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Schiff Base Complexes in Macromolecules

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Schiff base metal complexes are a class of compounds that have been studied extensively because of their attractive chemical and physical properties, and their wide-ranging applications in numerous scientific areas. Researchers have incorporated Schiff base complexes into polymers, generating new materials with useful mechanical, thermal, chemical, and electronic properties. This work comprehensively reviews the developments in macromolecules containing Schiff base metal complexes, emphasizing new synthetic strategies and characterization techniques that were used to prepare and study these polymers.

KEY WORDS: Schiff base; imine; coordination chemistry; salen

1. INTRODUCTION

There is tremendous interest in the development of polymers with novel electronic, magnetic, and catalytic properties [1]. Recent advances in conjugated organic polymer chemistry have led to their application in diverse emerging technologies such as organic light emitting diodes [2], photoconductors [3], and static dissipaters [4]. Metal-containing polymer chemistry is a growing field in which the synthetic materials are anticipated to offer properties unique from their individual organic and inorganic components. These polymers may have useful semiconducting, magnetic, and luminescence properties [5], and may serve as processable precursors to novel ceramics [6]. Moreover, the coordinating ability of the metal within the polymer backbone permits these materials to act as sensors [7], and as building blocks for supramolecular structures [8].

The preparation of metal-containing polymers has been delayed by the limited synthetic routes to these materials [9]. One strategy that has emerged is the polymerization of functionalized metal-containing complexes, such as phthalocyanines and porphyrins [10]. Phthalocyanine metal complexes have been studied extensively because of their potential applications as organic semiconductors. By organizing the complexes to maximize intermolecular π orbital overlap that allows delocalization of electrons, researchers strive to generate materials with high conductivities. This goal has been realized with the synthesis of 1-D phthalocyanine stacks (e.g., “shish-kebab” polymers), phthalocyanine-containing ladder polymers, and 2-D phthalocyanine sheets (“parquet” polymers), new materials with high conductivities [11]. Porphyrin complexes, another important class of compounds with useful biological and catalytic applications [12], have been incorporated into conjugated organic polymers such as poly(*p*-phenylenevinylene) (PPV), and poly(*p*-phenyleneethynylene) (PPE) to generate new materials with promising conductive, electroluminescent, and nonlinear optical (NLO) properties [13].

This paper is dedicated to the pioneering research of Dr. Ian Manners.

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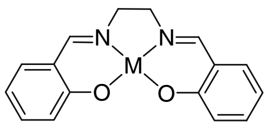

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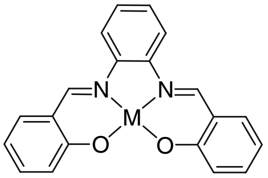

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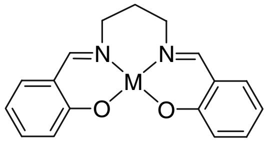

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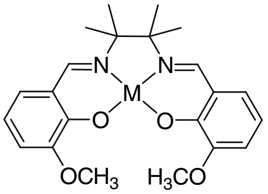

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Schiff base metal complexes are a broad class of compounds that have received much less attention than porphyrins or phthalocyanines for the incorporation into macromolecules. *N,N′*-Bis(salicylidene) ethylenediamine, **1** ("M(salen)"), is the archetype of this family of complexes, which are known to possess interesting magnetic [14], electroluminescent [15] , NLO [16], oxygen transport [17], and catalytic properties [18]. Related compounds, such as M(salphen) **2**, M(salpn) **3**, and M(3-MeOsaltMe) **4** demonstrate the breadth of chemical structures available within this class of compounds, maintaining the central N_2O_2 binding pocket that is formed by two imines and two phenoxides. For nearly 50 years, researchers have worked to integrate M(salen)-type complexes into polymers and oligomers in the hope of generating materials with favorable characteristics.

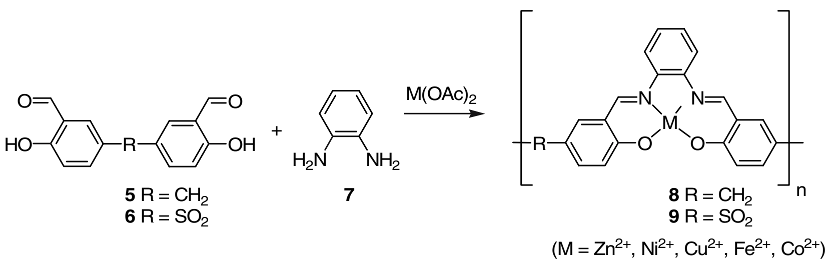
1.1. Scope of Review

This review covers the development of metal-containing polymers incorporating Schiff base complexes having the general structure related to **1**–**4**. In particular, polymers where the complex is either in the backbone of the polymer or attached directly to the main chain are emphasized. Early attempts to synthesize metal salen-containing polymers will be discussed first, although these materials are generally insoluble and poorly characterized. The discussion will then cover more recent research in chemically-prepared Schiff base polymers. For example, metal salen complexes have been copolymerized with various monomers to generate new materials with improved mechanical and thermal properties. Finally, salen-containing polymers that are prepared electrochemically, often as polymer-modified electrodes, and their applications as sensors, semiconductors, and electrochromic materials will be discussed. Some of these results have been covered in other reviews [19], but no comprehensive review on polymeric Schiff base complexes has previously appeared.

A note about nomenclature: To simplify the text, we often call macromolecules that include metal complexes of the sort exemplified by **1**–**4** "salen-type" or "salen-containing" polymers, recognizing that we do not specifically mean *N,N′*-bis(salicylidene)ethylenediamine, but more generally this family of complexes. It would be useful if there was a simple name for the central N_2O_2 ligand, as in "porphyrin", but unfortunately no such simple nomenclature exists.

2. EARLY RESEARCH

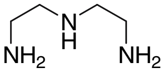
Marvel and Tarköy [20] reported the first example of polymeric Schiff base chelates containing Zn^{2+}, Ni^{2+}, Cu^{2+}, Fe^{2+}, and Co^{2+}. These polymers were prepared by condensation of bis(salicylaldehyde) **5** with *o*-phenylenediamine **7** to yield a polymeric organic Schiff base ligand that was subsequently metallated with metal acetate salts to yield insoluble polymers **8**, Scheme 1. These materials have high thermal stability (less than 2% weight loss at 300 °C), but, unfortunately, the insolubility of



Scheme 1. Synthesis of M(salphen)-containing polymers **8** and **9**.

these new materials made purification difficult and prevented proper characterization. Related polymers **9** were prepared from bis(salicylaldehyde) **6** and their thermal stabilities were compared.

Goodwin and Bailer [21], building on the work of Marvel, synthesized pentadentate and hexadentate Schiff base polymers from bis(salicylaldehyde) **5** and amines **10**–**12** employing similar polymerization procedures. Divalent (Cu^{2+}, Ni^{2+}, Co^{2+}) and trivalent (Co^{3+}, Al^{3+}, Cr^{3+}) ions were used to metallate the polymeric chelates. It was observed that the thermal stability of the insoluble polymers improves when the ionic charge of the metal is balanced by the charge on the chelating ligand.



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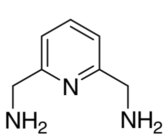

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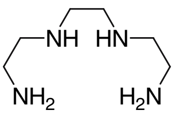

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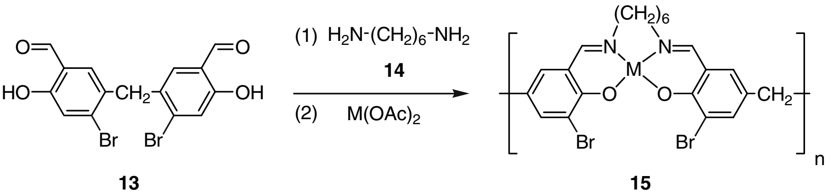
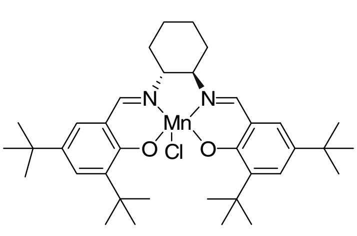
Sawodny and co-workers [22] prepared polymeric Schiff base complexes utilizing 1,4-diaminobutane. These organic Schiff base polymers were converted into their corresponding alkali salts by reaction with Li, Na, or K metal. Subsequent transmetallation with monovalent heavy metal ions (Tl^{+}, Cu^{+}, Hg_2^{2+}), divalent alkaline earth metals (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}), and a variety of transition metals yielded metal-containing polymers. Again, the poor solubility of these polymers limited characterization and hindered further research efforts.

Schiff base polymers **15** were prepared by Patel and co-workers [23] by condensation of bis(bromosalicylaldehyde) **13** with 1,6-diaminohexane **14**, and insoluble chelates of Cu, Ni, Co, Zn, and Mn were synthesized (Scheme 2). The authors determined the coordination geometry of the chelated metal ions via electronic reflectance spectroscopy and magnetic susceptibility measurements. It was reported that the Cu^{2+} metal center in the polychelates adopts a square-planar geometry, Co^{2+} ions are tetrahedral, while Mn^{2+} and Ni^{2+} have octahedral and distorted octahedral geometry, respectively. Thermal gravimetric analysis (TGA) indicated that decomposition occurs above ca. 250 °C. Not surprisingly, Schiff base polymers containing aliphatic amines are less thermally stable than their counterparts constructed from aromatic amines.



Scheme 2. Synthesis of Schiff base polymer **15** (M = Cu, Ni, Co, Zn, and Mn).



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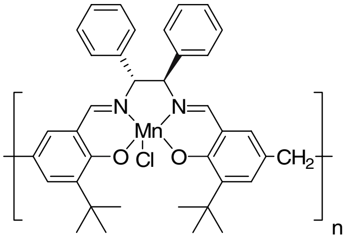

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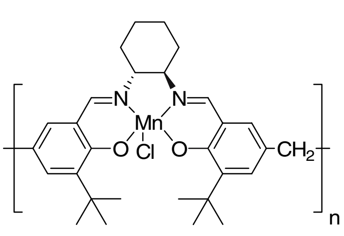

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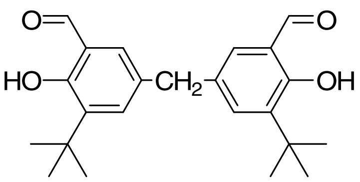

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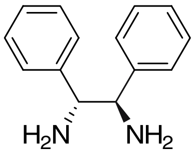

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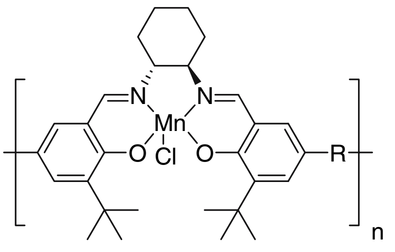
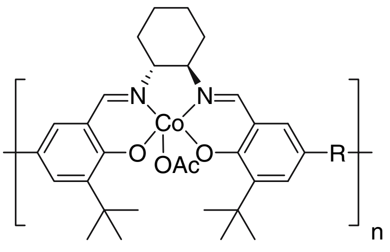
3. CHEMICALLY POLYMERIZED SCHIFF BASE POLYMERS

3.1. Salen-containing Homopolymers

Manganese salen complex **16** (Jacobsen's catalyst) is an effective catalyst for asymmetric epoxidation of alkenes [24]. Although the Mn^{3+} complex has good catalytic activity and enantioselectivity, there are often difficulties in the separation of catalyst and product, along with poor reusability of the catalyst. Kureshy and co-workers [25] prepared new heterogeneous polymeric catalysts in an attempt to overcome these disadvantages. Chiral Mn^{3+} Schiff base polymers **17** and **18** were prepared through condensation of bis(*tert*-butylsalicylaldehyde) **19** with 1S,2S-1,2-diaminocyclohexane or 1R,2R-1,2-diphenyl-1,2-diaminoethane **20**. The molecular weights of the polymers were determined by vapor pressure osmometry to be ca. 5000 Da (M_n). The polymers were tested as catalysts for enantioselective epoxidation of chromenes, indenes, and styrenes, and the polymers effectively catalyzed epoxidations of most of the compounds tested with near quantitative conversions and good enantiomeric selectivities (75–99% ee). After reaction, the polymers can be retrieved by precipitation, and they can be recycled up to five times without significant deterioration in catalytic activity. Other chiral Mn^{3+} Schiff base polymers **21**–**23** were prepared by Zheng and co-workers [26] using other derivatives of bis(salicylaldehyde) **19**. Catalytic activities and enantiomeric selectivities comparable to Jacobsen's catalyst were achieved.

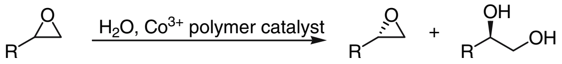


21 R = CH_2
22 R = CH_2O
23 R = $C(CH_3)_2$



24 R = CH_2
25 R = $C(CH_3)_2$

Zheng and co-workers [27] also investigated the use of cobalt(III) Schiff base polymers **24** and **25** as catalysts for hydrolytic kinetic resolution of terminal epoxides to yield the corresponding chiral epoxides and diols, Scheme 3. Excellent conversions (ca. 50%) and enantiomeric selectivities (>90% in most cases) were observed for the substrates tested. The authors observed dissolution of the polymeric catalyst into the aqueous phase during the course of reaction, and Et_2O could be used to precipitate the polymer when the reaction was complete. The recovered catalyst can be reused without significant loss of reactivity. No significant differences in catalytic performance were found between polymers bridged by methylene (polymer **24**) or dimethylmethylene (polymer **25**) groups.

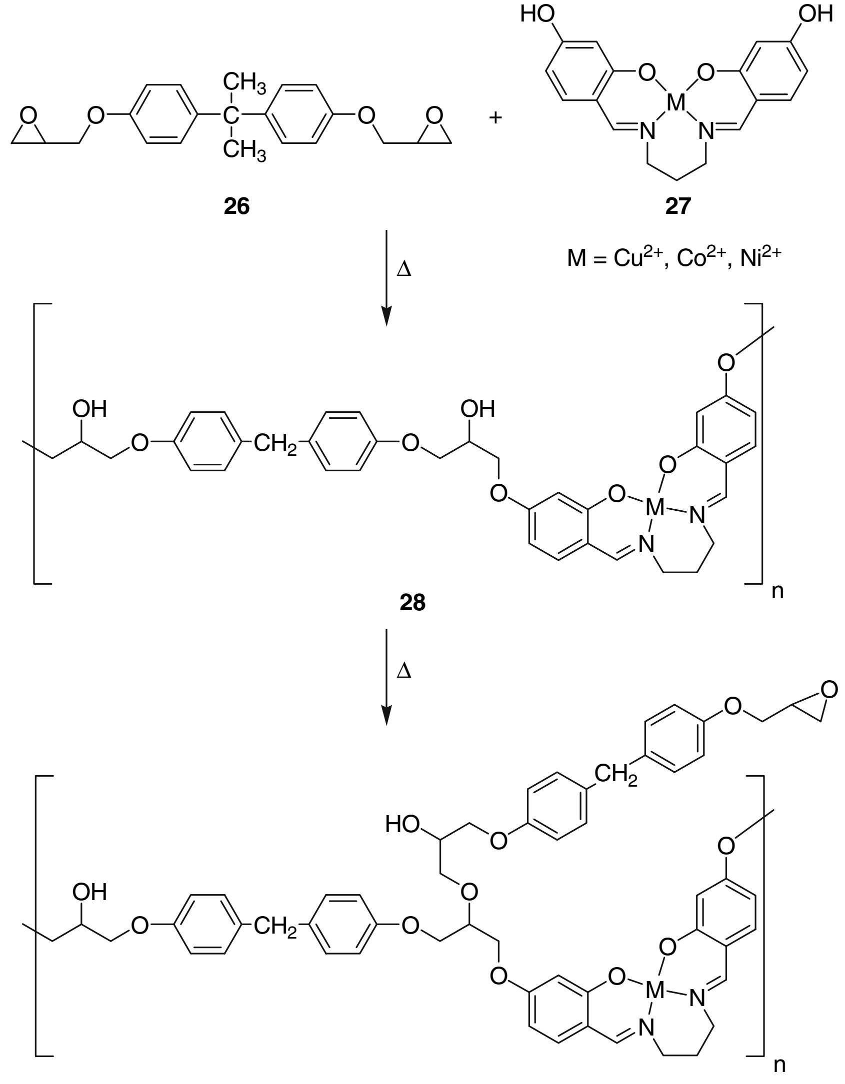


Scheme 3. Hydrolytic kinetic resolution of terminal epoxides catalyzed by **24** and **25**.

3.2. Salen-containing Copolymers

The copolymerization of salen complexes with other polymers may provide access to new materials with improved thermal, mechanical, and luminescent properties. In addition, it may enhance solubility of the otherwise intractable materials. Chantarasiri and co-workers [28] reported the synthesis of new salen-containing polymers from the diglycidyl ether of bisphenol A **26** and hydroxyl-functionalized Schiff base complexes **27**. The Schiff base monomers were synthesized by first condensing 2,4-dihydroxybenzaldehyde with 1,3-diaminopropane, followed by addition of the appropriate metal acetates and KOH in water. Attempts to isolate the organic Schiff base ligand were unsuccessful due to decomposition of the product. Polymers **28** were prepared by reacting **26** and **27** in the presence of Bu_4NOH, Scheme 4. Upon further reaction with **26**, crosslinked epoxy resins **29** were obtained. Curing of the polymers was monitored by IR spectroscopy with the disappearance of the band at 917 cm^{-1} corresponding to the opening of the epoxide groups of **26**. DSC studies indicated the use of Bu_4NOH lowers the curing temperature and shortens the reaction time. It was found that the copper-containing copolymer having a 12:1 molar ratio of **26**:**27** has the best thermal stability and highest tensile strength.

In a similar manner, polymers **31** were prepared using hexadentate Zn^{2+} and Ni^{2+} Schiff base complexes **30** and bisphenol A **26** [29]. The authors proposed the crosslinking mechanism involves breaking of the chelation between two of the amino groups on the tetraamine with the metal center, changing the denticity of the metal complexes from hexadentate to tetradentate, followed by condensation of the amino groups with epoxy groups of **26**. These polymers possess similar mechanical and thermal properties as polymer **29**; however, little work was done to confirm the structure of these polymers.



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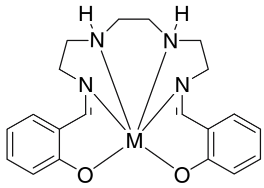
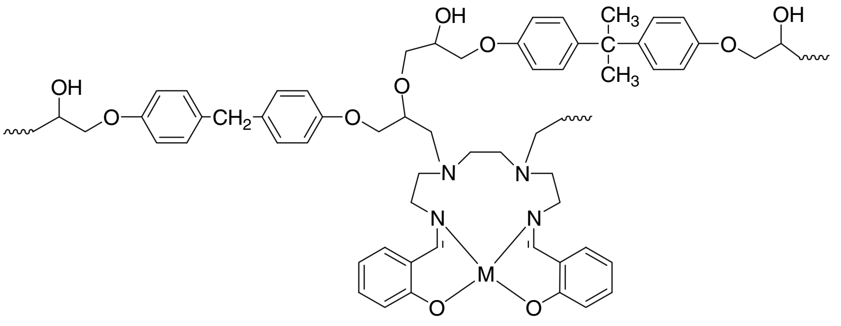
Scheme 4. Synthesis of copolymer **29** by thermal curing.



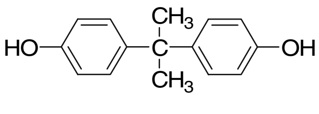
30 M = Zn^{2+}, Ni^{2+}



31 M = Zn^{2+}, Ni^{2+}

Chantarasiri extended this work by copolymerizing Schiff base monomers **27** and **30** with maleic anhydride **32** and bisphenol A **26** [30], and with urethane–ureas **33** [31]. The former polymers, in which ring-opened maleic anhydride forms ester linkages between the bisphenol A and the Schiff base complexes, have similar mechanical and thermal properties with polymers **29** and **31**. In contrast, the polyurethane-urea copolymers **34** are soluble, and the viscosity of the polymers could be measured. The authors investigated the possibility of using these polymers as flame-retardant materials, and it was found that increasing the metal content of the copolymers generally improves flame retardation.

Raghavan and co-workers [32] also reported the synthesis of new soluble salen-containing polyurethanes. The authors prepared new polymerizable monomer **38**, and subsequent copolymerization with diisocyanate **35** and poly(oxytetramethylene) glycol-2000 **36** afforded new metal-containing polyurethanes **39**, Scheme 5. Soluble in DMF and DMSO, the polymers have molecular weights between ca. 12,000–44,000 Da (M_n, GPC). TGA measurements of the metal-containing polyurethanes indicate the introduction of Schiff base complexes increases the overall thermal stability of the polymers. Mechanical properties such as tensile strength and elongation of the polymers were also reported, but no general trends were observed between the polymers of different metal content.



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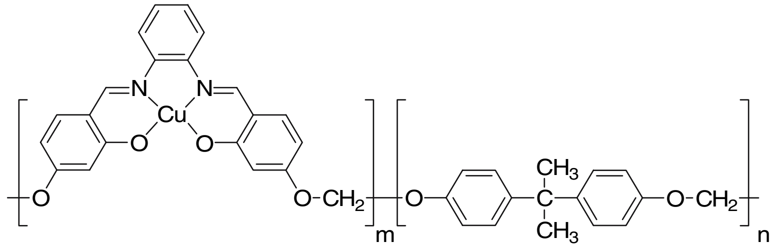
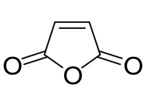


44 m:n = 1:10
45 m:n = 1:1

Copolymers of Cu salphen and polycarbonate or polyether were reported by Scamporrino and co-workers [33]. Interfacial condensation of **40** with 1,4-butanediol bischloroformate **41** in the presence of tetrabutylammonium bromide as a phase-transfer agent afforded alternating copolymer **42**, Scheme 6. These polymers were poorly soluble in organic solvents, and their polymeric structures were established by MALDI-TOF mass spectrometry. However, only short oligomers of the copolymers were observed in the mass spectra, and the molecular weight of the polymer remains undetermined. Random copolymers **44** and **45** were also synthesized by interfacial condensation of Cu salphen **40** and bisphenol A **43** with excess dibromomethane in the presence of tetrabutylammonium bromide. Polymer **42** did not exhibit any glass transition temperature (T_g) between −30 and 200 °C, above which temperature the polymer decomposed. Random copolymers **44** and **45** were stable to over 400 °C, with only **44** showing a T_g (at 88 °C) before decomposition. Although the authors incorporated Cu salphen to prepare new polymeric materials with NLO properties, no NLO measurements were reported.



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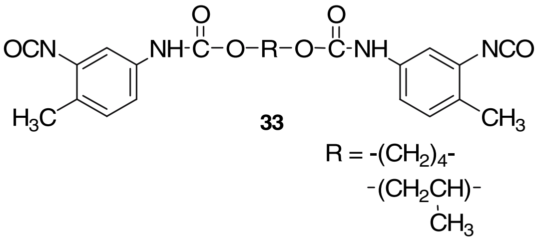

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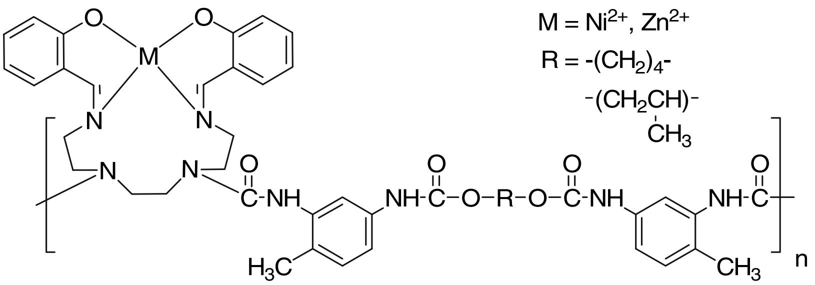

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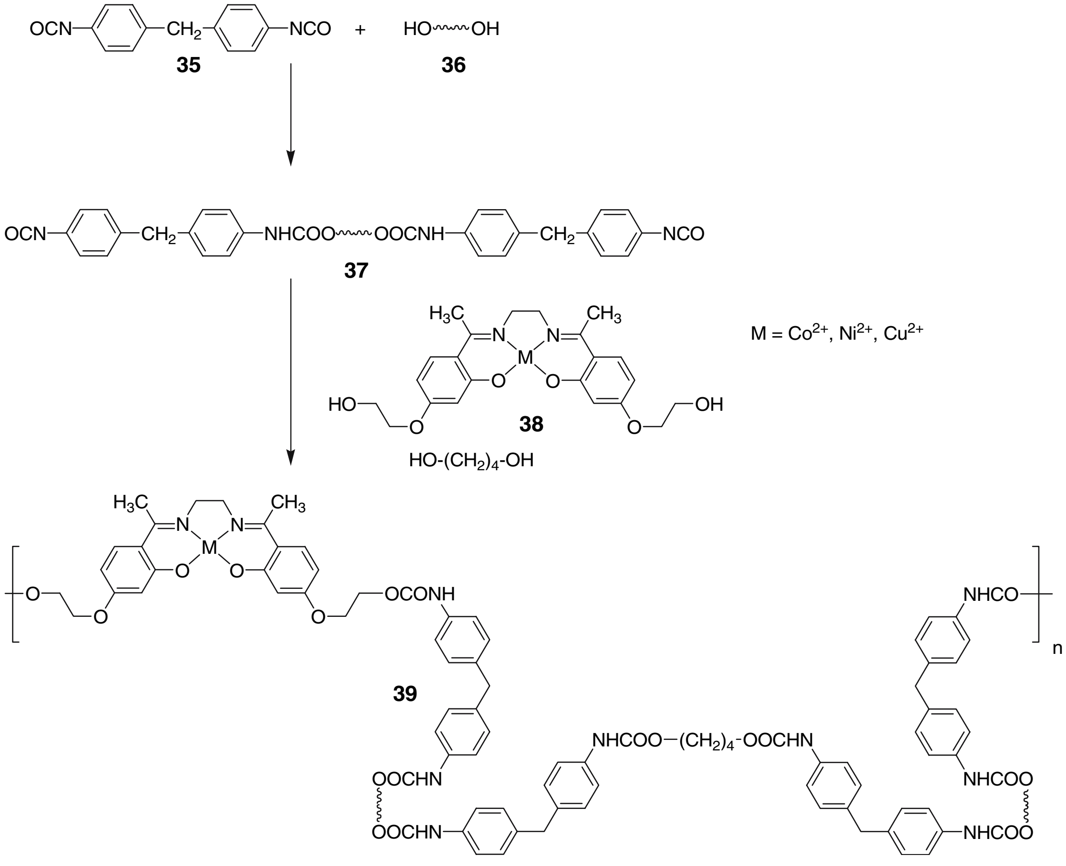
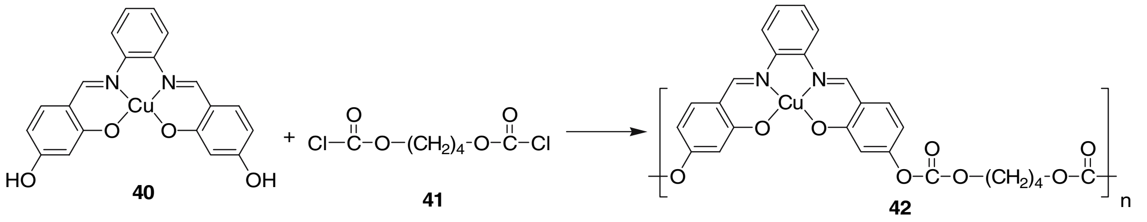


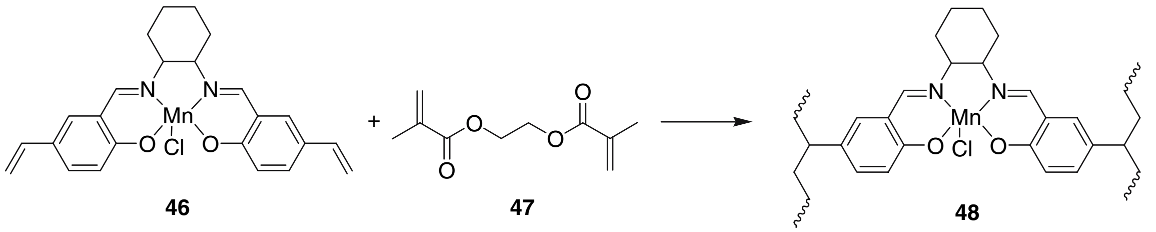
Scheme 5. Synthesis of salen–polyurethane copolymer **39**.



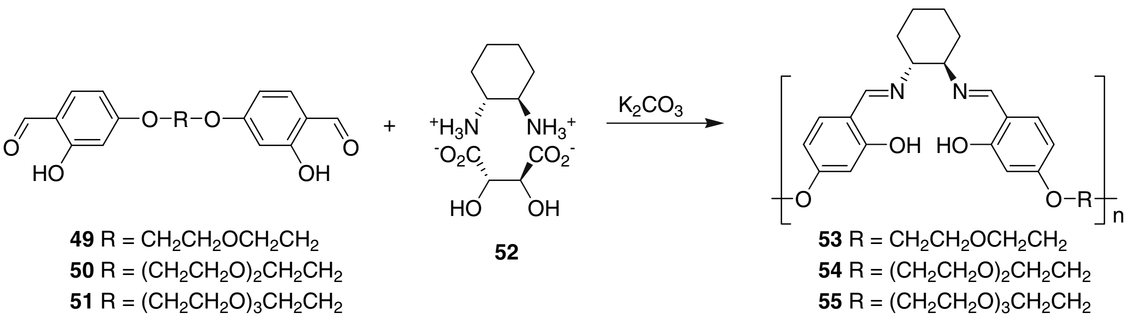
Scheme 6. Synthesis of Cu salphen–polycarbonate copolymer **42**.

Dhal and co-workers [34] copolymerized manganese(III) Schiff base complex **46** bearing two reactive vinyl groups with ethylene glycol dimethacrylate **47** via free-radical polymerization to yield insoluble crosslinked polymer **48**, Scheme 7. The ability of the polymer to catalyze epoxidation of various alkenes was evaluated, and product yields comparable to monomeric Mn(III) salen complexes were observed. However, the rate of epoxidation is relatively slow, and kinetics studies indicated that the reaction is a diffusion-controlled process.

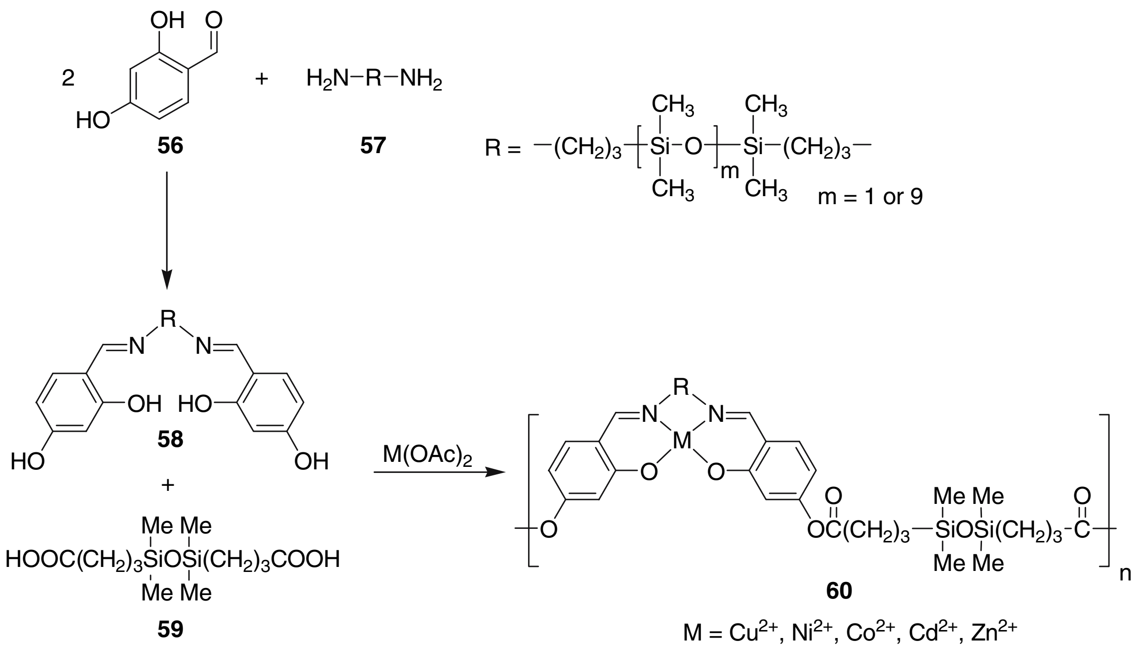
Praphairakait and co-workers [35] designed soluble salen polymers through coupling of various lengths of ethylene glycol units with chiral salen units, Scheme 8. The polymers were prepared by the condensation of bis(salicylaldehyde)s **49**–**51** with trans-diaminocyclohexane tartrate salts **52** to afford polymers **53**–**55** with molecular weights ranging from 5100–17,500 Da (M_n, GPC). Upon complexation of these poly(Schiff base)s with transition metals (Ni^{2+}, Mn^{3+}, Co^{2+}, and V^{4+}), it was observed that only polymers with tri- and tetra-ethylene glycol chains are soluble, with the exception of Co^{2+} polymers. The insolubility of the cobalt polymers is attributed to the preferred octahedral geometry of Co^{2+} ions that results in a crosslinked structure through coordination of oxygen atoms on the glycolic chains to the Co metal centers. The authors investigated the use of these metallopolymers as electrochemical sensors, casting the polymers directly onto carbon working electrodes and recording their cyclic voltammograms. The Ni^{2+} salen polymer electrode exhibited a quasi-reversible signal for the oxidation–reduction of Ni^{2+}, while the Mn^{3+} and V^{4+} polymer electrodes showed only irreversible oxidation–reduction processes. It was observed that the anodic signal for the nickel polymer is significantly shifted in the presence of pyridine.



Scheme 7. Synthesis of crosslinked copolymer **48**.



Scheme 8. Synthesis of copolymers **53**–**55**.

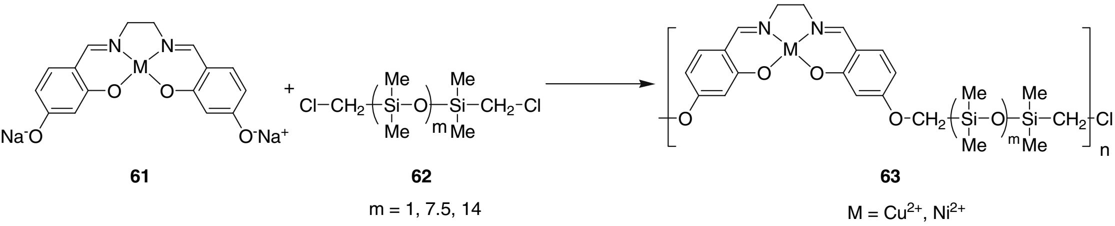


Scheme 9. Synthesis of siloxane-Schiff base copolymer **60**.

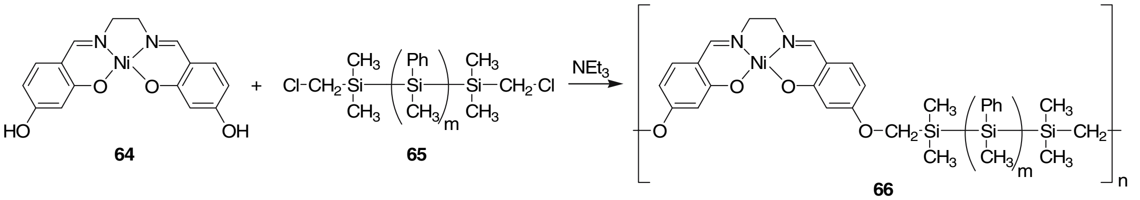
Cazacu and co-workers [36] prepared siloxane-Schiff base copolymers **60**. Polymerizable salen–siloxane ligand **58** was first prepared by condensation of 2,4-dihydroxybenzaldehyde **56** with siloxane-diamine **57,** Scheme 9. Polymerization was achieved by a dehydration reaction catalyzed by acetic anhydride or *N,N′*-dicyclohexylcarbodiimide (DCC) to afford soluble polymers that can be cast into yellow or brown films. The polymers were characterized by IR, UV–vis, and ^{1}H NMR spectroscopies, but no molecular weights were reported. Incorporation of short segments of polysiloxanes into the polymer induces good processability by improving solubility and lowering melting points.

Polysiloxane-Schiff base copolymer **63** was synthesized by a different strategy, Scheme 10 [37]. Copper and nickel salen-diol monomers were first converted to the corresponding alkali metal salt **61** through the addition of NaOH. Subsequent polycondensation with chloromethyl-terminated poly(dimethylsiloxane) **62** afforded the polymers as brown (Cu) and orange (Ni) solids. The polymers were characterized by IR, UV–vis, and ^{1}H NMR spectroscopies. TGA indicated copolymers with longer polysiloxane segments have improved thermal stability.

Polysilanes are known to exhibit σ-delocalization and these materials may be semiconducting [38]. Their incorporation into metallopolymers, such as poly(ferrocenylsilanes), have led to new materials that show both metal–metal interactions and σ-delocalization [39]. Sacarescu and co-workers [40] prepared polysilane–salen copolymers **66** by polycondensation of Ni(salen) diol **64** with chloromethyl-terminated polysilane **65** in the presence of triethylamine, Scheme 11. The polymers were characterized by ^{1}H NMR spectroscopy, and GPC analysis indicated the presence of low molecular weight materials (M_w = 5600 Da). TGA showed thermal decomposition of the polymer



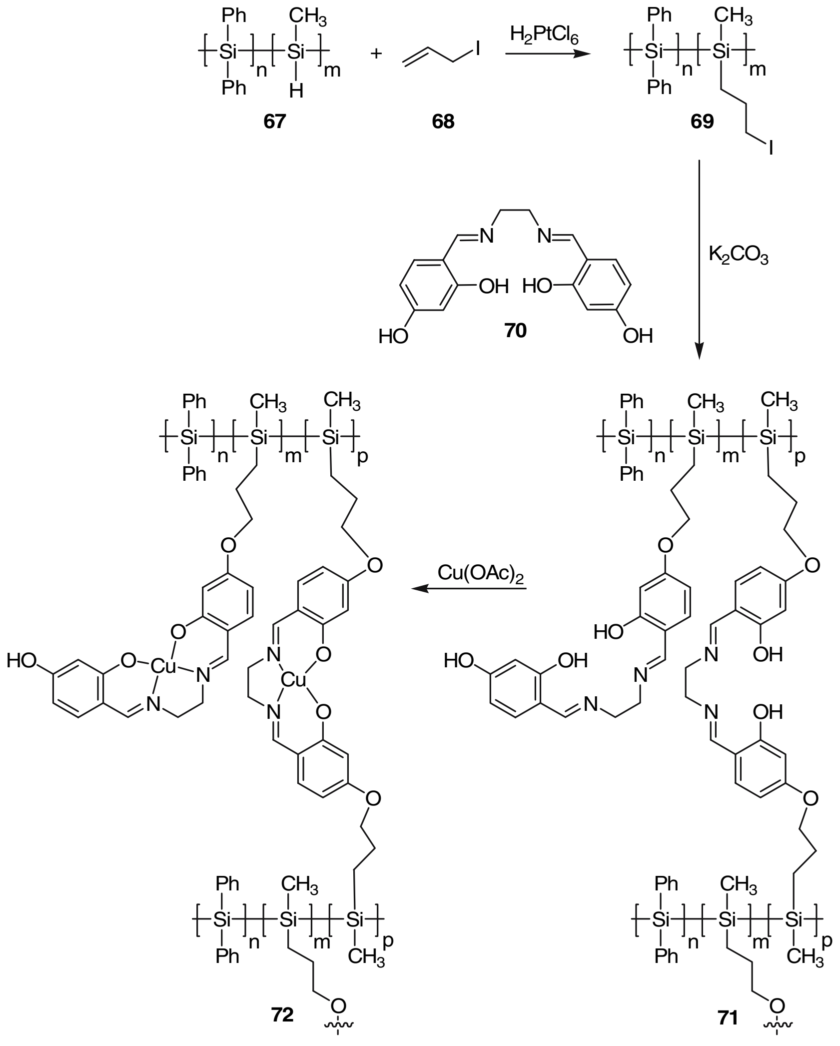
Scheme 10. Synthesis of siloxane-Schiff base copolymer **63**.



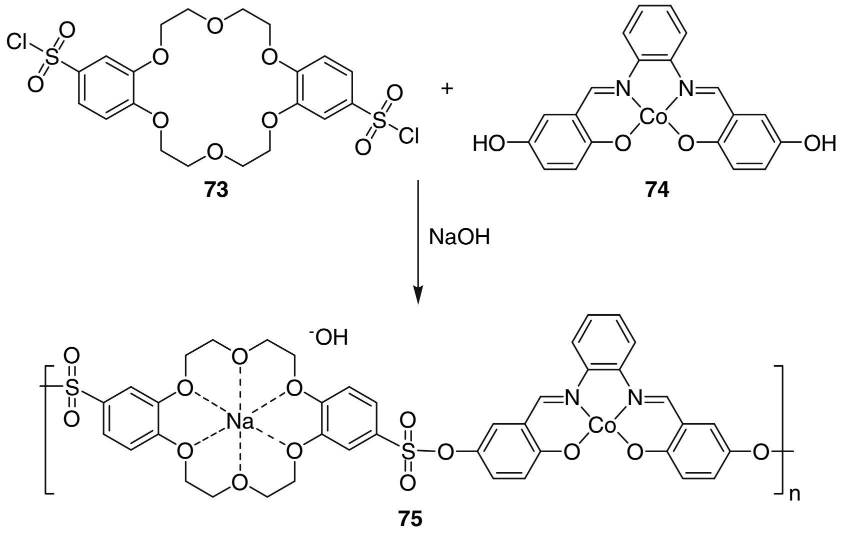
Scheme 11. Synthesis of polysilane–salen copolymer **66**.

beginning at 100 °C, possibly due to the loss of solvent trapped within the polymer matrix.

Crosslinked polysilane–salen copolymer **72** was synthesized according to Scheme 12 [41]. Polysilane **69** with pendant iodopropyl groups, prepared by Pt-catalyzed hydrosilylation of **67** with allyl iodide **68**, was condensed with Schiff base ligand **70** in the presence of K_2CO_3 to form crosslinked polymer **71**, which was then metallated to form copper-containing polymer **72**. The polymer was characterized with IR and ^{1}H NMR spectroscopies, although the peaks in the ^{1}H NMR spectra were severely broadened. GPC measurements indicated a bimodal molecular weight distribution (M_w ca. 9600 and 14,000 Da) characteristic of crosslinked polymers. It is very likely that the presence of highly crosslinked polymers formed by



Scheme 12. Synthesis of crosslinked polysilane–copper salen copolymer **72**.

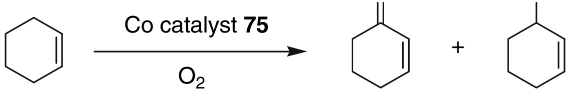


Scheme 13. Synthesis of crown ether–cobalt salphen copolymer **75**.

intermolecular condensation of the two hydroxyl functionalities on the salicylideneimine moiety contributed to the observed high molecular weight and bimodal distribution. As expected, the UV–vis spectrum of polymer **72** is nearly identical to the combination of the starting polysilane and Cu salen complex, indicative of minimal electronic communication between the polysilane backbone and the tethered Cu salen complex.

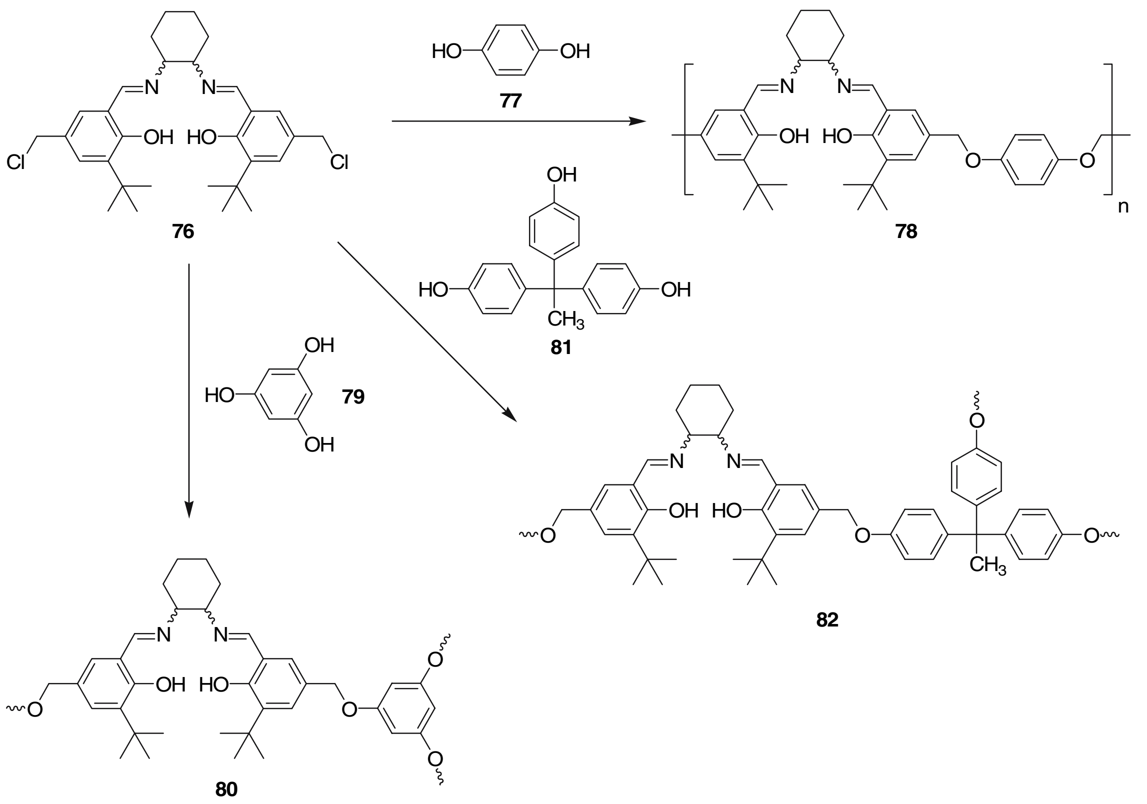
Wang and co-workers [42] synthesized new Schiff base polymer **75** incorporating both a crown ether and a Co(salphen) complex by interfacial polymerization of **73** and **74**, Scheme 13. The insoluble polymer was characterized by IR, XPS, TGA, and SEM, but no molecular weight information was reported. The solid polymer was tested for catalytic aerobic oxidation of cyclohexene, Scheme 14. It was found that the new polymer oxidizes cyclohexene in the allylic position to give a mixture of its corresponding ketone and alcohol.

Kim and co-workers [43] synthesized cobalt(III) Schiff base polymers by polymerizing ligands **76** with hydroquinone **77**, phloroglucinol **79**, and 1,1,1-tris (4-hydroxyphenyl)ethane **81** to yield linear polymer **78**, and crosslinked polymers **80** and **82**, respectively (Scheme 15). The polymeric ligands were then metallated with $Co(OAc)_2$ and the Co^{2+} metal was oxidized to Co^{3+} using a ferrocenium salt. The polymers were characterized by IR spectroscopy and were tested for catalytic activities for enantioselective hydrolysis of terminal epoxides to diols. Upon testing the catalytic activity of the polymers with epichlorohydrin, styrene oxide, 1,2-epoxybutane, and 1,2-epoxyhexane, it was found that they were effective in producing a mixture of approximately equal amounts of the corresponding epoxides and diols with excellent ee in the range of 97–99%. The polymeric catalysts can be reused up to seven times without significant loss in catalytic activity after simple filtration from the reaction mixture. No significant difference in catalytic performance was observed between linear or crosslinked polymers.



Scheme 14. Aerobic oxidation of cyclohexene catalyzed by **75**.

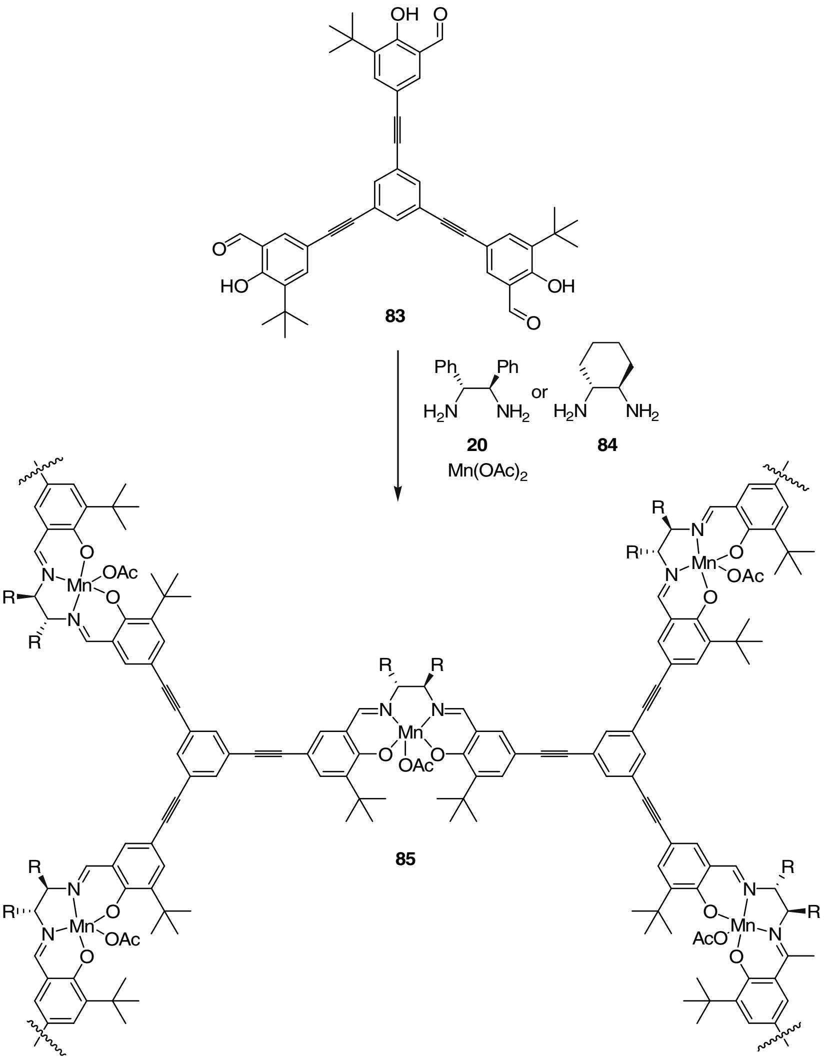
Gothelf and co-workers [44] synthesized conjugated hyperbranched Schiff base polymers **85** through a one-pot condensation of an aromatic trialdehyde **83** and diamines **20** or **84,** Scheme 16. The organic polymers formed were insoluble, but solid-state NMR and powder synchrotron X-ray diffraction data obtained were consistent with the presence of a rigid polymeric network with a small degree of local order. When the reaction was performed in the presence of $Mn(OAc)_2$, insoluble metal-containing polymers precipitated and were tested as chiral catalysts for asymmetric epoxidation of alkenes. The epoxidation of cis-2-methylstyrene in the presence of this catalyst afforded 73% conversion, and the enantioselectivity for the cis isomer is 57%.



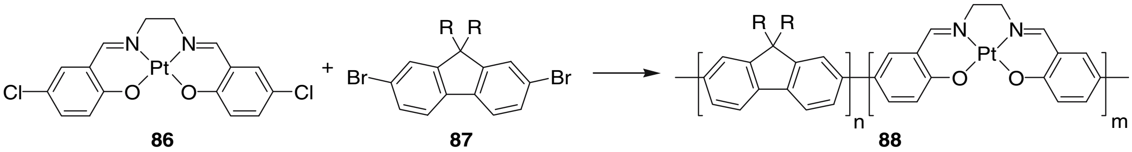
Scheme 15. Synthesis of linear polychelates **78** and crosslinked polychelate **80** and **82**.

Platinum-containing Schiff base complexes are known to exhibit intense yellow–green phosphorescence in solution, and their incorporation into electroluminescent devices was successful in generating white light with high efficiency [45]. Statistical copolymers **88** containing Pt(salen) monomer **86** were synthesized by Scherf and co-workers [46], Scheme 17. Yamamoto-type Ni(0)-mediated aryl-aryl coupling of **86** and **87** was accomplished in THF using a microwave heat source to synthesize the high molecular weight copolymers (M_n ca. 24,000–170,000 Da) in short reaction times (ca. 12 min). The molar ratio of incorporated Pt(salen) units was determined from ^{1}H NMR spectra to be only 2.1–8%. Although the solution emission spectra of the copolymers were dominated by poly(fluorene) emission, phosphorescence originating from the Pt(salen) complex was observed in the solid state (575 nm). When copolymers **88** were employed in OLED devices, the observed electroluminescence (EL) efficiencies were low (ca. 0.1–0.3 cd A^{-1}), probably due to the presence of aggregate quenching. Blending the copolymer into a poly[9,9′-bis(2-ethylhexyl)fluorene] matrix improved the EL efficiency of the device to ca. 3–6 cd A^{-1}.

Thus far, all of the polymers discussed possess organic backbones. Although a number of studies of inorganic polymers have involved the synthesis of materials with metal-organic bonds in the backbone [47], there have been very few studies of this type with Schiff base complexes. Typically these interactions are weaker and are expected to reduce the stability of the polymers. Tong and Archer reported block copolymers containing zirconium Schiff base complexes and poly(tetrahydrofuran) [48]. Novel eight-coordinated Zr-containing Schiff base monomer **91** was obtained through addition reaction of complex **89** with tolylene-2,4-diisocyanate **90**, Scheme 18. The resulting Zr complex contained two reactive isocyanate groups, which were subsequently condensed with poly(THF) **92** to afford new block copolymer **93** as an orange–red transparent film. It is noteworthy that the Zr monomers were copolymerized with an excess of low molecular weight poly(THF) (~1000 Da) to obtain low molecular weight materials for easy characterization. The copolymer was characterized by IR, ^{1}H NMR and UV–vis spectroscopies. GPC analysis showed a molecular weight (M_w) of 10,300 Da, indicative of polymers with an average of five repeat units. The novel Zr Schiff base monomers with



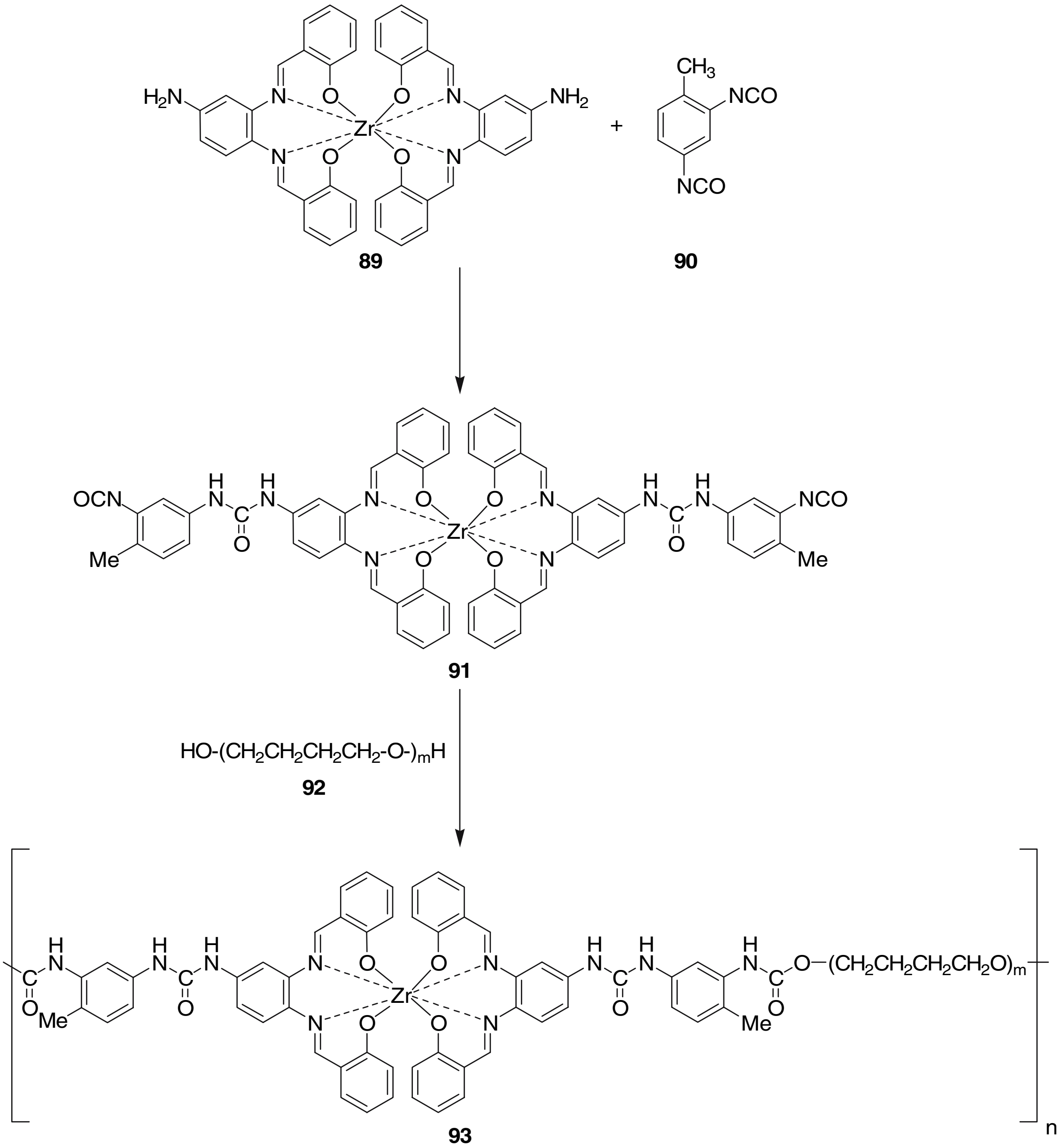
Scheme 16. Synthesis of manganese Schiff base crosslinked polymers **85**.



Scheme 17. Synthesis of platinum salen–fluorene copolymer **88**.

pendant isocyanate functional group should readily react with a variety of primary alcohols and amines, allowing facile assembly of linear Zr-containing copolymers.

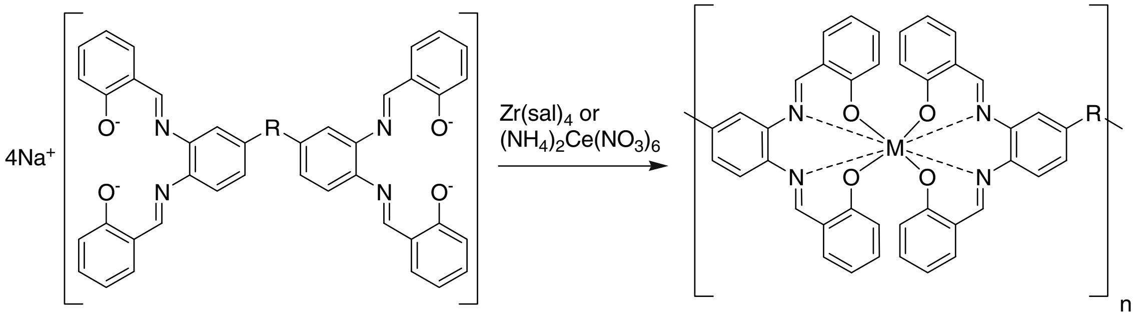
Archer also prepared new Zr Schiff base polymers from bis(tetradentate) Schiff base ligands **94**–**96** [49]. The ligands were first deprotonated with NaOH, followed by addition of a zirconium precursor to afford the new homopolymers **97**–**99**, Scheme 19. GPC analysis revealed molecular weights (M_n) of ca. 9000–20,000 Da, and the molecular weights were also confirmed by ^{1}H NMR end-group analysis after capping the polymers with excess salicylaldehyde. Analogous cerium polymers were prepared by a similar



Scheme 18. Synthesis of zirconium salphen–poly(tetrahydrofuran) block copolymer **93**.

strategy [50], although it was found that the polymers can be prepared from simple metallation of the ligand with $Ce(acac)_4$, or from a two-step method by first adding salicylaldehyde to Ce^{4+} metal salts followed by condensation with the appropriate tetraamine. Cerium-containing polymers with molecular weights as high as 30,000 Da (M_n, GPC and ^1H NMR end group analysis) were reported. Films of both the Ce and Zr polymers were examined with scanning electron microscopy, revealing a featureless and continuous morphology. TGA revealed that these polymers have excellent thermal stabilities, with the Zr polymers retaining >95% of their mass at 400 °C, while the Ce counterparts are stable to 350 °C, retaining more than 98% of their original mass. Conductivities measured using a two-probe instrument indicated that these polymers have high intrinsic (ca. 10^{-7} S cm^{-1}), and doped (I_2, 10^{-3} S cm^{-1}) conductivities.

Highly luminescent analogues of polymers **97** and **98** can be prepared according to Scheme 19 with Eu^{3+} and Y^{3+} metals [51]. These polymers have molecular weights (M_n) of ca. 7000–20,000 Da, as

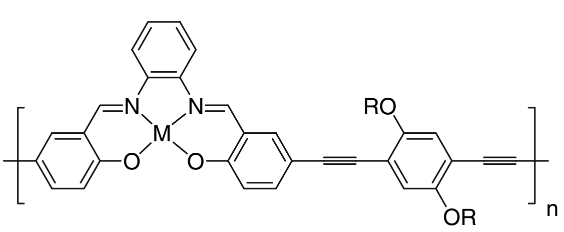


94 R = -
95 R = CH_2
96 R = SO_2

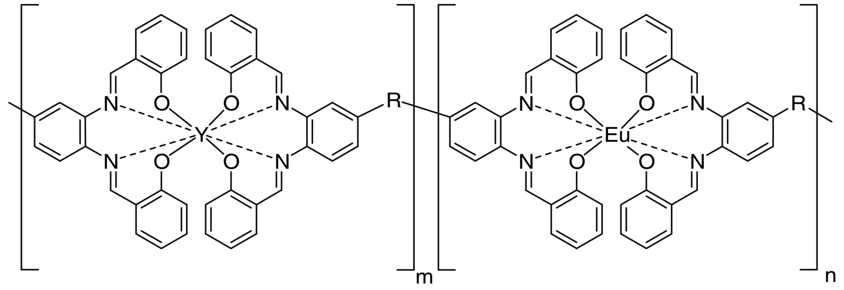
97 R = - M = Zr, Ce
98 R = CH_2
99 R = SO_2

Scheme 19. Synthesis of zirconium and cerium Schiff base polymers **97**–**99**.

measured by GPC and ^1H NMR end group analysis. Polymers **100** and **101** were prepared by addition of both metal salts (Eu, Y) in various ratios during polymerization; copolymer **101** ($m = 1$, $n = 4$) has the highest quantum yield (74%) of the series. The authors proposed the improvement in luminescence is likely due to additional intramolecular energy transfer from yttrium centers to the europium ions, analogous to the antenna effect. Excellent thermal stability and luminescence characteristics make this class of Schiff base polymers good candidates for applications requiring luminescent polymers (e.g., lasers, LEDs).



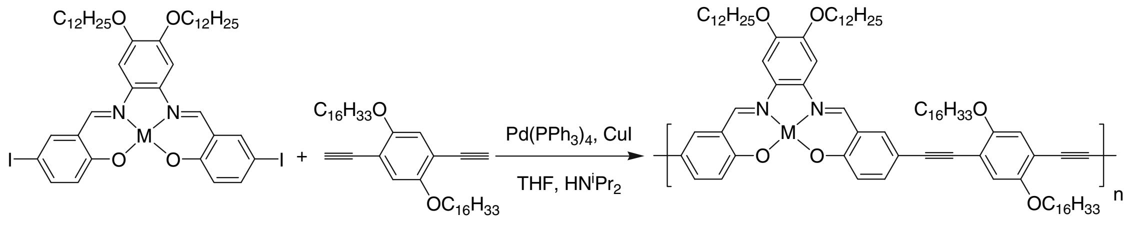
102 M=Zn, Ni; R = C_8H_{17}



100 R = -
101 R = CH_2

In 2002, Lavastre and co-workers [52] reported a large library of new fluorescent conjugated polymers from a combinatorial synthesis and screening method. Among these polymers, the postulated structures **102** incorporating Schiff base Zn^{2+} and Ni^{2+} complexes were prepared using Pd(0)-catalyzed Sonogashira coupling of the appropriate dibromosalphen complexes and diethynyldialkoxybenzene. These polymers showed high quantum yields, suggesting that they may be excellent candidates for application in LEDs. However, these polymers were of low molecular weights (3000–6000 Da, GPC), poorly soluble, and the measured luminescence may have originated from unreacted monomeric species.

Following this report, MacLachlan and co-workers [53] prepared soluble derivatives of polymer **102** by Sonogashira coupling of diiodosalphen monomers **103** with diethynyldialkoxybenzene **104** to afford new poly(salphenyleneethynylene)s **105,** Scheme 20. Long alkoxy substituents were attached to both the salphen and diethynylbenzene monomers to render these polymers soluble. These polymers have high molecular weights (M_w ca. 17,000–84,000 Da, GPC) and form red, free-standing films, Fig. 1. Wide-angle X-ray analysis indicated that the



103 M = Zn, Ni, VO **104** **105**

Scheme 20. Synthesis of poly(salphenyleneethynylene)s **105**.

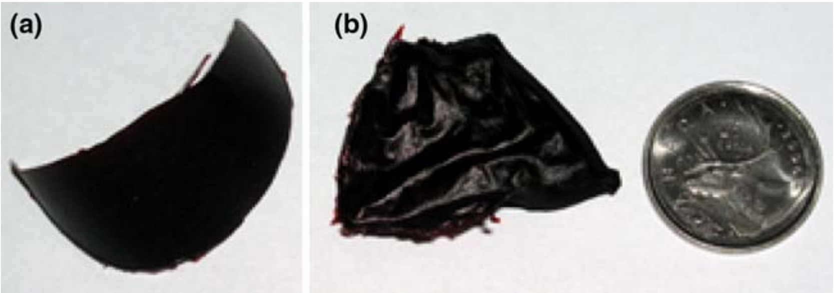
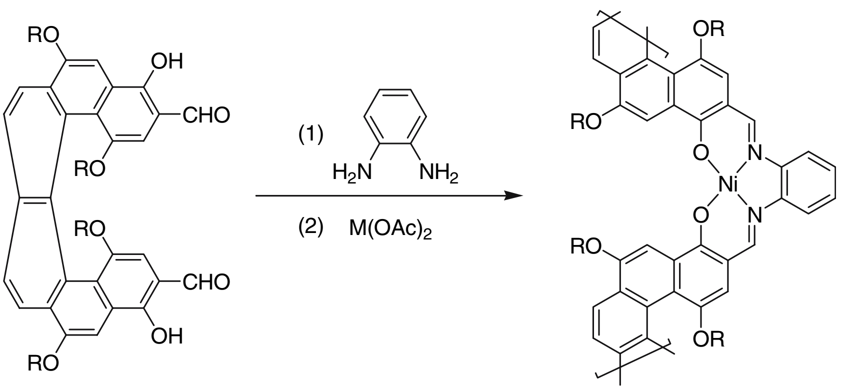


Fig. 1. Polymeric films of **105** where (a) M = Zn, and (b) M = Ni. A quarter is shown for size comparison.

polymers are amorphous. Fluorescence studies were carried out on all of the polymers, but only polymer **105** metallated with Zn is weakly luminescent in solution. Energy transfer from the polymer absorption into localized states of the metal complexes is likely responsible for the poor emission properties of these materials.

3.3. Helical Schiff Base Polymers

Katz and co-workers [54] synthesized the first fully conjugated ladder polymers that have a helical structure. Helicene bis(salicylaldehyde) **106**, prepared in 7 steps, was condensed with *o*-phenylenediamine and metal acetates to afford polymers **107** with helical structures, Scheme 21. It was necessary to first synthesize the organic polymer backbone and subsequently react the polymeric ligand with metal salts. The polymeric structure of Ni polymer **107** was confirmed using ^{1}H NMR, ^{13}C NMR, and IR spectroscopies as well as MALDI-TOF mass spectrometry. The MALDI-TOF mass spectra of the polymers showed peaks corresponding to oligomers, terminated with either the expected salicylaldehyde end group or end groups that are likely benzimidazoles **108** and **109**. The molecular weight estimated by ^{1}H NMR end group analysis was ca. 5000 or 10,000 Da (M_n) depending on whether the polymer is capped by one or two salicylaldehyde groups, respectively.



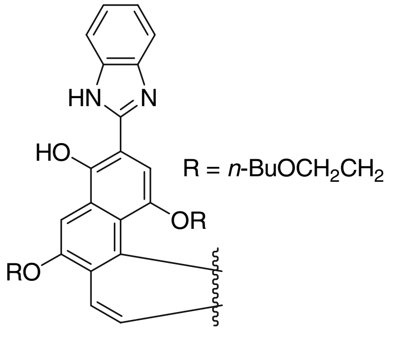
106

R = *n*-BuOCH$_2$CH$_2$

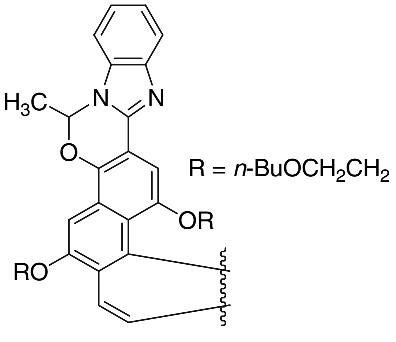
107

M = Ni, Cu, Co
R = *n*-BuOCH$_2$CH$_2$

Scheme 21. Synthesis of helical ladder polymer **107**.

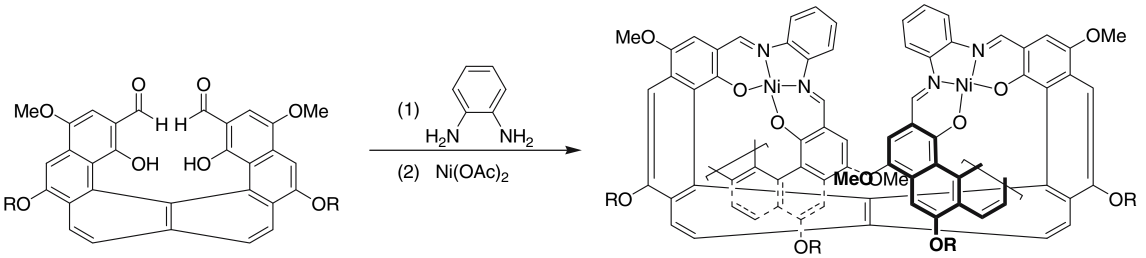


108



109

Helicene bis(salicylaldehyde) **110**, having the orientation of its aldehyde and hydroxyl functional groups switched in comparison to **106**, was employed to prepare a different helical polymer **111** using a similar procedure, Scheme 22. Figure 2 illustrates the different structures of polymers **107** and **111**. Based on GPC measurements and ^{1}H NMR end group analysis, the molecular weight of polymer **111** is ca. ~7000 Da (M_n). The circular dichroism spectra of the two polymers **107** and **111** are very similar, and the absorptions associated with metal-to-ligand charge transfer are very large in comparison to monomeric Ni(salphen) complexes.



110 R = n-BuOCH$_2$CH$_2$

111 R = n-BuOCH$_2$CH$_2$

Scheme 22. Synthesis of helical ladder polymer **111**.

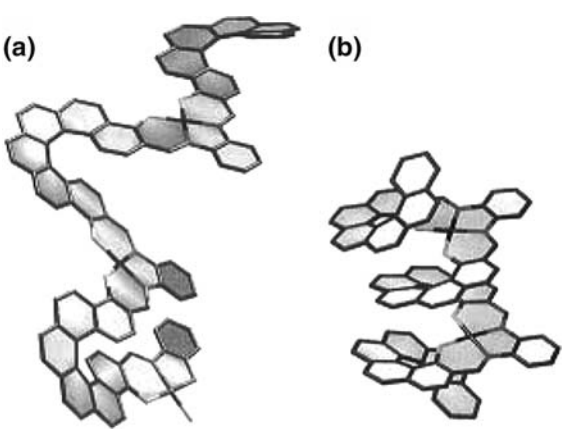
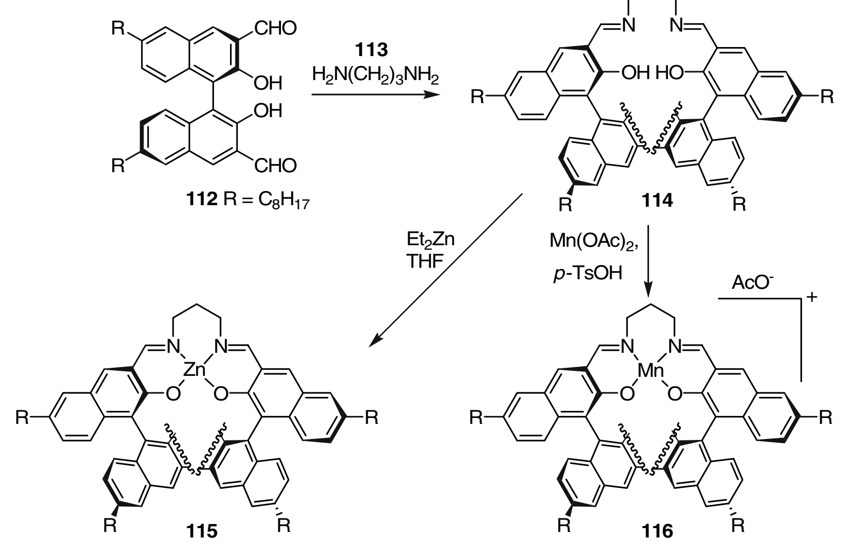


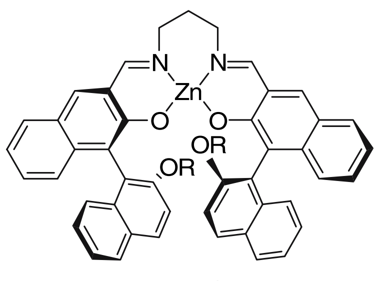
Fig. 2. 3-D representation of nickel helical polymer (a) **107** and (b) **111**. Reprinted with permission from reference 54b. Copyright 1997 American Chemical Society.

Takata and co-workers [55–57] synthesized chiral salen polymers **115** and **116** by the condensation of chiral binaphthyl bis(salicylaldehyde) derivative **112** with diamine **113**, Scheme 23. The predisposed chirality of the binaphthyl unit leads to the formation of helical polymers which are synthesized in two steps by first preparing the organic backbone **114** followed by the insertion of the appropriate transition metal. Notably, the metal-free polymeric Schiff bases have high molecular weights (M_w up to 13,000 Da), while a considerable drop in molecular weight (M_w = 1800 Da for **115**, 1700 Da for **116**) was observed after the incorporation of M(OAc)$_2$. The authors attributed this observation to the inability of GPC to correct for the polyionic structure of the polymer, in addition to changes in conformations to form compact helices. Model compounds **117** and **118** were synthesized and their UV–vis and CD spectra were compared with the polymers. It was found that the absorption band of the naphthalene unit exhibited a significant red shift in the polymers compared to the model compounds, in agreement

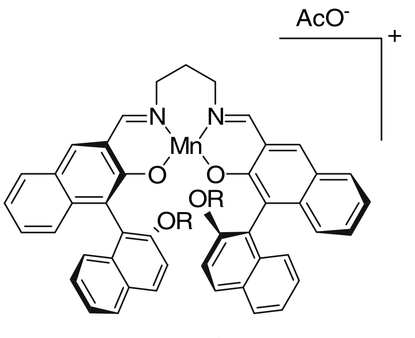


Scheme 23. Synthesis of helical zinc and manganese polymers **115** and **116**.

with the proposed helical structure for which the naphthalene units are in close proximity. The change in Cotton effect in the CD spectra of the polymer in comparison to the model compounds also supports the helical structure.



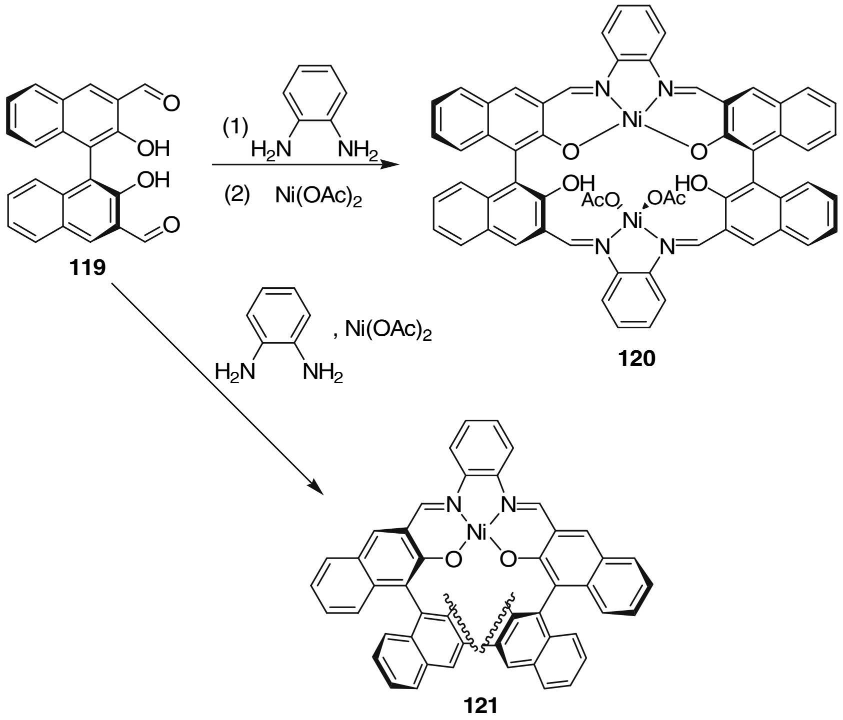
117 R = C_4H_9



118 R = C_4H_9

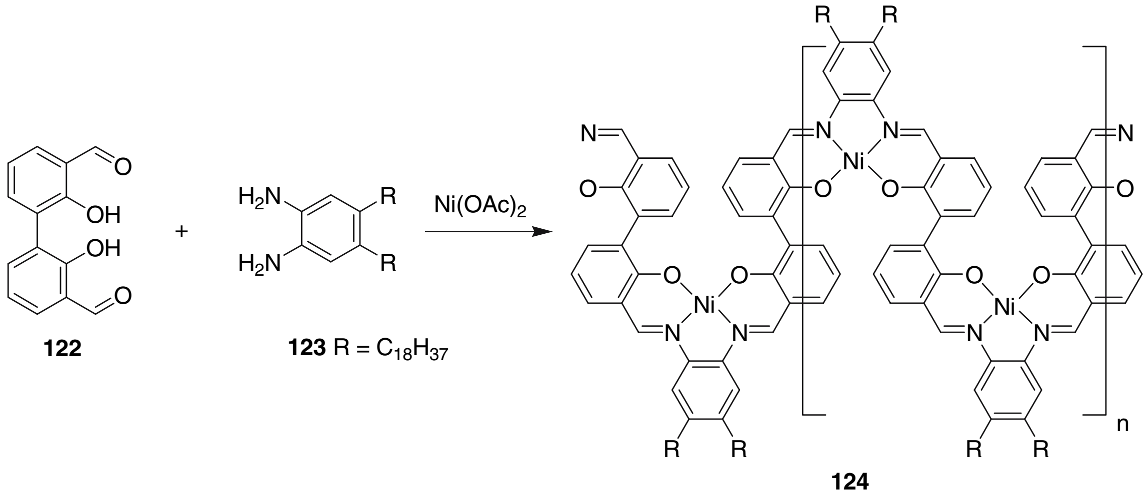
Takata explored the use of these new helical metallopolymers for asymmetric catalysis. The addition of 5 mol% of Zn polymer **115** catalyzed the addition of diethylzinc to benzaldehyde with enantioselectivity up to 95% ee, compared to only 5% ee with Zn model compound **117**. Manganese polymer **116** catalyzed the epoxidation of alkenes using Jacobsen's protocol, but low catalytic activities and low enantioselectivities were observed.

Pu and co-workers [58] attempted to synthesize soluble conjugated Ni(salphen) polymers from BINOL dialdehyde **119** and bis(salicylaldehyde) **122**. When BINOL monomer **119** is reacted with *o*-phenylenediamine, a macrocyclic product is formed instead of the anticipated polymeric product, and the addition of $Ni(OAc)_2$ yields a paramagnetic product with proposed structure **120**, Scheme 24. The authors suggested the formation of macrocycle **120** containing both square-planar and tetrahedral Ni^{2+} centers results from steric congestion of the macrocyclic product. Condensation of **119** with *o*-phenylenediamine in the presence of $Ni(OAc)_2$ afforded low molecular weight polymers (M_w ca. 3600 Da, GPC). The oligomers are also paramagnetic, suggesting the presence of non-planar coordination of Ni^{2+} units. Condensation of **122** with bis(octadecyloxy)phenylenediamine **123** yielded soluble polymers **124** with

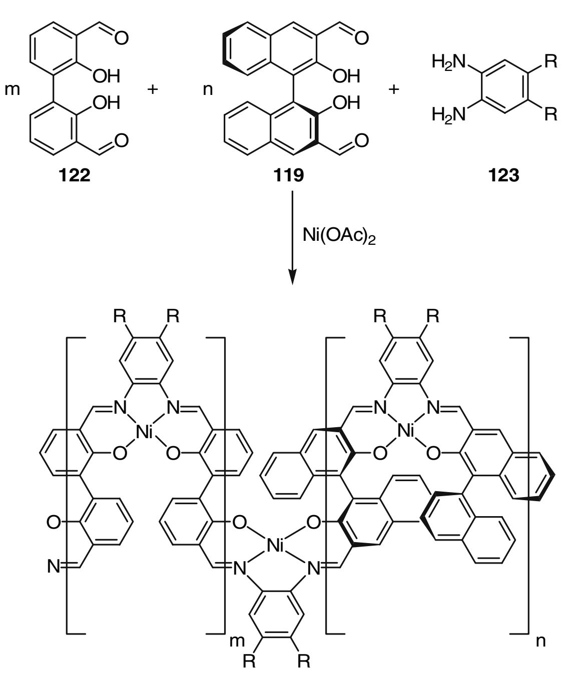


Scheme 24. Synthesis of macrocycle **120** and oligomer **121**.

low molecular weights (M_w ca. 4900 Da, GPC), Scheme 25. The polymer is also paramagnetic or strongly aggregated since no NMR signals could be detected in the expected region. A broad absorption band was observed at 700–1200 nm in the UV–vis spectrum of **124,** which is not present in the UV–vis spectra of square-planar Ni(salphen). Copolymerization of the phenylenediamine **123** with both **119** and **122** was conducted to determine whether the chirality of the binaphthyl units can induce a helical chiral structure in copolymer **125,** Scheme 26. CD spectra of the copolymers, which had low molecular weights (M_w ca. 3400–5400 Da, GPC), showed a linear increase in the CD peak maxima with the increase of chiral binaphthyl monomer content. This result indicates that the introduction of chiral binaphthyl



Scheme 25. Synthesis of Ni polymer **124**.



125 R = $C_{18}H_{37}$

Scheme 26. Synthesis of copolymer **125**.

units cannot induce the formation of a main chain helix, probably due to the presence of non-planar Ni centers.

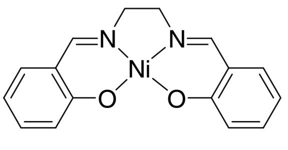
Insoluble double-helical metallopolymer **128** was synthesized by Houjou and co-workers [59a] by a one-pot precipitation polymerization of bis(salicylaldehyde) **126**, dianiline **127**, and copper(II) acetate, Scheme 27. Surprisingly, SEM images revealed that the brown powdery solid was composed of nearly monodisperse microspheres with average diameter of 1.35 μm. These metal-bound polyimine microspheres can be fabricated with different dimensions using different metal salts: Co, 0.80 μm; Ni, 1.34 μm; and Zn, 0.51 μm, Fig. 3. The microspheres have high thermal stability, with TGA showing no significant degradation below 300 °C. SEM images of the materials after pyrolysis at 500 °C showed no change in the shape of the particles. Bimetallic microspheres were also investigated using mixtures of Zn^{2+} and Cu^{2+} [59b]. Based on microanalysis of individual particles, the researchers deduced that the particles have a gradient Zn/Cu composition originating from differential rates of coordination to the polyimine. This is potentially an elegant route to developing microspheres with tunable magnetic properties.

A model compound **131** of the double helical polymer was prepared by reacting bis(salicylaldehyde) **129** with p-methoxyaniline **130** in the presence of $Cu(OAc)_2$, Scheme 28. A single crystal X-ray structure (Fig. 4) of this Cu complex confirmed the two imine ligands assembled into a double helix bridged by Cu atoms, which are coordinated in a distorted square-planar geometry. Based on the crystal structure of the model compound, the authors proposed that the formation of colloidal microspheres may be a result of helical entanglement of the polyimine chains to form highly crosslinked structures.

4. ELECTROCHEMICALLY PREPARED SCHIFF BASE POLYMERS

The development of polymer-modified electrodes is of great interest to researchers because of their potential applications in electrocatalysts, chemical sensors, and electrochromic displays. One common strategy for electrochemical synthesis of metal-containing polymers is to attach polymerizable groups such as thiophene or pyrrole functionalities onto metal complexes [60]. In the case of salen-type polymers, these extra synthetic steps can be avoided because Schiff base complexes can be conveniently polymerized by direct electrolysis.

Murray and co-workers [61] reported the first electrochemically synthesized polymers containing Schiff base metal complexes. Aniline-substituted salen complexes (meansalen) **132** were electropolymerized in a “tail to tail” fashion to form non-conjugated polymers **133**, Scheme 29. Nickel and cobalt monomers of **132** were polymerized by potential scanning between 0 and + 0.8 V in 0.1 M Et_4NBF_4/MeCN, whereas formation of the manganese polymer of **133** required scanning to a slightly higher potential (+0.9 V). The voltammograms obtained during polymerizations of all of the monomers exhibited peaks at +0.5 V, which is very close to the formal potential (+0.45 V) of *N,N*-dimethylaniline dimerization to form *N,N,N′,N′*-tetramethylbenzidine, confirming that the polymerization proceeds through tail-to-tail coupling of the aniline moieties. Thin films of Ni and Co polymers of **133** exhibited CV traces that resembled their corresponding monomers, while Mn polymers produced poorly defined electrochemical responses. The authors attributed the poor electroresponsiveness of the Mn polymer to the slow electron transport rate for the $Mn^{2+/3+}$ couple.



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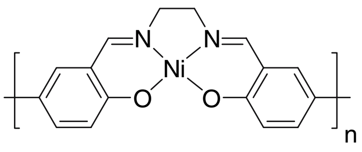

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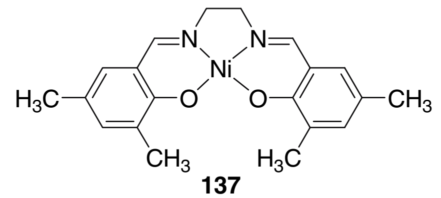

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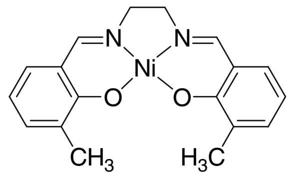

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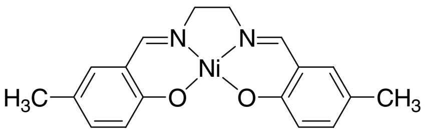
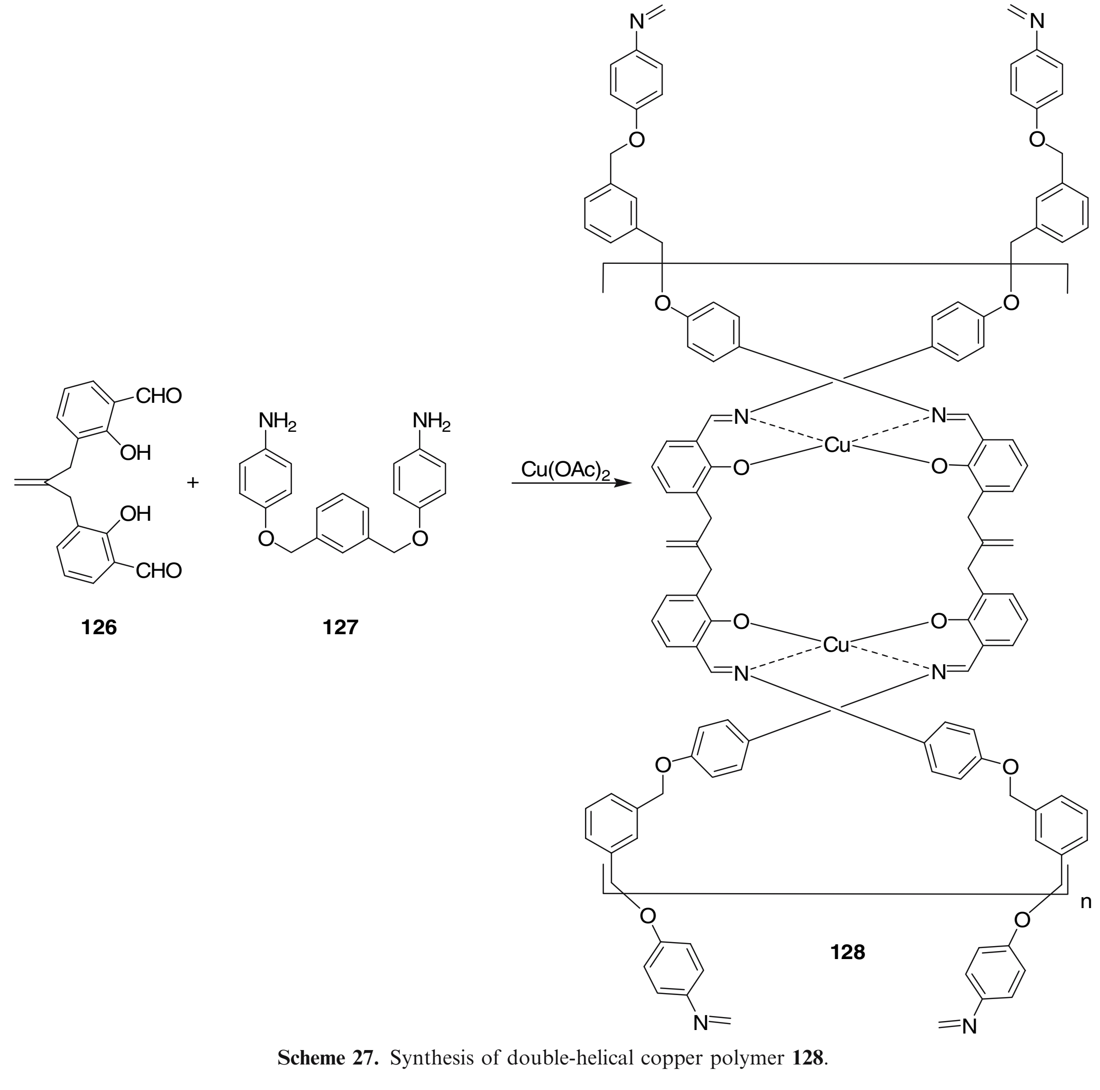


139

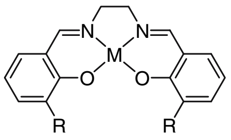
Goldsby and co-workers [62] demonstrated for the first time that Ni(salen) complexes **135** can be directly electropolymerized in weak donor solvents such as acetonitrile, acetone, and dichloromethane to form insoluble yellow thin films of polymer **136**. Energy dispersive X-ray spectroscopy was used to



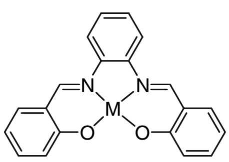
126 **127** **128**

Scheme 27. Synthesis of double-helical copper polymer **128**.

confirm the presence of Ni in the polymer film, and UV–vis spectra of polymer **136** coated on ITO surfaces showed characteristics of Ni(salen) complex **135**. Goldsby proposed the polymerization mechanism occurs via oxidative carbon-carbon coupling *para* to the phenolic oxygen. Salen complexes **137**–**139** were prepared to elucidate the site where polymerization occurs. It was observed that only Ni(salen) **138** with unsubstituted *para* positions on the phenolic ring underwent polymerization, thus providing indirect evidence to the molecular structure of polymer **136**.



140 M = Ni, R = CH_3
141 M = Ni, R = OCH_3
142 M = Cu, R = CH_3
143 M = Cu, R = OCH_3



144 M = Ni
145 M = Cu

Goldsby electropolymerized Ni and Cu salen-containing complexes **140**–**143** by cycling a platinum electrode in the potential region 0.4–1.4 V, and 0.5–1.4 V, respectively [63]. It was observed that the film growth of Ni complexes **140** and **141** increased linearly for several scans, followed by a gradual decrease in the rate of film growth. After ca. 50 scans, film growth stopped and the electrode became passivated. Polymer film growth of Cu monomers **142** and **143** was similar to that of **140** and **141**, although passivation of the electrodes occurred much earlier. A number of weak donor solvents, including acetone, dichloromethane, and propylene carbonate, were tested as solvents for the electropolymerizations. The resulting Ni and Cu polymer films exhibited similar electrochemical behaviors regardless of the initial solvents used for polymerizations. Nickel polymers of **144** prepared with phenylenediamines were electrochemically more stable than the corresponding polymers prepared from **135**, **140**, and **141** bridged by ethylenediamines, whereas the Cu polymers were considerably less stable. Scanning electron microscopy (SEM) revealed all of the polymer films have surface structures comprised of small amorphous spheres. Polymers **136** prepared in acetonitrile were observed to be extensively aggregated, polymers prepared in acetone were moderately aggregated, and a more uniform film structure was observed for polymers prepared in dichloromethane, Fig. 5. Attempts to polymerize the organic ligands resulted in poly(phenyl ether) films, and subsequent metallations were unsuccessful.

Following Goldsby's report, Audebert and co-workers further investigated the electropolymer-

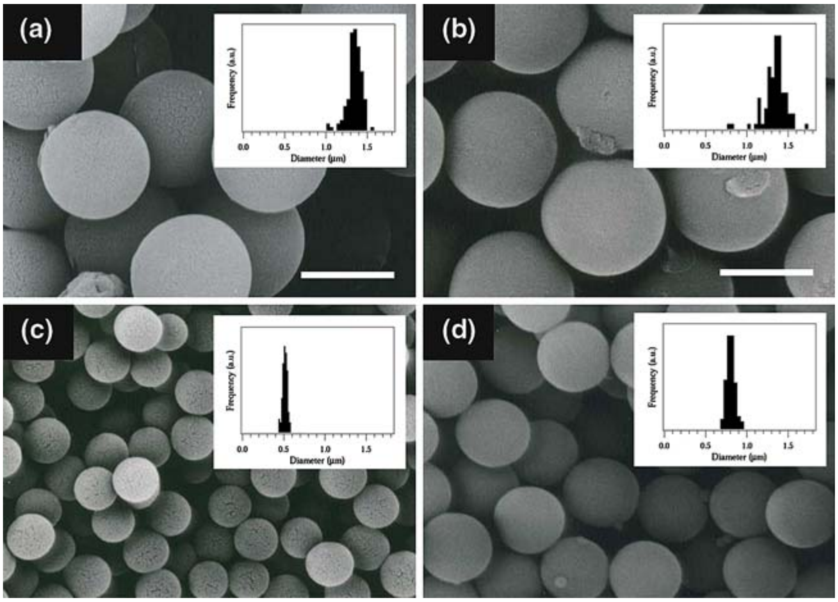
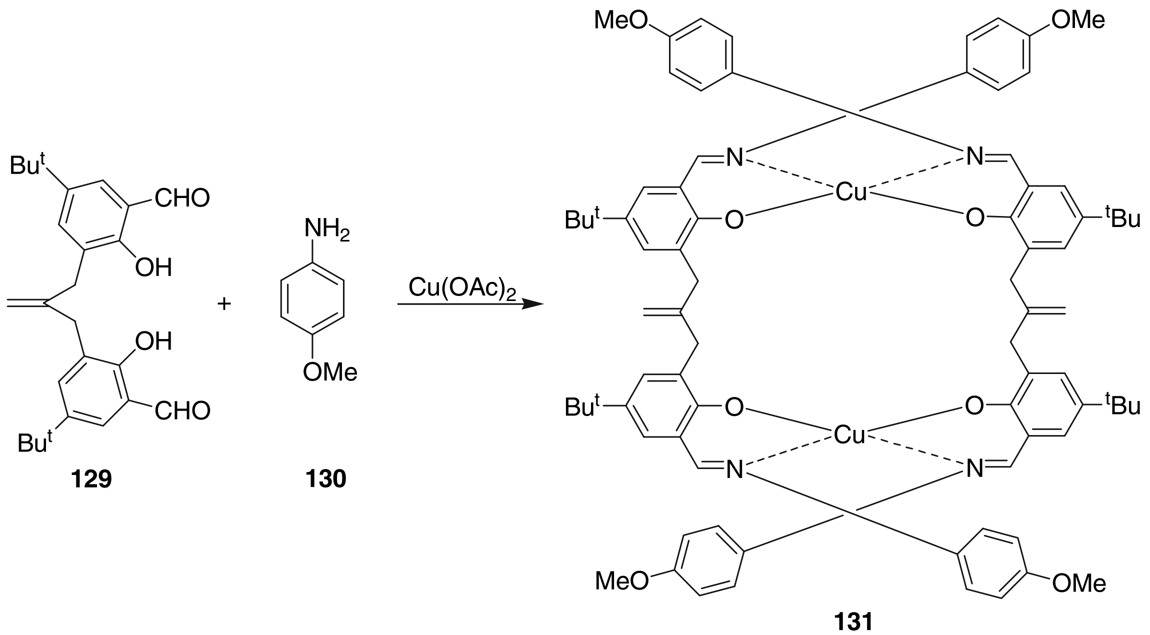


Fig. 3. SEM images of (a) Cu polymer **128** and analogous (b) Ni (c) Zn and (d) Co polymer. Scale bar represents 1 μm, and the inset shows the frequency of the microspheres' diameters. Reprinted with permission from reference 59a. Copyright 2003 Wiley-VCH.



Scheme 28. Synthesis of model compound **131**.

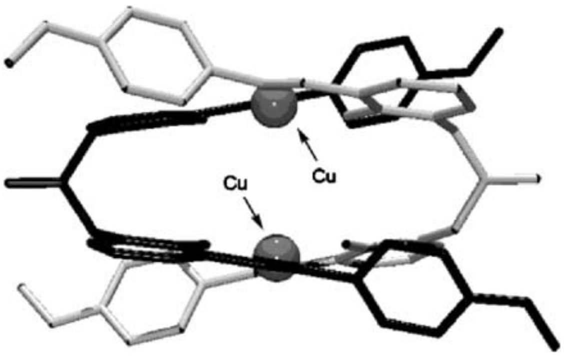
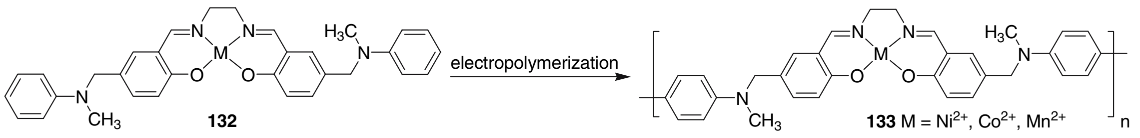


Fig. 4. Structure of model compound **131** as determined by X-ray crystallography. Hydrogen atoms and *tert*-butyl groups are omitted for clarity. Reprinted with permission from reference 59a. Copyright 2003 Wiley-VCH.

izations of Cu Schiff base complexes **143**, **145**–**148**, Ni complexes **135** and **141**, Co complexes **149** and **150**, and Zn complexes **151** and **152** [64]. All of the Schiff base complexes were polymerized by applying a constant potential or by successive potential sweeps in 0.1 M Et_4NClO_4/MeCN, with the exception of insoluble Zn(salen) **151**, which did not undergo polymerization. Thick films of these polymers could be easily prepared, showing typical increase in polymer-layer electroactivity throughout the course of polymerization. For Co polymers of **149** and **150**, the first oxidation step only led to oxidation to Co^{3+}, but it was possible to electropolymerize the Co^{3+} salen by further oxidation. However, it was difficult to produce thick deposits with Co(salen) derivatives. Similarly, only thin films of Zn polymer were deposited on the electrode surface, possibly due to the insulating character of the polymer. Conductivity measurements indicated polymers of Cu, Ni, and Co salens with methoxy substituents were highly conductive, with conductivities in the order of 10^{-3} S cm^{-1} in the dry state. In addition, all of the polymers prepared from methoxy-substituted Schiff base complexes **141**, **143**, **148**, **150**, and **152** exhibited electrochromic behavior, changing from transparent green in the reduced state to dark green in the oxidized state (red for Cu poly(salphen)), as characterized by *in situ* spectroelectrochemical studies of the



Scheme 29. Preparation of electropolymerized polymer **133**.

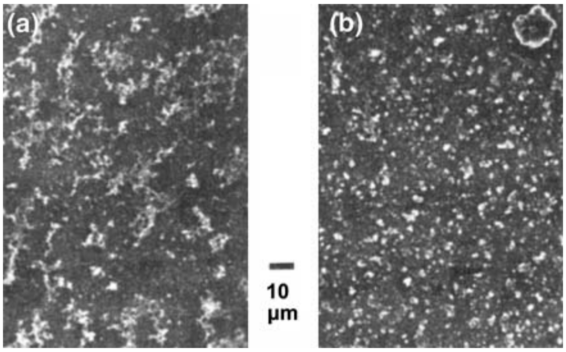
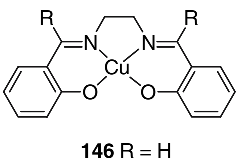


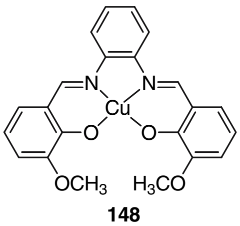
Fig. 5. SEM images of poly(**135**) electrochemically synthesized in (a) MeCN and (b) CH_2Cl_2. Reprinted with permission from reference 63. Copyright 1989 American Chemical Society.

polymer films. Audebert further asserted that direct electropolymerization occurs *para* to the hydroxyl moieties; demetallation of the polymers with sodium hydrosulfite and sodium bicarbonate followed by treatment with dilute sulfuric acid to cleave imine bonds led to the isolation of bis(salicylaldehyde) **154**. A small amount of salicylaldehyde was also detected, likely due to cleavage of imine bonds in terminal groups of the polymers, providing evidence that high degrees of polymerization were achieved. In the same year, Devynck and co-workers also reported the synthesis of Co^{2+}, Ni^{2+}, and Mn^{3+} salen polymers by potential scanning in MeCN electrolytes on glassy carbon electrodes [65]. The Co^{2+} and Ni^{2+} poly(salen)s exhibited electrochemical behaviors similar to those reported by Audebert. Again, Mn^{3+} poly(**153**) has poorly defined CV traces, having only small peaks corresponding to the redox of the Mn centers.

Vilas-Boas and co-workers combined electrochemical techniques with spectroscopic techniques to further characterize Ni(salen) polymers **136** [66]. *In situ* UV–Vis and FTIR spectroscopies were employed to explore the film structure and electronic properties as a function of applied potential. *Ex situ* EPR experiments were performed to elucidate the oxidized species involved in the polymerization. Ultimately, it was found that the electropolymerization of **135** is a ligand-based process that takes place through the phenyl moiety. It was observed that the polymer exhibited poly(phenylene)-like physical and chemical properties, with the Ni^{2+} ion acting as a bridge between biphenylene moieties. Polymer **136** was also prepared by Peters and coworkers, and it was found that thin films **136** on carbon electrodes were capable of catalyzing reductions of a wide range of dihaloalkanes [67]. Applying a static potential (−1.00 V) to the coated carbon electrodes in 0.05 M Me_4NBF_4/MeCN electrolyte with catalytic acetic acid promoted the reductions of various dihaloalkanes, affording the corresponding alkanes in good yields. Other nickel Schiff base derivatives **155** and **156** were also prepared by Vilas-Boas, and their dynamic electrochemical polymerizations were carefully studied by spectroelectrochemistry [68]. It was found that the polymerization and redox switching of **155** involves ligand-based processes as in the case of **135**, and coulometric studies showed that one positive charge is delocalized through each monomer unit. SEM revealed the polymer has a continuous layered morphology, and its morphology does not change upon oxidation of the polymer films. The addition of methoxy substituents in poly(**156**) invoked a more



146 R = H
147 R = CH_3



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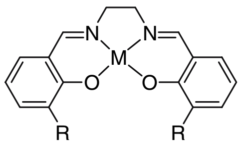
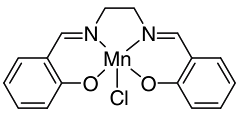


149 M = Co; R = H
150 M = Co; R = OCH_3
151 M = Zn; R = H
152 M = Zn; R = OCH_3



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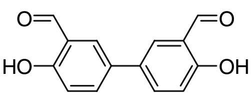
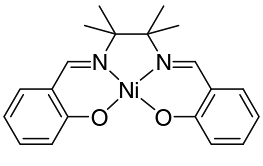


154

complex voltammetric response in comparison to polymer **136** and poly(**155**). Spectroelectrochemical studies indicated that film polymerization and redox switching of **155** involve transfer of two electrons per three monomer units.



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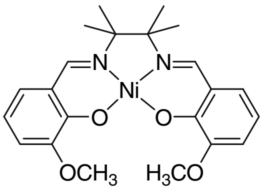
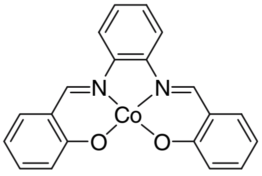


156

Shagisultanova and co-workers also studied electrochemically prepared Ni(salen) and Ni(salphen) polymers [69]. They found that polymerization in the potentiostatic mode occurs most rapidly at ca. + 1.1 V for both poly(**135**) and poly(**144**). Photovoltaic measurements using a polychromic light source indicated reduced polymer films of **136** and poly(**144**) ca. 30 μm thick were capable of generating maximum potentials of 250 and 190 mV, respectively. In a separate report, salen and salphen polymers containing Pt^{2+}, Pd^{2+}, Cu^{2+}, Mn^{2+}, and Mn^{3+} were electrochemically polymerized, and reduced films of Pd(salen) polymer were found to exhibit the largest potential shifts (450 mV) in photovoltaic studies [70].



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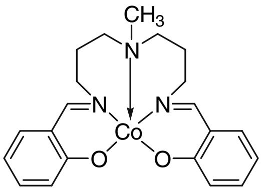
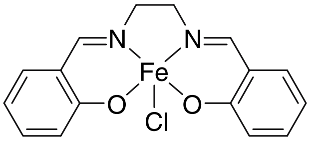


158

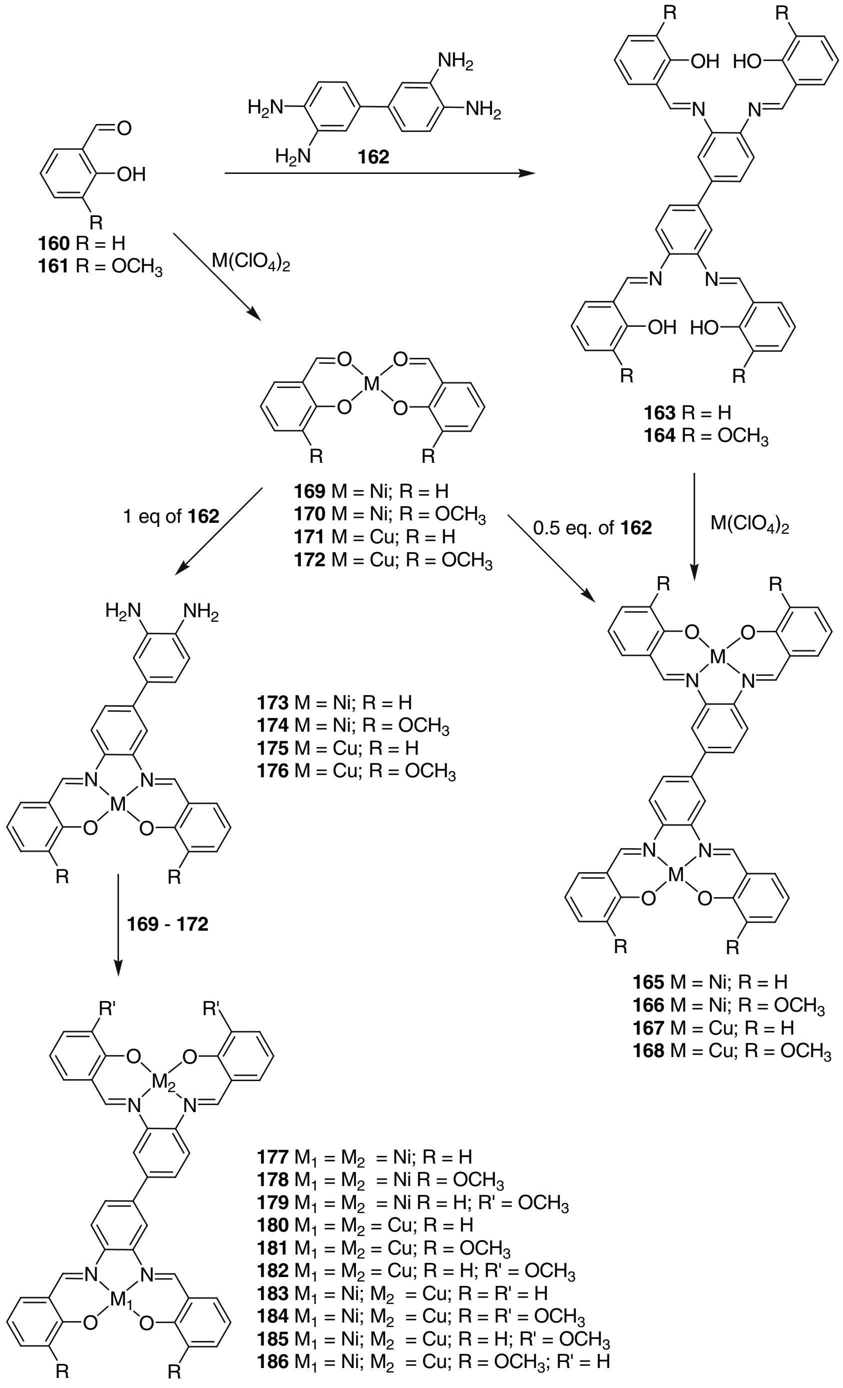
Okada and co-workers [71] electropolymerized cobalt Schiff base complexes **149**, **157** and **158** on pyrolytic graphite electrodes, and the films were tested as oxygen reduction catalysts in aqueous solutions. Cyclic voltammograms of the polymer-modified electrodes were measured in aqueous solutions of various pH values saturated with 1 atm O_2, and a current corresponding to O_2 reduction appeared around 0.6–0.9 V. Good catalytic performance was observed in neutral or basic media, but the polymers behaved poorly in acidic media. Polymers of Co(salen) were the most effective catalysts among the three polymers tested, catalyzing a 67 % conversion of O_2 to H_2O.

Iron Schiff base complexes are well known for their ability to catalyze oxidation or reduction reactions, such as aerobic oxidation of hydrocarbons [72], and oxidative polymerization of bisphenol A [73]. Audebert reported the electropolymerization of iron salen **159**, and the ability of the resulting thin films to catalyze electroreductions of hydrogen peroxide and oxygen were investigated [74]. Electropolymerization of **159** was found to be very difficult in MeCN, but thin films can be obtained in 0.1 M Et_4NClO_4/CH_2Cl_2 electrolyte, although the polymerization stopped after only a few cycles. Thin films of poly(**159**) grown on ITO were studied by CV in MeCN, and the traces revealed peaks corresponding to oxidation of the ligand (+ 0.95 V) and reduction of Fe^{3+} (–0.35 V), but the electroactivity is poor and the $Fe^{3+/2+}$ couple diminished after a few cycles. More stable electroactivity of the film was observed in aqueous electrolyte. The electrocatalytic behavior of the films toward reduction of H_2O_2 and O_2 was studied in a phosphate buffer solution, and reductions of the substrates were evident from the shifts in reduction potential (ca. + 120 mV for reduction of H_2O_2 and 400 mV for O_2). Based on measurements of current and potential, catalytic efficiency is high for reduction of O_2, but occurred rather slowly for the reduction of H_2O_2.



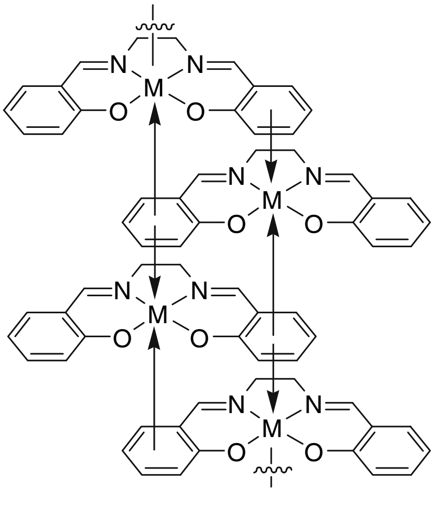
159

Audebert reported the synthesis of ladder polymers containing Schiff base complexes [75]. Templated synthesis allowed the preparation of numerous derivatives such as symmetric bimetallic bis(salphen) complexes **165**–**168**, the bis(salphen)s with methoxy substituents on only one of the salphen moieties (**179**, **182**, **185** and **186**), and bis(salphen)s containing two different metals **183**–**186**, Scheme 30. However, the poor solubility of the Cu^{2+} complexes and mixed-metal Cu^{2+}/Ni^{2+} bis(salphen) complexes impeded electrochemical polymerization. As a result, only polymers of Ni complexes were reported. Electropolymerizations of the ladder polymers were performed at a controlled potential or upon repeated cycling in 0.1 M Et_4NClO_4/MeCN electrolyte as in typical



Scheme 30. Preparation of bis(salphen)s **165**–**168** and **177**–**186**.

electropolymerization of salen complexes. The bis(salphen) complexes behave as two independent salphens, possibly due to the weak conjugation through the tetraamine bridge. The authors reported that the degree of polymer crosslinking depends on the synthesis potential. When a given polymer was synthesized at relatively low potential, CV in fresh electrolyte revealed that the first few scans (ca. 5) were very different from the stabilized voltammogram. The authors attributed this behavior to overoxidation of the polymer films to form highly crosslinked polymers. This interesting characteristic of the ladder polymers should allow easy control of polymer properties via controlling the electropolymerization potential. More interestingly, if the solubility of the mixed-metal monomers can be improved, new bimetallic materials may be synthesized.



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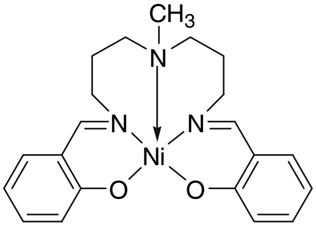


188

Timonov and co-workers [76] electrochemically synthesized Ni and Pd Schiff base polymers. Despite the strong evidence provided by Goldsby and Audebert for the formation of linear Schiff base polymers, Timonov proposed poly(salen)s to have the stacked structure **187**. Interestingly, when non-planar Ni Schiff base complex **188** was subjected to electropolymerization in DMF, no product formation occurred. The authors attributed the inability for non-planar Schiff base complexes to form polymers as evidence that the polymers have a stacked structure. However, the structure of the electrochemically prepared Schiff base polymers probably contained aggregated linear polymer chains. Electropolymerized Ni(salen) and Pd(salen) were fabricated into nanostructures by Timonov [77], Fig. 6. These highly conductive nanostructured polymers are well aligned and ordered, containing few defects in the polymer structure. Polymeric nanowires were synthesized using microporous alumina membranes as the template. The microporous alumina membrane was first sputtered with a thin layer of gold, and subsequent repeated cycling between potentials of −0.3 and +0.4 V in the presence of H_2PtCl_6 in dilute sulfuric acid afforded short segments of Pt nanowires in the pores of the membrane. Poly(salen)s were then deposited on the Pt nanowires by potential cycling between 0 and 1.1 V in 0.1 M Bu_4NBF_4/MeCN electrolyte. Alternatively, the polymers could be electrochemically polymerized by applying a constant potential at which the maximum rate of polymer growth was observed. SEM images of cross-sections of the Ni poly(salen) revealed the lengths of the polymer fibers were ca. 0.6 ± 0.1 μm, and the alumina templates can be dissolved in 2 M NaOH to afford a brush-like nanostructure. Conductivities of nanostructured Ni poly(salen) that are 20 nm in diameter are 5 times higher than bulk samples of the same polymer.

Reddinger and Reynolds [78] prepared new Schiff base complexes incorporating a thiophene

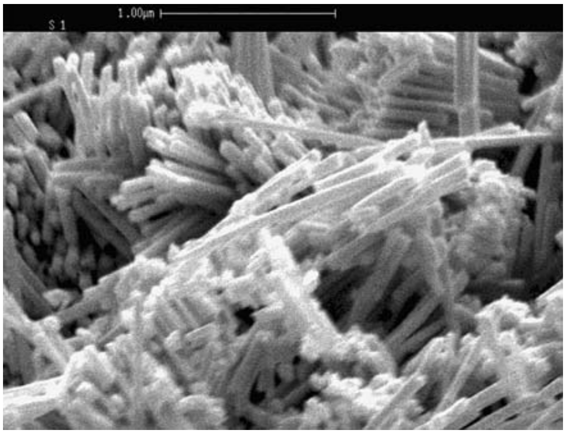
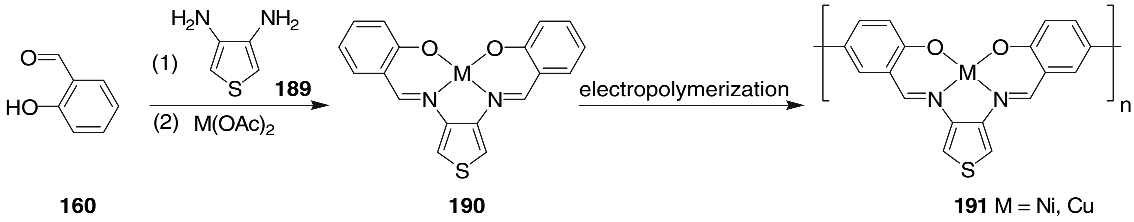
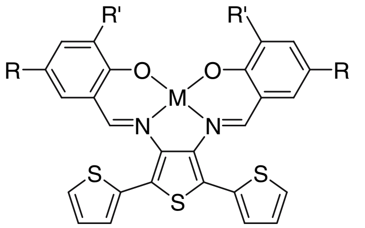


Fig. 6. SEM image of polymeric Pd(salen) nanostructure. Reprinted with permission from reference 77. Copyright 2003 American Chemical Society.

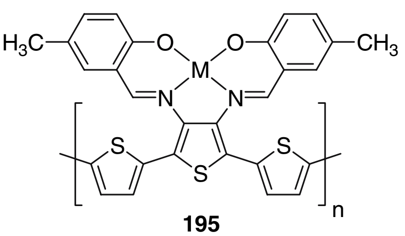


Scheme 31. Electrochemical synthesis of polymer **191**.

moiety by condensation of 3,4-diaminothiophene **189** with salicylaldehyde followed by addition of metal acetates, Scheme 31. Nickel and copper monomers **190** were subjected to repeated potential cycling between −0.5 V and + 0.9 V in 0.1 M Bu_4NClO_4/CH_2Cl_2 to form thin films. Increases in potential peaks corresponding to polymer oxidation (+0.55 V) and reduction (+0.50 V) after repeated potential scanning indicated the formation of polymeric product. Films of polymers **191** grown on platinum electrodes were found to be very redox stable, exhibiting less than 7% loss of electroactivity after 50 repeated scans in the potential range of −0.5 to +1.0 V. The same polymers were prepared on ITO electrodes for the study of their electrochromic behavior. The Cu polymer is transparent light green in its reduced state and transparent dark green in its oxidized state, and the Ni polymer toggles between transparent orange (reduced) and transparent green (oxidized).



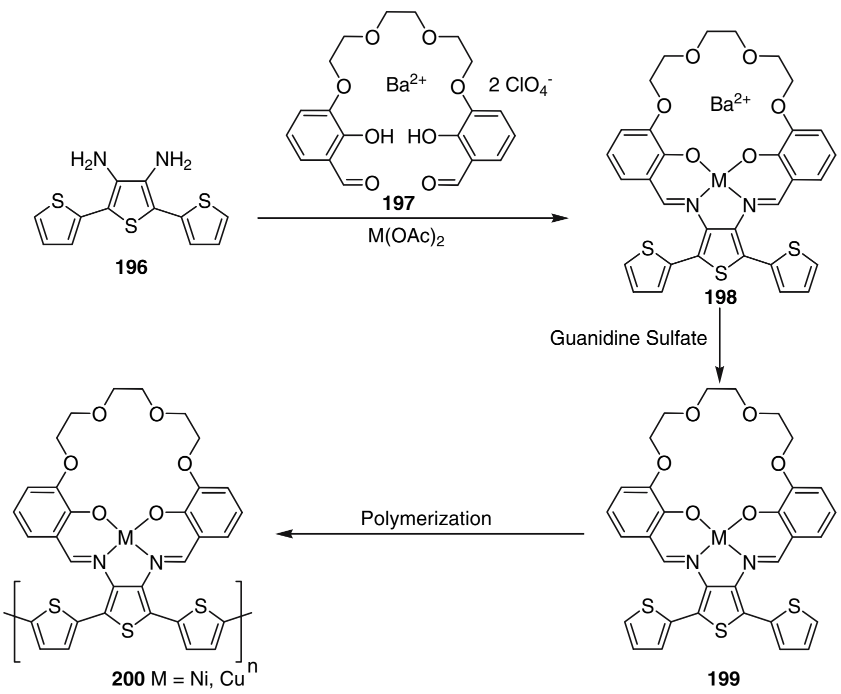
192 M = Cu, R = H, R' = H
193 M = Cu, R = Me, R' = H
194 M = Cu, R = Me, R' = Me



195

Reynolds determined the structure of polymers **191** employing a similar strategy used by Goldsby of placing methyl substituents on positions where the polymeric linkage can possibly occur. As expected, it was found that blocking the position *para* to the phenolic oxygen in monomer **190** inhibited polymerization, thereby indirectly confirming the structure of polymer **191**. The electropolymerization of other monomers **192**–**194** containing terthiophenes was investigated. Copper complex **192** exhibited similar electrochemical behavior at slightly higher potentials than **191**, and the CV traces suggested the polymer contains both phenyl and thiophene linkages. When the *para* position of the phenolic ring in Cu complex **193** was blocked, electropolymerization proceeded and redox activities different than **191** and **192** were observed at lower potentials. When both the *ortho* and *para* position to the phenolic position were blocked, as in complex **194**, polymerization occurred with electrochemical behavior closely resembling that of complex **193**. The authors attributed these observations to the formation of Schiff base polymers **195** with a polythiophene backbone. It is interesting that these monomers can be functionalized to build either polymers with poly(phenylene) linkages or poly(thiophene) linkages.

Reynolds [79] synthesized new salen-type polymers **200** containing crown ether moieties to afford new conjugated polymers that are capable of complexing multiple metal ions. Schiff base complexes **199** were synthesized using a templation method, Scheme 32. Due to the instability of the Schiff base ligand, bis(salicylaldehyde) **197** bridged by a glyme chain was complexed with Ba^{2+} prior to condensation with diamine **196** and metallation with transition metals. The complexed template Ba^{2+} ions can then be removed by treatment with guanidine sulfate to afford monomer **199**. Polymers **200** were prepared as thin films by repeated potential cycling between −0.3 and + 0.8 V in 0.1 M Bu_4NClO_4/CH_2Cl_2. The

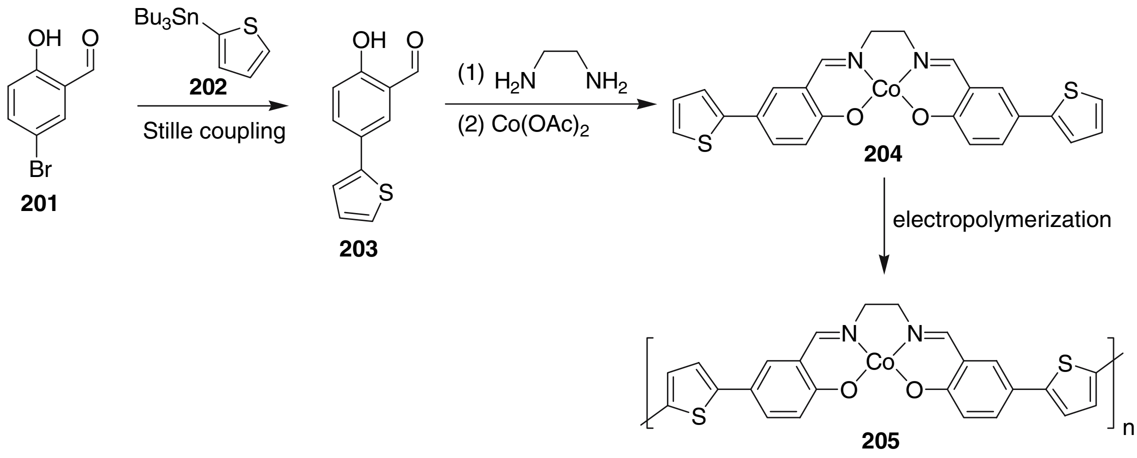


Scheme 32. Electrochemical synthesis of polymer **200**.

ability of the polymers to sense alkali metals was tested on polymers grown on platinum electrodes in electrolytes containing alkali and alkaline earth perchlorate salts. Relatively small shifts in the anodic and cathodic peak potential were observed for polymers exposed to alkali cations (10–80 mV), and the complexed ions can be exchanged by simply stirring the polymer films in electrolytes containing the new alkali ions. Incorporation of alkaline earth cations resulted in larger shifts in the anodic and cathodic peak potentials (70–140 mV); however, the coordination appeared to be irreversible since no change occurred in the cyclic voltammograms when the electrode was exposed to electrolyte containing alkali cations. In addition to cation sensing, the polymers are also capable of detecting Lewis bases. Voltammograms of the Ni polymer modified electrodes in the presence of dilute pyridine solution showed ca. 75% loss in electroactivity. The authors attributed this behavior to the formation of adducts between the transition metal ion and the Lewis base, which inhibits electronic interaction between the polymer chains.

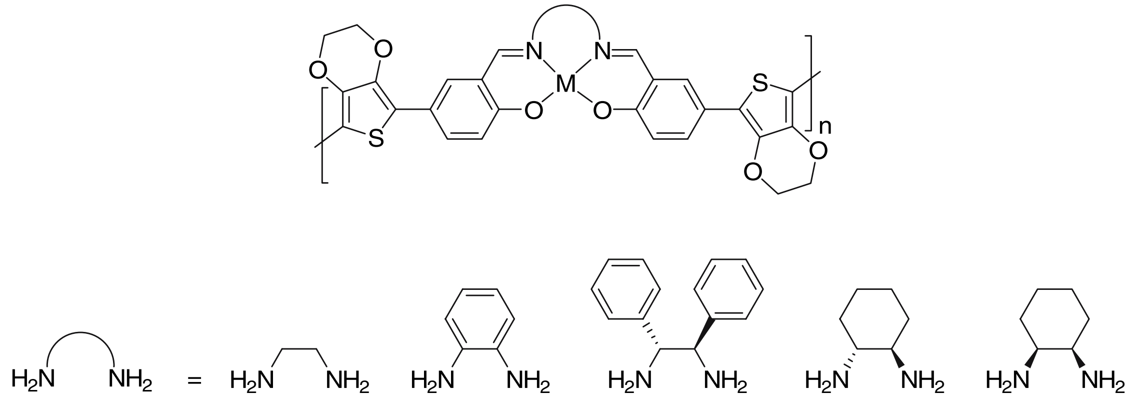
Swager and co-workers [80] prepared new monomer **204** having pendant thiophene groups via palladium-catalyzed Stille coupling of **201** and **202** followed by condensation with ethylenediamine and then metallation with $Cu(OAc)_2$, Scheme 33. Cobalt complex **204** was electrochemically polymerized in MeCN by scanning the potential between −0.75 and + 0.85 V to afford yellow films. Conductivity measurements indicated that polymer **205** has a conductivity of 40 S cm^{-1}; however, *in situ* conductivity measurements indicated that the $Co^{2+/3+}$ redox couple did not contribute to the overall conductivity. Analogous polymer **209** with 3,4-ethylenedioxythiophene (EDOT) was synthesized using a similar strategy to the preparation of **205**, Scheme 34. The redox potential of the organic polymer backbone was shifted toward lower potential to coincide with the $Co^{2+/3+}$ redox wave. Conductivity measurements revealed polymer **209** has high conductivity of 250 S cm^{-1}. Interestingly, exposure of the polymers to Lewis base such as pyridine and 2,6-lutidine resulted in a significant loss in conductivity (ca. 66% decrease), as observed for polymer **200**.

Swager and co-workers [81] systematically investigated the relationship between interchain interactions (i.e., π aggregation) and the bulk conductivity of salen-type polymers. A series of Cu, Ni, and UO_2 polymers **210**–**224** with diamine bridges of varying steric bulk were prepared. Cyclic voltammetry indicated varying interchain spacing with substituents of different sizes on the polymer to have a large effect. Copper polymer **211** with the least sterically

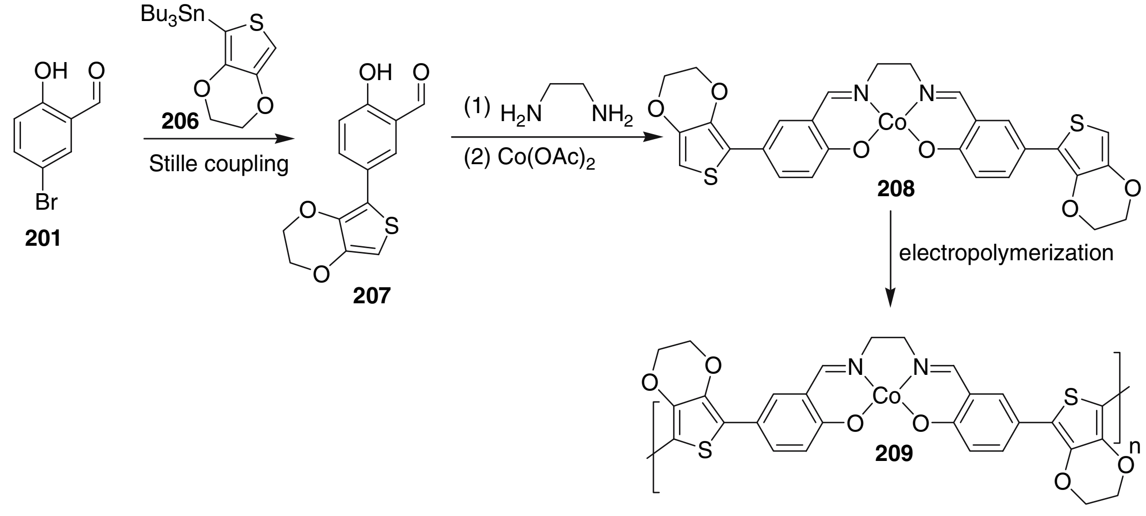


Scheme 33. Electrochemical synthesis of polymer **205**.

encumbered ethylenediamine bridge displayed four one-electron redox processes, whereas polymers with sterically hindering diamine substituents such as **217** displayed only two redox waves. These results from CV, together with spectroelectrochemistry and *in situ* EPR measurements indicate that the increase in bulkiness of the substituents on the polymers has a large effect on the ability of the polymers to form π aggregates, which in turn affects electronic communication between polymer chains. Conductivity measurements indicate a decrease in conductivity in the order of **210** ≈ **213** > **219** > **222** > **216**, correlating well with the bulkiness of the substituents. On the contrary, the Ni polymers all displayed high conductivities, and they appeared to be less sensitive to the steric hindrance of the substituents. The authors attributed these observations to the rigid square-planar geometry of the Ni complexes and the available d_{z^2} orbital facilitating electron hopping between polymer chains.



Cobalt polymer **209** was investigated for potential applications as an oxygen-reducing electrocatalyst [82] and as a nitric oxide sensor [83]. The development of materials capable of electrocatalytic reduction of O_2 to H_2O is relevant to fuel cell technologies. Films of polymer **209** coated on glassy carbon surfaces were studied with CV in 0.1 M KH_2PO_4/K_2HPO_4 buffer solutions. It was observed that in the presence of O_2, a new reduction peak (+0.05 V) emerges in the cyclic voltammogram.



Scheme 34. Electrochemical synthesis of polymer **209**.

Rotating ring-disc voltammetry measurements suggested the polymer catalyzes a four electron process to reduce O_2 to H_2O, without significant production of H_2O_2 as a side product. However, polymer degradation is observed in acidic media typical to conditions found in fuel cells, which is likely due to hydrolysis of the imine functionality. Polymer **209** was also investigated as a sensing material for nitric oxide (NO). When the polymer is exposed to NO in a 0.1 M Bu_4NPF_6/MeCN electrolyte, CV revealed that the $Co^{2+/3+}$ couple shifted slightly toward positive potential such that there is a better overlap between the $Co^{2+/3+}$ couple and the redox potential of the organic polymer framework. This electrochemical response to NO is reversible, as the CV of the polymer film quickly returned to its original state when the film is placed into fresh NO-free electrolyte. In addition, the polymer exhibited reversible changes in conductivity by ca. 30% upon exposure to NO, which is probably due to better redox matching of the conducting polymer backbone and the transition metal center.

5. CONCLUSIONS AND OUTLOOK

Since the first report of insoluble polymers containing Schiff base complexes by Marvel and Tarköy 50 years ago, the emergence of new synthetic methods and characterization techniques have allowed major developments in the field of metal-containing polymers. Although Schiff base complexes were demonstrated to have unique catalytic, nonlinear optical, luminescent, conductive, and sensory properties, their integration into macromolecules remains difficult due to their inherent insolubility. Through copolymerization with soluble monomers, and addition of solubilizing groups onto the metal complexes, soluble high molecular weight polymers can be prepared and their chemical and physical properties have been carefully studied. By choosing appropriate co-monomers, mechanical, thermal, chemical, and electronic behavior of the polymers can be tailored to meet specific applications. The discovery of electrochemically polymerized metal Schiff base polymers by Goldsby presented a new strategy to form stable polymeric films on a large variety of electrode surfaces. A great deal of effort has been devoted to elucidating the mechanism of electropolymerization, and studying redox and charge transport properties of the polymer films. Several potential applications for these polymer-modified electrodes have been proposed in the area of catalysis, conductivity, electrochromism, and sensors for small molecules.

In the past two decades, the discovery of conductive π-conjugated polymers has spurred extensive research effort to incorporate a variety of functional molecules into polymeric π-conjugated frameworks. Among the large amount of literature on conjugated polymers, the combination of metal complexes such as metalloporphyrins and phthalocyanines has drawn much attention as these materials have properties that are not found in other organic-based polymers. Surprisingly, there are only a few reports of π-conjugated polymers containing metal

Schiff base complexes despite the attractive properties exhibited in their molecular or non-conjugated polymeric counterparts. It is clear that the poor solubility of Schiff base complexes and synthetic difficulties in obtaining polymerizable monomers have hindered the development of these polymers. These challenges were met when Katz reported helical conjugated Schiff base type metal-containing ladder polymers, demonstrating clever strategies to overcome both the solubility and synthetic difficulties. Although work in this area has proven to be demanding, it also provides researchers with tremendous opportunities for exploration and discovery. With new ideas and insights, it is expected that we will soon see this field blossom into a mature state ripe for a plethora of exciting developments.

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