was employed. The specific weight ratio (χ_w) in the THF-hexane mixture at room temperature, under which the complex can be precipitated out, was first determined. Meanwhile, χ_w was also determined for precipitating its corresponding precursor polymer an amount of the crude polymer complex was dissolved in THF weighed in advance to give a clear solution, hexane was added dropwise to the clear polymer complex solution (the amount of hexane added can be calculated using χ_w for the complex and the amount of THF used).



Scheme 8. Schematic Representation for Preparation of Tris(2,2'-bipyridine)ruthenium(II)-Cored Star-Shaped Polymers

The preparation of amphiphilic star-shaped metallopolymer **44**, the polystyrene macroligand **32** was reacted with excess $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ using a solvent mixture of DME/ CHCl_3 (10:1 v/v) at 120°C under argon for 2 days to give the polymeric complex **42**. The polystyrenic complex was further purified by washing with water and diethyl ether to remove excess $\text{Ru}(\text{DMSO})_4\text{Cl}_2$ and uncomplexed polystyrene macroligand precursor. The pure polystyrenic complex **42** was reacted with more than 2 equivalents of the PNIPAM macroligands **35** in DME/MeOH (10:1 v/v) at 120°C under argon for 4 days. Dehalogenating with AgPF_6 resulted in the formation of the targeted metallopolymer **44**. The crude metallopolymer was preliminarily purified by centrifugation in THF to remove the remaining inorganic salts, and further purified by centrifugation in water to remove the uncomplexed PNIPAM macroligands. As a result, pure metallopolymer was obtained.

The purified metallopolymer **43-45** were characterized by UV-vis and fluorescence techniques. The UV-vis spectra of metallopolymer are different from that of their corresponding starting polymer precursors. For example, the starting precursor **42** has an absorption band at 398 nm

originated from the mono-pyridine coordinated ruthenium ion $\text{Ru}(\text{bpy})(\text{DMSO})_2\text{Cl}_2$. However, the amphiphilic metallopolymer **44** formed by its reaction with PNIPAM macroligand **35** shows an absorption band at 435 nm, which is a characteristic peak of metal-to-ligand charge transfer (MLCT) of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex. This indicates that the mono-pyridine coordinated ruthenium ion $\text{Ru}(\text{bpy})(\text{DMSO})_2\text{Cl}_2$ complexed with the other two equivalent bipyridine groups of the polymer precursors to lead to the formation of tri-pyridine coordinated ruthenium $[\text{Ru}(\text{bpy})_3]^{2+}$. Therefore, such a star-shaped metallopolymer of one core of $[\text{Ru}(\text{bpy})_3]^{2+}$ connecting three polymer chains can be formed through metal-ligand interaction. The other two metallopolymers **43** and **45** also show $[\text{Ru}(\text{bpy})_3]^{2+}$ characteristic absorption bands at 442 and 432 nm, respectively. Compared with standard tris(bipyridine)ruthenium(II) ($[\text{Ru}(\text{bpy})_3]^{2+}[\text{PF}_6]_2^{2-}$) complex, the maximum absorption peaks assigned to metal-to-ligand charge transfer (MLCT) of these metallopolymers show little shift towards low wavelengths from 451 nm. This indicates that the three bipyridine end-functionalized polymer precursors combined with a metal ion have changed the environment of the metal complex and resulted in the shift in the MLCT maximum characteristics peaks. The formation of the ruthenium ion $[\text{Ru}(\text{bpy})_3]^{2+}$ located at the core of metallopolymers was evidenced by the emission spectra of the metallopolymers which show only the well-known $[\text{Ru}(\text{bpy})_3]^{2+}$ band with $\lambda_{\text{max}} \approx 600$ nm under the excitation of multi-wavelength lights such as 465 nm. However, the emission spectra of the macroligand precursors showed a band with $\lambda_{\text{max}} = 350$ nm for polystyrenes, and a band with $\lambda_{\text{max}} = 330$ nm for PNIPAM polymers, and no band at $\lambda_{\text{max}} = 600$ nm. Moreover, the emission maximum of the standard $[\text{Ru}(\text{bpy})_3]^{2+}[\text{PF}_6]_2^{2-}$ complex is at 605 nm. The difference between the emission maxima of these metallopolymers and the standard complex originated from the microenvironment change of the metal complex in these metallopolymers. They show the successful formation of star-shaped metallopolymers through metal coordination between the bipyridine end-functionalized polymers and ruthenium ions.

Self-assembly of Amphiphilic Metallopolymers

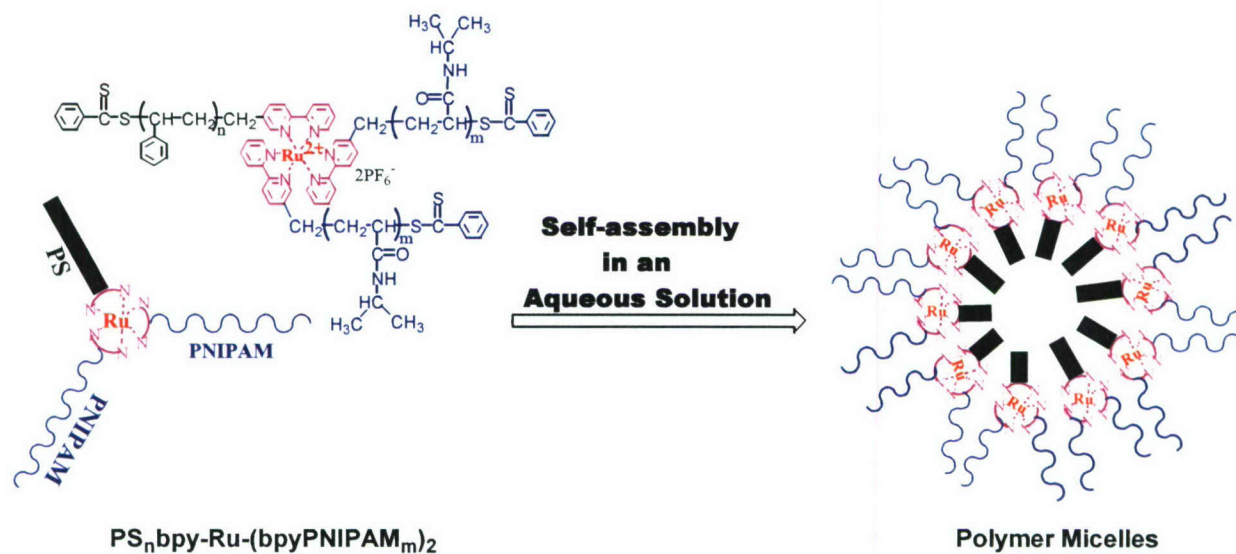


Figure 3. Schematic illustration of the formation of a micelle with metal ions interface from amphiphilic tris(2,2'-bipyridine)ruthenium-cored star-shaped metallopolymers of styrene with N-isopropylacrylamide.

Amphiphilic tris(2,2'-bipyridine)ruthenium-cored star polymers of polystyrene and poly(N-isopropylacrylamide) **44** are found to self-assemble into core-shell micelles in which the ruthenium ions are located on the interface between core and shell (Figure 3). The effects of polymer concentration and hydrophilic poly(N-isopropylacrylamide) block length on the size and shape of the micelle aggregates were directly observed by dynamic light scattering (DLS) and tunneling electron microscope (TEM). The amphiphilic star-shaped metallopolymer with longer PNIPAM blocks can form micro-sized aggregates at high concentration (Figure 4a). However, the amphiphilic metallopolymer with a shorter PNIPAM block can only self-assemble into normal-sized aggregates (Figure 4b). The polymer concentration within the studied range has no distinct effect on the self-assembly of the latter.

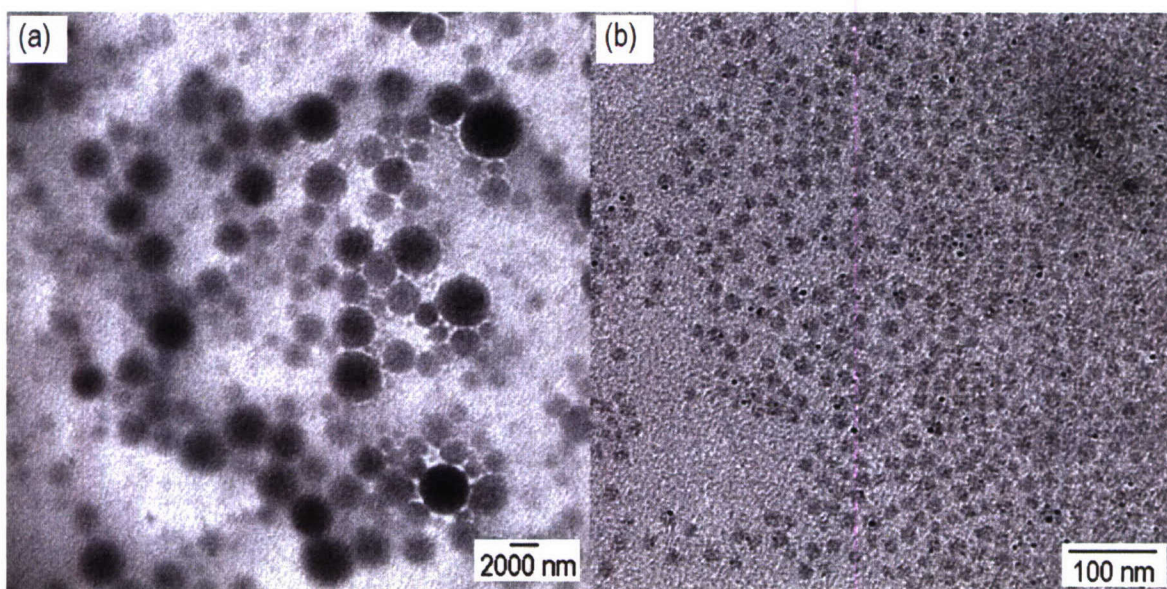


Figure 4. TEM images of the amphiphilic metallopolymers **44** with longer PNIPAM segments (a) and shorter PNIPAM segments (b).

Similarly, the diblock amphiphilic metallopolymer **41** has a strong tendency to form micelles due to its structural amphiphilic property. Atomic force microscope (AFM) was used on solid substrates to observe the surface morphology. Figure 5 shows the AFM image of the diblock metallopolymer **41**. Spherical particles from micelle aggregation were observed, some formed self-assembled arrays. This further demonstrates the formation of amphiphilic diblock metallopolymer via the connectivity of $\text{Ru}(\text{tpy})_2(\text{II})^{2+}$ complex.

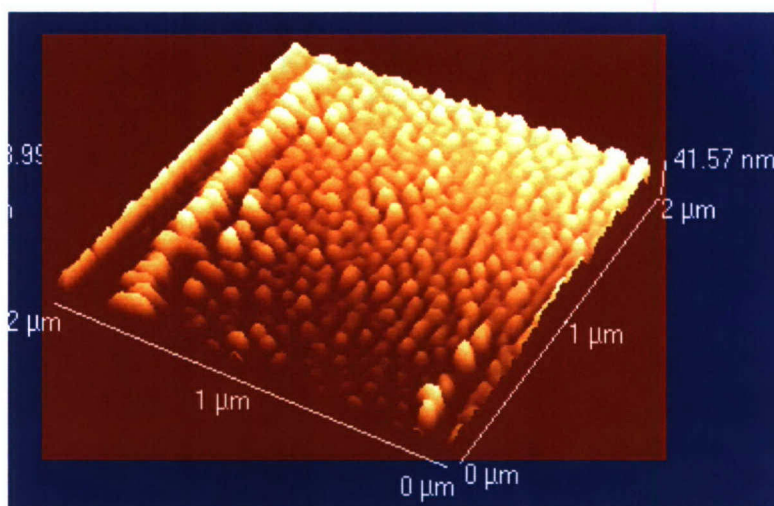


Figure 5. AFM image of the bis(terpyridine)ruthenium complex-connected polystyrene(PS) and poly(N-isopropylacrylamide) (PNIPAM) diblock metallopolymer **41**.

Ligand-Functionalized Initiators

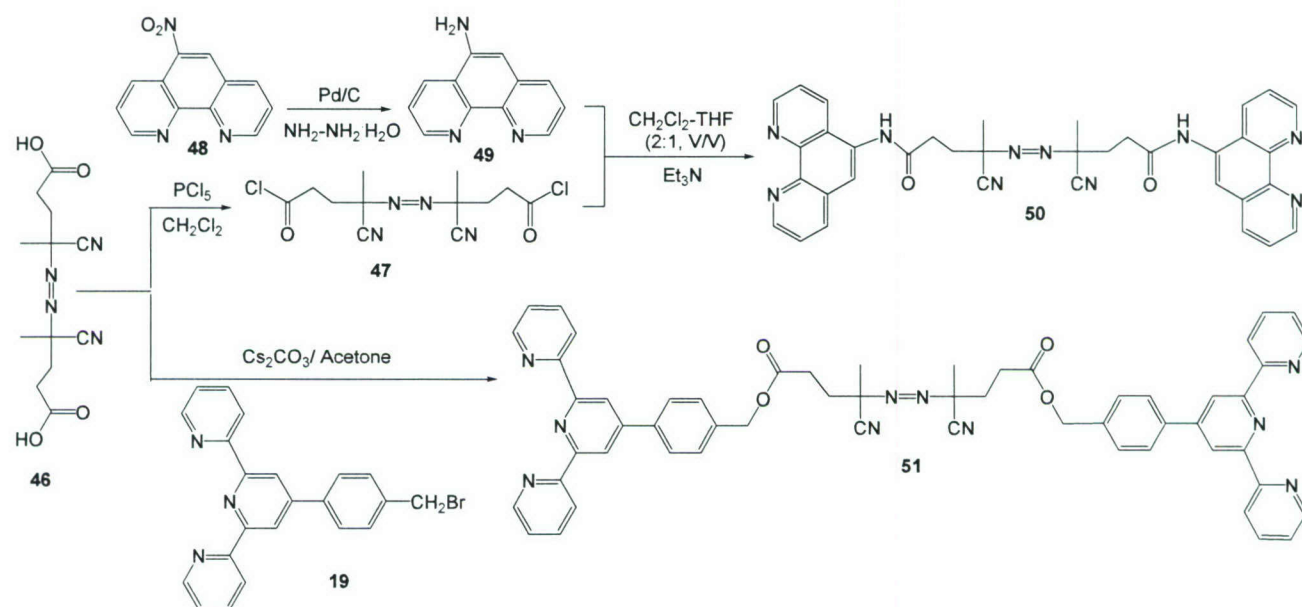
It is well known that an initiator plays an important role in radical polymerization since it determines the polymerization rate, the molecular weight, and other characteristics of polymers. Many ethylenically unsaturated monomers are polymerized by the use of free radical initiators, i.e. those having aliphatic azo or peroxide groups. However, the azo initiator is most commonly used because of its favorable kinetics of decomposition. Particularly, the functionality of the polymer chain ends derived from the initiator used can affect or alter the properties of the polymers.

Therefore, there is still a need for a compound which is capable of initiating ethylenically unsaturated monomers to prepare some polymers having ligand terminal groups. These ligand end-functionalized polymers can further complex with metal ions to form supramolecular materials. To prepare ligand-endfunctionalized polymers, we here synthesized two ligand-functionalized initiators (Scheme 9).

4,4'-Azobis(4-cyanopentanoic acid chloride) **47** was prepared by treatment of commercially available 4,4'-azobis(4-cyanopentanoic acid) **46** with PCl_5 , further reacted with 1, 10-phenanthroline-5-amine **49**, which was obtained by the reduction of 5-nitro-1,10-phenanthroline **48**, with triethylamine as catalyst using CH_2Cl_2 -THF (2:1, v/v) as a reaction solvents to produce the bipyridine-functionalized initiator **50**.

Commercially available initiator **46** reacted with 4'-(4-bromomethylphenyl)-2,2':6',2''-terpyridine **19** with catalytic cesium carbonate to produce the terpyridine-functionalized initiator **51**. A little amount of water can accelerate the reaction and result in higher yield. The crude initiator was further purified by column chromatography (Al_2O_3) using ethyl acetate-hexane (3:2, v/v) as eluent. The singlet peak at 5.20 ppm in its $^1\text{H-NMR}$ spectrum which is typically a characteristic peak of the methylene of the benzyl ester group ($\text{Ph-CH}_2\text{OC(O)-}$), proved the formation of the new initiator. The two new initiators **50** and **51** possess strong fluorescent property.

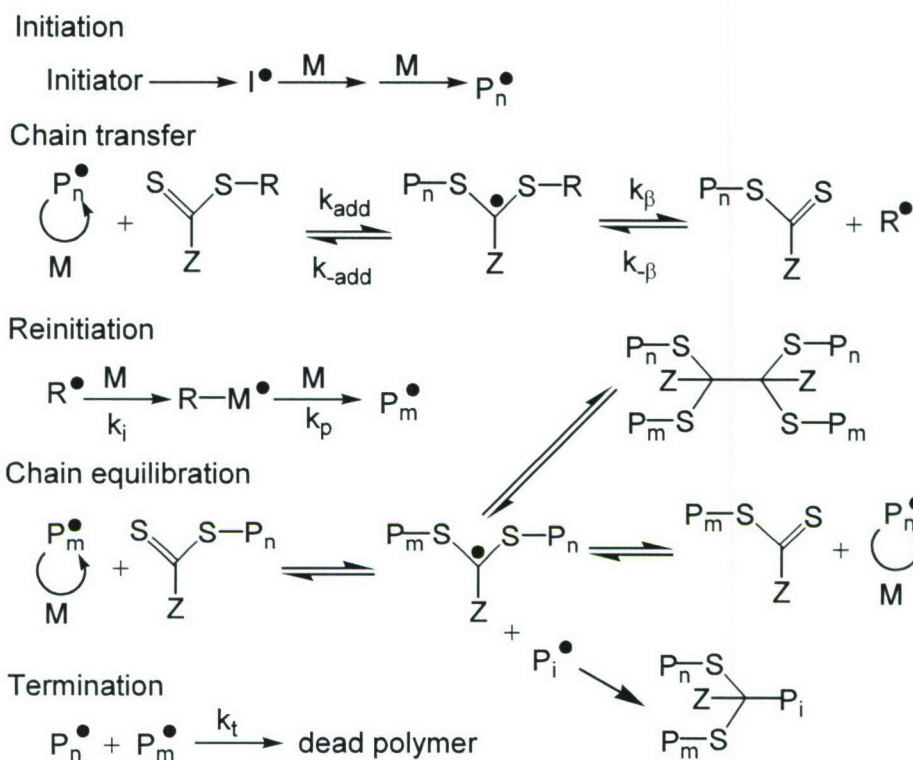
The two ligand-functionalized initiators will be used to prepare ligand-endfunctionalized polymers which further complex with some transition metal ions to produce new metallopolymers.



Scheme 9. Synthetic Route for Ligand-Functionalized Initiators

Confirmation of RAFT Polymerization

Reversible addition fragmentation chain-transfer process (RAFT) was first reported by Rizzardo in 1998. Since then, various research groups have attempted to elucidate the RAFT polymerization mechanism through different approaches including NMR, UV-vis, electron spin resonance (ESR) spectrometry and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) as well as, computation modeling. In order to elucidate RAFT polymerization mechanism shown in Scheme 10, several polystyrene polymers were prepared by RAFT polymerization of styrene using two different RAFT agent-initiator systems, and then further characterized by NMR and SEC as well as MALDI-TOF-MS techniques. The data indicated that most of the polymer chains are terminated by the active groups (Ph-C(=S)-S-) derived from RAFT agents, and few of the polymer chains bear initiator fragments at the other end. Most importantly, the structures arising from the intermediate RAFT radicals and their cross-termination adducts were detected. Also, the MALDI-TOF-MS analysis shows that the combination termination between two macromolecular radicals is minor, and the amount of dead chains is quite low. Thus, narrow molecular weight distribution is obtained. This analysis confirms the operation of the Rizzardo mechanism including the Monteiro intermediate radical termination (IRT) model for the RAFT polymerization.



Scheme 10. Mechanism of RAFT Polymerization.

Synthesis of Mesoporous Materials as Potential Anticorrosion Inhibitors

The objective of this project is to synthesize nanocrystals of highly acidic zeolite Y nanoclusters, encapsulate them within the channels of mesoporous (nanoporous) silicates or nanoporous organosilicates, and evaluate the “zeolite Y/Nanoporous host” as delivery vehicles for corrosion inhibitors. The project consists of three major tasks as follows: 1) synthesis of the nanoparticles of zeolite Y (of various chemical compositions) using various techniques such as the addition of organic additives to conventional zeolite Y synthesis mixtures to suppress zeolite Y crystal growth; 2) synthesis of nanoporous silicate host materials of up to 30 nm pore diameter, using poly (alkylene oxide) copolymers, which when removed will yield a mesoporous material; and 3) investigation of the zeolite Y/Nanoporous composite materials as hosts for corrosion inhibitors.

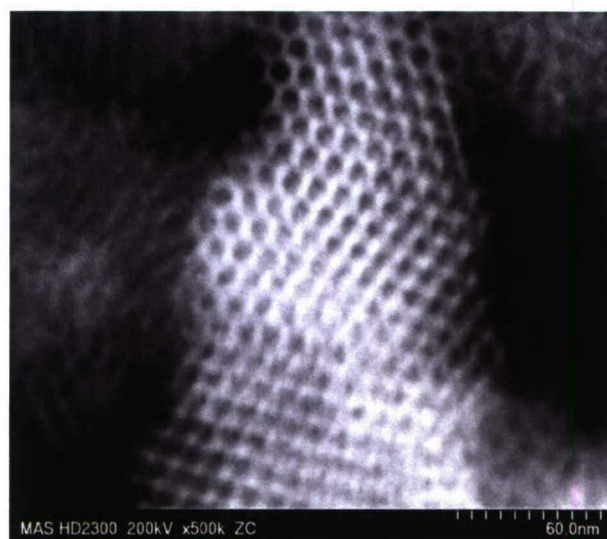


Figure 1. High Resolution Transmission Electron Micrograph of Al-SBA-15 synthesized with 3.0 g of zeolite precursor added to SBA-15 mixture. The precursor was aged for 3 days at room temperature, then 24 hr at 100°C.

Thus Al-SBA-15 mesoporous materials containing strong Brönsted acid sites and Al stabilized in a totally tetrahedral coordination were synthesized from the addition of hydrothermally aged zeolite Y precursor to SBA-15 synthesis mixture under a mildly acidic condition of pH 5.5 (Figure1). The materials possessed surface areas between 690 and 850 m²/g, pore sizes ranging from 5.6 to 7.5 nm and pore volumes up to 1.03 cm³, which were comparable to the parent SBA-15 synthesized under similar conditions. Two wt % Al was present in the catalyst that was obtained from the reaction mixture that contained the highest Al content. The Al remained stable in totally tetrahedral coordination after calcination at 550°C. The Al-SBA-15 mesoporous catalyst showed significant catalytic activity for cumene dealkylation. The catalytic activity was found to increase as the amount of zeolite precursor added to the SBA-15 mixture was increased. The activity of the catalyst was not affected by the aging time of the precursor for up to the 24-hour aging period. This method of introducing Al and maintaining it in a total tetrahedral coordination is very effective when compared to other direct and post synthesis aluminations methods reported.

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PUBLICATIONS:

Journal

1. Zhou, G.; He, J.; Harruna, I. I. “*Self-assembly of Tris(2,2'-bipyridine)ruthenium-Cored Amphiphilic Star-Shaped Polymers*”, *Journal of Polymer Science: Part A: Polymer Chemistry*, 45(18), 4204-4210, 2007.
2. Zhou, G.; He, J.; Harruna, I. I. “*Synthesis and Characterization of Tris(2,2'-bipyridine)ruthenium-Cored Star-Shaped Polymers via RAFT Polymerization*”, *Journal of Polymer Science: Part A: Polymer Chemistry*, 45(18), 4225-4239, 2007.
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5. Ghirmazion, Y.; Mehreteab, T.; Ingram, C. W., “*Mesoporous Aluminosilicate Catalysts from FAU Precursor under Mild Acidic Conditions and with Al in Totally Tetrahedral Coordination*,” *Journal of Porous Materials*, 14, 7-17, 2007.
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7. Ingram, C. W. “*Adsorption of Heavy Metals and Organic Contaminants on Functionalized Periodic Mesoporous Organosilicates*, Proceedings of the Spring 2006 Meeting of the Materials Research Society, 2006.
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9. Zhou, G.; Harruna, I. I. “*Synthesis and Characterization of Polymers with Side-chains of Schiff-Base-Functionalized Ruthenium Bipyridine Complexes*”, *Polymer Preprints (American Chemical Society, Division of Polymer Chemistry)*, 47(1), 307-308, 2006.
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11. Zhou, G.; Harruna, I. I. “*Synthesis and Characterization of Bis(2,2':6',2''-terpyridine)ruthenium(II)-Connected Diblock Polymers via RAFT Polymerization*”, *Macromolecules*, 38(10), 4114-4123, 2005.
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13. Zhou, G.; Harruna, I. I. "Synthesis and Characterization of Tris(2,2'-bipyridine)ruthenium(II)-Centered Polystyrenes via Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization", *Macromolecules*, 37(19), 7132-7139, 2004.
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19. Zhou, G.; Harruna, I. I.; Aicher, W. K., Geckeler, K. E., "Viability of Human Mesenchymal Stem Cells in the Presence of Nanostructured Polymeric Fullerenes," in preparation.
20. Zhou, G., He, J., Harruna, I. I., "Synthesis and Characterization of Fullerene and Ruthenium Dual End-Functionalized Thermosensitive," in preparation.

Book Chapters:

Harruna, I. I.; Petzold, O. N. "Polyamides containing metals", in *Macromolecules Containing Metal and Metal-Like Elements* (2005), 5(Metal-Coordination Polymers), 297-341.

PATENT APPLICATIONS:

Zhou, G.; Harruna, I. I. "Ligand-Functionalized/Azo Compounds and Methods of Use Thereof", US Patent, Filed, June 2006.

PRESENTATIONS:

1. "Phenols Sorption on Functionalized Periodic Mesoporous Organosilicates," presented at the 15th International Zeolite Conference (15th IZC), Beijing, China, August 12-17, 2007.
2. "Sulfonated ACF on fiberglass for Pb²⁺ removal from water," 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007.
3. "Anti-Microbial Activity of Silver-Impregnated Alumina in a Hard Water Environment," 233rd ACS National Meeting, Chicago, IL, March 25-29, 2007.

4. "Development of functionalized nanoporous inorganic-organic sorbents for removal of phenols and heavy metals from water, 233rd ACS National Meeting," Chicago, IL, March 25-29, 2007.
5. "A Novel Approach to Blue Light Emitting Polymers," 232nd ACS National Meeting, San Francisco, CA, United States, Sept. 10-14, 2006.
6. "Fullerene and Ligand End-Functional Polymers," 1st European Chemistry Progress, Budapest, Hungary, 27-31 August 2006.*
7. "Synthesis and Characterization of Polymers with Side-Chains of Schiff-base-Functionalized Ruthenium Bipyridine Complexes," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
8. "A Novel Phenanthroline-Functionalized RAFT agent," 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006.
9. "A Comparative Look at the Synthesis and Characteristics of Sodium Titanosilicates by Different Hydrothermal and Synthetic Parameters using XRD," SERMACS 2006, Augusta, GA Nov 1-4, 2006.
10. "Development of Nanoporous Inorganic-Organic Materials as Adsorbents for Water Purification," SAFEWATER2006, October 21-23, 2006 Rio de Janeiro, Brazil.
11. "Development of potential gas oil cracking catalysts by incorporating tetrahedral aluminum in SBA-15," American Chemical Society 232nd National Meeting September 10 - 14, 2006, San Francisco, CA USA.
12. "Synthesis and Applications of Zeolites and Related Porous Materials as Absorbents and Catalysts," Presented at the University of the West Indies, Mona Campus, Jamaica, July 6, 2006.*
13. "On the Incorporation of Tetrahedral Aluminum in SBA-15 from Zeolitic Seeds," XXIX Annual British Zeolite Association Meeting, Ambleside, UK, 30 Jul - 4 Aug 2006.
14. "Absorption of Heavy Metals and Organics Contaminants on Functionalized Periodic Mesoporous Organosilicates," Spring 2006 Material Research Society Meeting, San Francisco, April, 2006
15. "Synthesis and Characterization of Well-Defined Metallopolymers via RAFT polymerization," The 4th Singapore International Chemical Conference (SICC-4), Singapore, December 8-10, 2005.*
16. "Technologies for Safe Water Distributions in Local Rural Communities," International Conference on Safe Water, San Diego, CA, October, 2005.*

17. *Preparation of Nanosized micro/mesoporous composites via sequential synthesis of zeolite Y/SBA-15 phases*; Yohannes Ghirmazion and Conrad W. Ingram, to be presented at the ACS National Meeting, Washington DC, August, 2005
18. "Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host," University Coal Research/HBCU/MIs Contractors' Review Conference, June 7-8 2005, Pittsburgh, Pennsylvania.
19. "Functionalized Mesoporous Organosilicates and Their Adsorption Properties for Heavy Metals and Organics," Division of Environmental Chemistry for the 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005.
20. "Synthesis of Mesoporous Solids Containing Zeolitic Phase from Hydrothermal Treatment of Colloidal Zeolite Y Precursors," Pacificchem 2005, Hawaii, December 2005.
21. "Synthesis and Catalytic Properties of Hierarchical Mesoporous Aluminosilicate Assembled from Zeolite Y Precursors," Singapore International Chemical Conference 4, December 8-10, 2005, Singapore.
22. "Enhancing the Catalytic Properties of Ordered Nanoporous Silicate Using Hydrothermally Treated Zeolitic Precursors," Nanomaterials and Composites: Synthesis, Properties and Applications II 57th Southeast / 61st Southwest, Joint Regional Meeting of the American Chemical Society, November 1 - 4, 2005, Memphis, Tennessee.
23. "Nanoporous Aluminosilicate Clinoptilolite for Ammonia Removal in Shoreline Aquaculture System," 32nd Annual National Organization of Black Chemists and Chemical Engineers (NOBCCHE) conference, March 20-26, 2005, Orlando, FL.
24. "Mesoporous Composites from the Sequential Combination of Hydrothermally Treated Colloidal Zeolitic Silicate Precursors," Division of Colloid and Surface Chemistry for the 230th ACS National Meeting, in Washington, DC, Aug 28-Sept 1, 2005.
25. Inorganic and Organosilicate Composites for Selective Removal of Trace Contaminants, Center of Advanced Materials for Purification of Water with Systems 2nd Annual Symposium, April 14-15, 2004, University of Illinois Urbana-Champaign, IL.
26. "Characterization of High Performance Polyimides Containing the Bicyclo[2.2.2]Oct-7-ene Ring System," presented at the 17th International Symposium on Polymer Analysis and Characterization, Heidelberg, Germany, June 2004.*
27. "Characterization of Ruthenium (II)-Centered Polymers Prepared via Reversible Addition-Fragmentation Transfer (RAFT) Polymerization," 17th International Symposium on Polymer Analysis and Characterization (ISPAC-2004), Heidelberg, Germany, June 7-9, 2004.*
28. "Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host," University Coal Research/HBCU/MIs Contractors' Review Conference, June 7-8 2004, Pittsburgh, Pennsylvania.

29. "Phenylene-Bridged Mesoporous Organosilicate from Nonionic Surfactant Templated Synthesis," 4th International Mesostructured Material Symposium, Cape Tow, South Africa, 2004, Extended Abstract 82, Pages 224-225.
30. "Synthesis of Aromatic Bridged Ordered Mesoporous Organosilicate with Cetyltrimethylammonium Cation as Templating Agent," 4th International Mesostructured Material Symposium, Cape Town, South Africa, 2004.
31. "Nanoporous Aluminosilicate Clinoptilolite for Ammonia Removal in Shoreline Aquaculture System", NOAA EPP/MSI Education & Science Forum, October 21-23, 2004, City College of the City University of New York.
32. "On the Synthesis of Zeolite Y Nanocrystals in the Presence of Tetramethylammonium Bromide," presented at the 227 American Chemical Society meeting, Anaheim, CA March, 2004.
33. "Improved Catalysts for the Heavy Oil Upgrading Based on Zeolite Y Nanoparticles Encapsulated in Stable Nanoporous Host," University Coal Research Contractors Review Conference June 3-4 2003, Pittsburgh, Pennsylvania.
34. "Removal of Trace Organic Contaminants from Water Using Naturally Occurring Organically Modified Microporous Aluminosilicate" *Development of Adsorbents for Air and Water Treatment Conference*, 226th American Chemical Society (ACS) National Meeting, New York, NY, September 7-11, 2003.
35. "Surfactant Enhanced Extraction of Polychlorinated Biphenyl from Soils," 55th Southeast Regional Meeting (SERMACS), Atlanta, GA, Nov. 16-19, 2003.
36. "Non Ionic Surfactant Mediated Templated Synthesis of Phenylene-Bridged Organosilicate," 55th Southeast Regional Meeting (SERMACS), Atlanta, GA.
37. "A Comparison of Synthesis Strategies for Aryl Functionalized Ordered Nanoporous Organosilicates using Nonionic and Cationic Surfactants," 55th Southeast Regional Meeting (SERMACS), Atlanta, GA.
38. "Synthesis of a Novel Ligand-Functionalized Dithioester for RAFT Polymerization," presented at the National Meeting of the American Chemical Society, New York, NY, September 2003.
39. "Durability of Fiber Reinforced Polymer Composites Under Varying Environmental Exposure," presented at The Canadian-International Conference on Composites (CANCOM 2003), Ottawa, Canada, 19-22 August 2003.

*** invited presentations**

NUMBER OF STUDENTS SUPPORTED:

Postdoctoral Fellow 1 fellow
Graduate (Ph.D.) 3 students (2 graduated, 1 to graduate May 2008)
Graduate (M.S.) 5 students (graduated)
Undergraduate 4 students (graduated)

MAJOR INSTRUMENTS PURCHASED:

1 Cyclic Voltammeter