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Organoiron Polynorbornenes with Pendent Arylazo and Hetarylazo Dye Moieties

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Summary: Organoiron polynorbornene containing arylazo or hetarylazo dye chromophores has been prepared via ring opening metathesis polymerization using Grubbs' catalyst. The obtained polymers were isolated as brightly colored materials and displayed good solubility in polar organic solvents. The colors of these polymers were affected by the nature of the incorporated azo chromophores. Thermogravimetric analysis of these materials showed that the cleavage of the cyclopentadienyliron ($CpFe^+$) moieties was between 225 and 231 °C, while the degradation of the polymer backbones occurred between 400 and 450 °C. UV-vis studies in DMF showed that the organoiron polymers containing arylazo dyes exhibit wavelength maxima around 425 nm. However, the replacement of these arylazo moieties with hetarylazo dyes displayed substantial bathochromic shifts in the λ_{max} values (≈ 511 nm).

Keywords: arene complexes; arylazo dyes; cyclopentadienyliron; hetarylazo dyes; polynorbornene

Introduction

Ring opening metathesis polymerizations (ROMP) of cycloalkenes and bicycloalkenes have been extensively explored.[1-16] The development of highly active metal carbene catalysts allows for controlling the molecular weight and the backbone configurations of the resulting polymers.[3-8] To date, norbornene remains one of the most studied molecules due to its facile functionalizations and high reactivity in ROMP. [1-16] The introduction of various substituents to norbornene monomers and polymers allows for varying the physical and the chemical properties

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of these materials. Some of the properties include liquid crystallinty, redox, luminescence as well as biological properties. [9-16]

The past few decades have seen tremendous attention given to the development of metal-containing polymers. This interest stems from the unique properties that this class of polymers possess. For example, the incorporation of metal moieties into the macromolecules backbone and side chains enhances the solubility of these materials and offers interesting properties such as hardness, magnetism, catalytic behavior and redox activity. [17-29]

Our research has focused on the design of novel iron-based macromolecules using the cyclopentadienyliron methodology. The exceptional electron-withdrawing ability of the cationic iron moieties facilitates the nucleophilic aromatic substitution reactions of the chloroarene complexes and allows for the isolation of novel monomeric and polymeric material under mild conditions.[17, 20-22, 26-32] Recently we have reported the synthesis of thermally stable polynorbornene containing pendant etheric linkages.[30-32] Polynorbornenes functionalized with organometallic moieties in their side chains have also been investigated. Albagli and coworkers[11] have reported the synthesis of electrochemically-active polynorbornenes containing ferrocenyl moieties in their side chains. We also synthesized the first examples of polynorbornenes substituted with side chains containing $CpFe^+$ complexes.[30]

Currently, we are exploring the incorporation of arylazo moieties into macromolecules backbones and side chains. Polymers containing azo dyes are potential candidates for reversible optical storage systems, electrooptic modulators, and photorefractive switches.[33-40] In one of our recent articles, we reported the first example of cationic iron-coordinated polyaromatic ethers and thioethers functionalized with azo dyes in their side chains.[41] As well, we have also reported ring opening metathesis polymerization of novel organoiron norbornene monomers containing arylazo moieties using Grubbs catalyst.[42] Addition polymerization of norbornene monomers functionalized with arylazo chromophores have also been reported.[39]

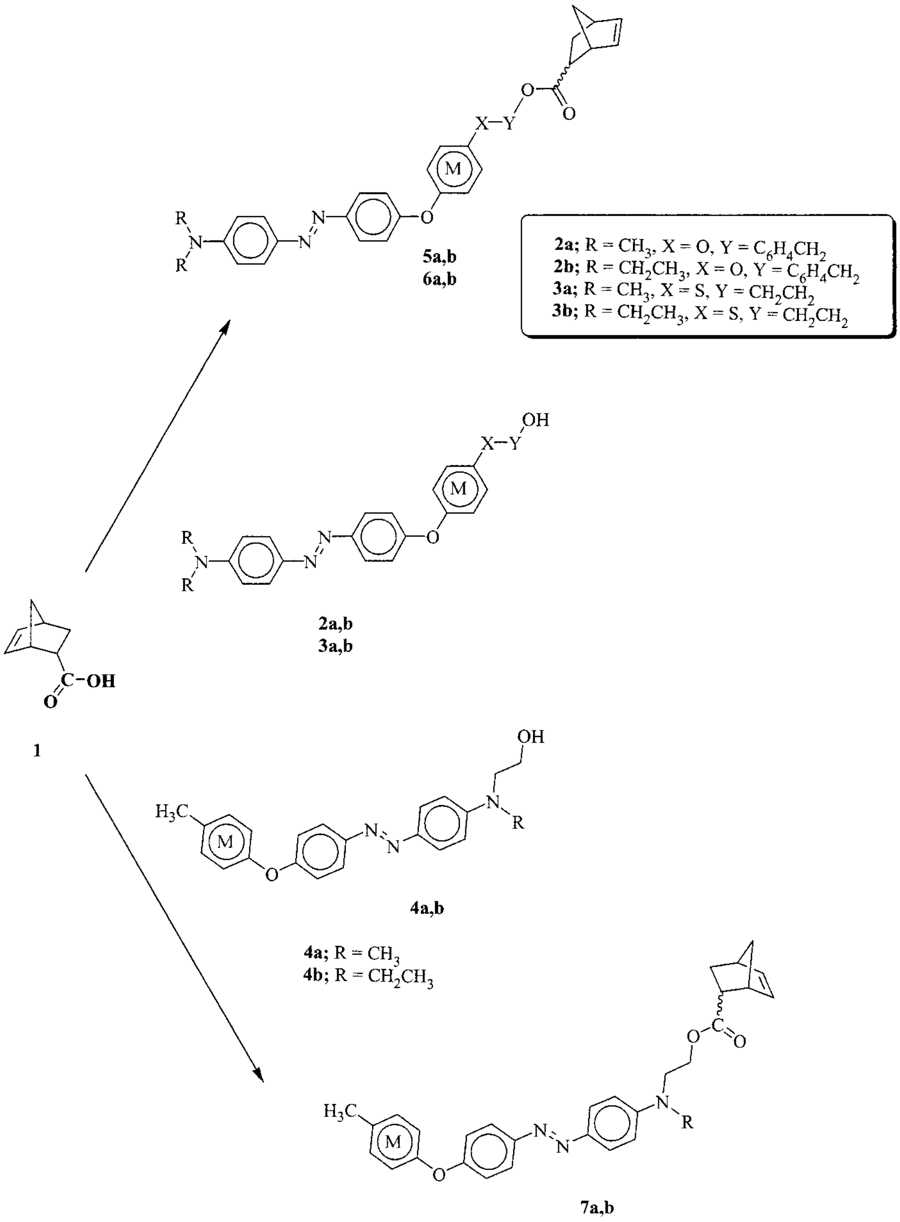
This article is focused on the introduction of hetarylazo dyes into the norbornene monomers. The colour of the resulting organometallic polymers containing these dyes ranged from reddish-violet to blue depending on the nature of the dye moiety. Herein, we will describe the synthetic strategies, spectroscopic and analytical characterizations of the monomeric and polymeric materials.

Results and Discussion

Monomer Synthesis

Using metal-mediated nucleophilic aromatic substitution reactions, various monometallic complexes containing arylazo moieties with terminal hydroxyl groups have been prepared. Scheme 1 shows the design of organoiron norbornene monomers functionalized with the arylazo chromophores. Reactions of chloroarene complexes with phenolic arylazo molecules resulted in the formation of organoiron arylazo complexes containing terminal hydroxyl groups (**2a,b-4a,b**). These complexes were subsequently reacted with *exo-*, *endo-*5-norbornene-2-carboxylic acid (**1**) resulting in the formation of novel norbornene monomers functionalized with cyclopentadienyliron-dye complexes **5a,b-7a,b**.

Characterizations of these monomeric species were determined using one- and two-dimensional NMR spectroscopy due to the existence of the *exo-* and *endo-*isomeric structures. For example, Figure 1 shows the HH COSY NMR of the aliphatic protons of monomer **5a**. Identification of *endo* and *exo* isomers was determined based on the assignment of the olefinic protons H_6(n) and H_5(n), which are strongly coupled with each other and resonate between 5.86 and 6.15 ppm respectively. The bridgehead protons H_1(n) (3.21 ppm) and H_4(n) (2.81ppm) appeared as broad singlets and identified via their coupling with H_6(n) and H_5(n). The connectivities between H_4(n) and the H_3 protons as well as the strong coupling between H_3(x) and H_3(n) protons led to the assignment of H_3(x) to the multiplet at 1.89-1.93 ppm and H_3(n) to the multiplet at 1.27-1.41 ppm. The H_{7a}(n) and H_{7s}(n) were also strongly coupled to each other and resonated within the multiplet at 1.27 to 1.41 ppm and the doublet at 1.50 ppm. The remaining norbornene protons were determined using the same methodology.


5a,b
6a,b
2a; R = CH3, X = O, Y = C6H4CH2
2b; R = CH2CH3, X = O, Y = C6H4CH2
3a; R = CH3, X = S, Y = CH2CH2
3b; R = CH2CH3, X = S, Y = CH2CH2
2a,b
3a,b
1
4a,b
4a; R = CH3
4b; R = CH2CH3
7a,b
M
R
N
O
X
Y
OH
C
H3C

Scheme 1

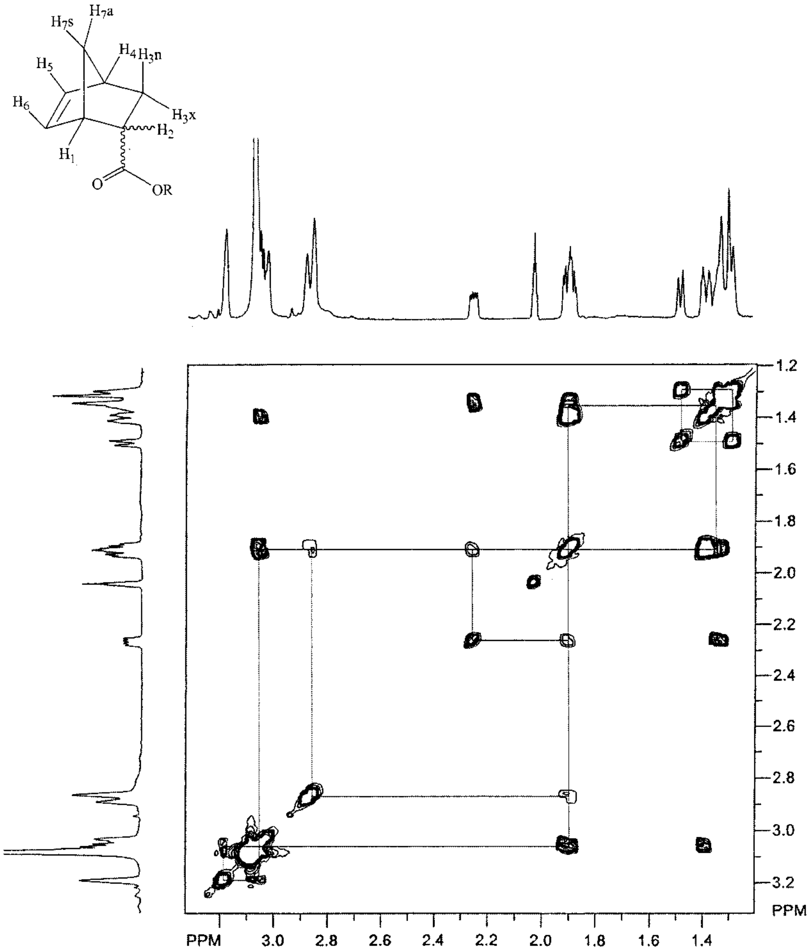
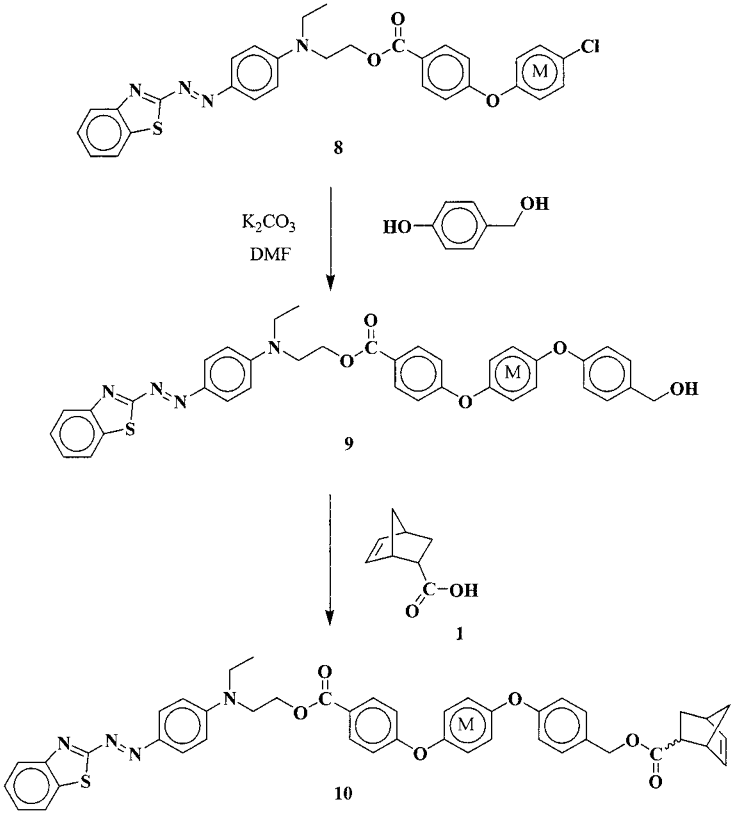


Figure 1. HH COSY NMR spectrum of monomer **5a**.

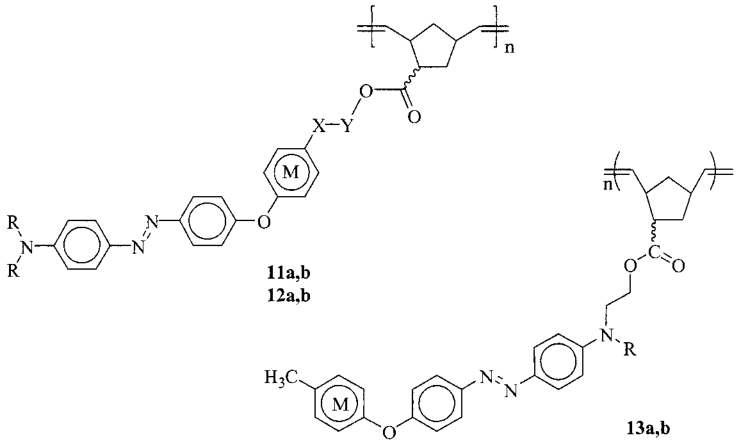
Condensation reactions of cyclopentadienyliron complexes containing carboxylic groups with hydroxyl groups benzothiazole azo dyes allowed for the isolation of novel organoiron complexes incorporating hetarylazo dyes. These complexes were reacted with 4-hydroxy benzyl alcohol and then capped with the norbornene molecules to form the first example of organoiron norbornene monomers functionalized with hetarylazo dye chromophores as shown in Scheme 2. The monomeric units were isolated in good yields, and identified using spectroscopic analysis.



Scheme 2

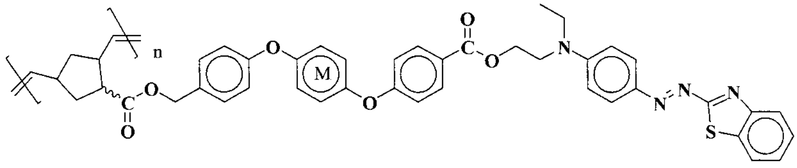
Polymerization

Ring opening metathesis polymerization of norbornene monomers (**5a,b**, **6a,b**, **7a,b**, **10**) using Grubbs' catalyst with monomer/initiator ratio [20]:[1] led to the isolation of metallated polynorbornenes containing azo dyes in the side chains. The obtained polymers displayed excellent solubility in DMF, DMSO and acetonitrile. While polymers **11a,b-13a,b** were orange solids, polymer **14** was isolated as purple solid. This change in color was attributed to the incorporation of benzothiazole azo chromophore into the side chain of polynorbornene.



11a,b
12a,b

13a,b



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Characterizations of the polymeric materials were performed using spectroscopic and thermal techniques. As an example, the ^1H NMR spectra of the resulting polymers showed disappearance of the olefinic protons from the norbornene monomer between 5.78 and 6.18 ppm, and the presence of a new set of peaks between 5.00 and 5.37 ppm, which is consistent with the double bond formation of the polymer backbone and thus verified the success of the polymerization.

Photolytic demetallation of the organoiron polymers was performed prior to the molecular weight determination due to the interaction of the cyclopentadienyliron moieties with the gel permeation chromatography (GPC) columns. The molecular weights of the organic polymers were determined using GPC and were in the range of 9 200-21 800 which corresponds to M_w of 14 300-31 600 for the metallated analogues. Thermal stability of the metallated and demetallated functionalized polymers was examined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA data of the metallated polynorbornene showed that the cationic organoiron moieties cleave between 225 and 231 °C, while the degradation of the polymer backbones occurred between 400 and 450 °C. Differential scanning calorimetric studies illustrated that the glass transition temperatures (T_g) of the resulting polymers was affected by the length of the side chains, the position of the cationic iron moieties and the substituted azo chromophores. The T_g's values for the metallated polymers were in the range of 140-178 °C while their organic analogues exhibit T_g's between 75 and 104 °C. Polymer **12b** shows a T_g at 140 °C (Figure 2).

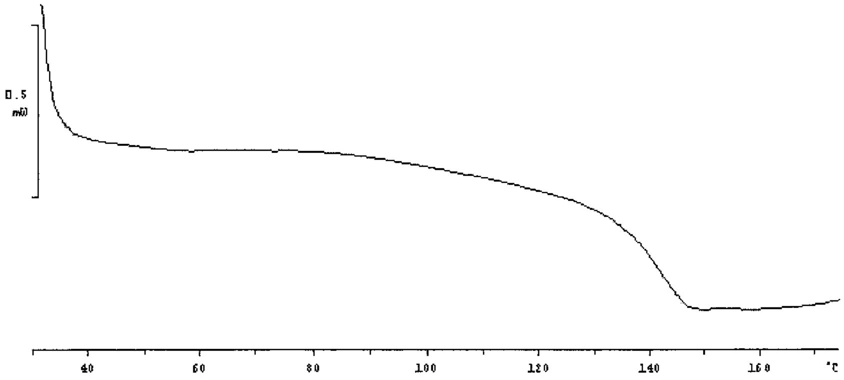

Figure 2. DSC thermogram of polymer **12b**.

UV-visible spectroscopic analysis of the colored organoiron polynorbornene was examined. The wavelength maxima of the obtained polymers were influenced by the nature of the azo chromophore moieties. For example, the incorporation of benzothiazole based chromophore instead of an arylazo dye into the polymer side chain displayed substantial bathochromic shifts in the λ_{max} values. This strong bathochromic effect may be attributed to the d-orbitals of the sulfur. The λ_{max} of polymers **13a** in DMF occurs at 424 nm, while polymer **14** exhibits wavelength maximum at 511 nm (Figure 3, curve **a** and **b** respectively). These values increased after the addition of a hydrochloric acid solution due to the formation of the azonium ions.[43] Polymers **13a** show λ_{max} at 520 nm while the maximum of polymer **14** occurred at 608 nm with a shoulder at 574 nm, which is consistent with the π-π* transition of azo dyes (Figure 3).

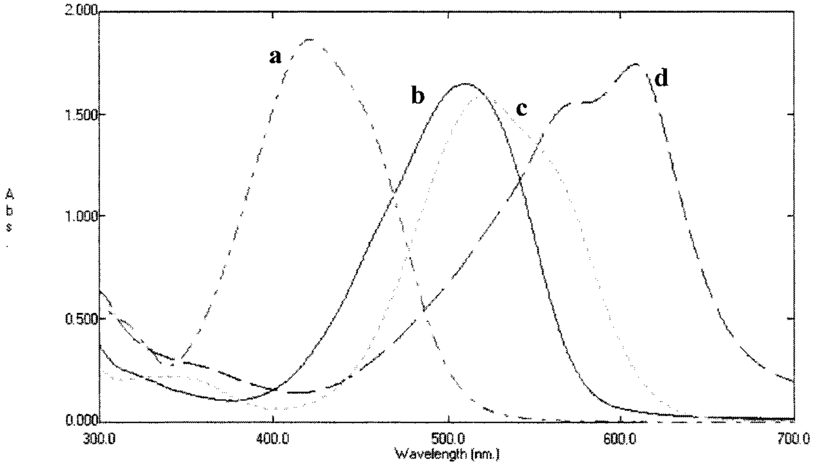

Figure 3. UV-vis spectra of (a) polymer **13a** in DMF, (b) polymer **14** in DMF, (c) polymer **13a** in DMF/HCl and (d) polymer **14** in DMF/HCl.

Conclusions

Novel organoiron polynorbornene functionalized with arylazo and hetarylazo dyes have been synthesized. The molecular weight of the metallated polymers was estimated to be in the range of 14 300-31 600. Differential scanning calorimetry showed that the T_g's of the organoiron polymers ranged from 140 to 178 °C, while their organic analogues displayed T_g values from 75 to 104 °C. Visible spectra of the resulting colored polymers in DMF and DMF/HCl solutions showed that the nature of the incorporated azo chromophore influences the wavelength maxima of these materials.

Acknowledgements

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