Macromol. Symp. **196**, *89–99 (2003)*

Organoiron Polymers Containing Azo Dyes

Alaa S. Abd-El-Aziz, Erin K. Todd, Rawda M. Okasha, Tarek H. Afifi*

Department of Chemistry, The University of Winnipeg, Winnipeg, Manitoba, Canada
R3B 2E9
E-mail: a.abdelaziz@uwinnipeg.ca

Summary: The synthesis of cationic organoiron polymers with azobenzene moieties in their side chains has been accomplished via nucleophilic aromatic substitution and ring-opening metathesis polymerization (ROMP) reactions. Polyaromatic ethers and thioethers with azobenzene moieties in their side chains were functionalized with different chromophores to yield yellow-, orange- and red-colored polymers. Polynorbornenes with azobenzene-containing side chains were isolated following ROMP of their monomeric analogs. All of the organoiron polymers were soluble in polar organic solvents and underwent reversible electrochemical reduction processes. Photobleaching of the azobenzene-containing polymers was achieved in the presence of hydrogen peroxide. The metallated polymers had glass transition temperatures approximately 50 to 80 °C higher than their organic analogs.

Keywords: azobenzene; cyclopentadienyliron complexes; organoiron polymers; poly(aromatic ethers); polynorbornene

Introduction

Organoiron polymers are one of the most important classes of metal-containing polymers.[1-4] This class of polymer has been the topic of numerous studies in light of their interesting properties and applications. The focus of our research is on the use of cyclopentadienyliron-coordinated chloroarenes in the design of iron-based monomers and polymers.[2, 5] The mild reaction conditions associated with the nucleophilic aromatic substitution reactions of complexed chloroarenes as well as the variety of dinucleophiles used in these reactions has allowed for an efficient route to the synthesis of functionalized monomers and polymers. Photolytic demetallation of organoiron monomers resulted in the decoordination of the cyclopentadienyliron moieties and the isolation of the free organic monomers. Our research has utilized both the cationic organoiron, and their corresponding organic monomers to produce polymeric materials. For example, oligomeric ether complexes containing terminal naphthyl groups were demetallated

CCC 1022-1360/00/$ 17,50+.50/0

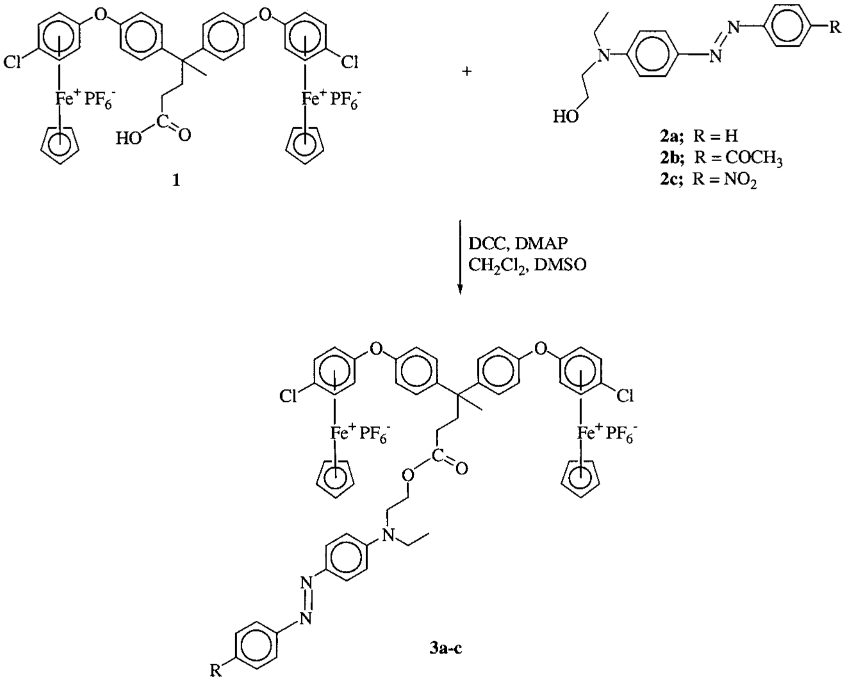
and subsequently polymerized using ferric chloride to yield polyaromatic ethers.[6] Substituted norbornene monomers were also synthesized using cationic arene cyclopentadienyliron complexes.[7-10] These monomers were either demetallated and then subjected to ring-opening metathesis polymerization, or the organoiron monomers were polymerized directly. The organoiron-coordinated polynorbornenes were also demetallated using photolytic techniques in order to conduct molecular weight measurements on these materials. Radical polymerization of methacrylate monomers functionalized with cyclopentadienyliron complexes has also produced high molecular weight cationic organoiron polymethacrylates.[11, 12] The direct polymerization of dichloroarene complexes with bisphenols and bisthiols produced polyaromatic ethers and thioethers with cyclopentadienyliron cations pendent to the polymer backbone.[13, 14] It was found that the organoiron groups increased the solubility of these polymers relative to their corresponding organic analogs. The electrochemical properties of oligomeric and polymeric materials containing arene complexes of cyclopentadienyliron have been examined using cyclic voltammetry and it was found that the cationic eighteen-electron iron complexes underwent reversible reduction steps.[15] We have also found that cationic organoiron polymers exhibit polyelectrolyte effects in polar organic solvents.[16]

Currently, there is considerable interest directed towards the synthesis of polymers containing azobenzene moieties in their backbones and side chains.[17-27] While a number of different classes of organic polymers have been studied, there has been very little research detailing azobenzene-modified organometallic polymers. However, Manners has reported the synthesis and liquid crystalline properties of polyferrocenylsilanes incorporating azobenzene groups in their side chains.[28] Recently, we have been investigating the incorporation of azobenzene chromophores into the side chains of cationic organoiron polymers.[29, 30] This article will describe the synthesis and properties of azobenzene-containing organoiron polymers via metal-mediated nucleophilic aromatic substitution reactions and ring-opening metathesis polymerization.

Results and Discussion

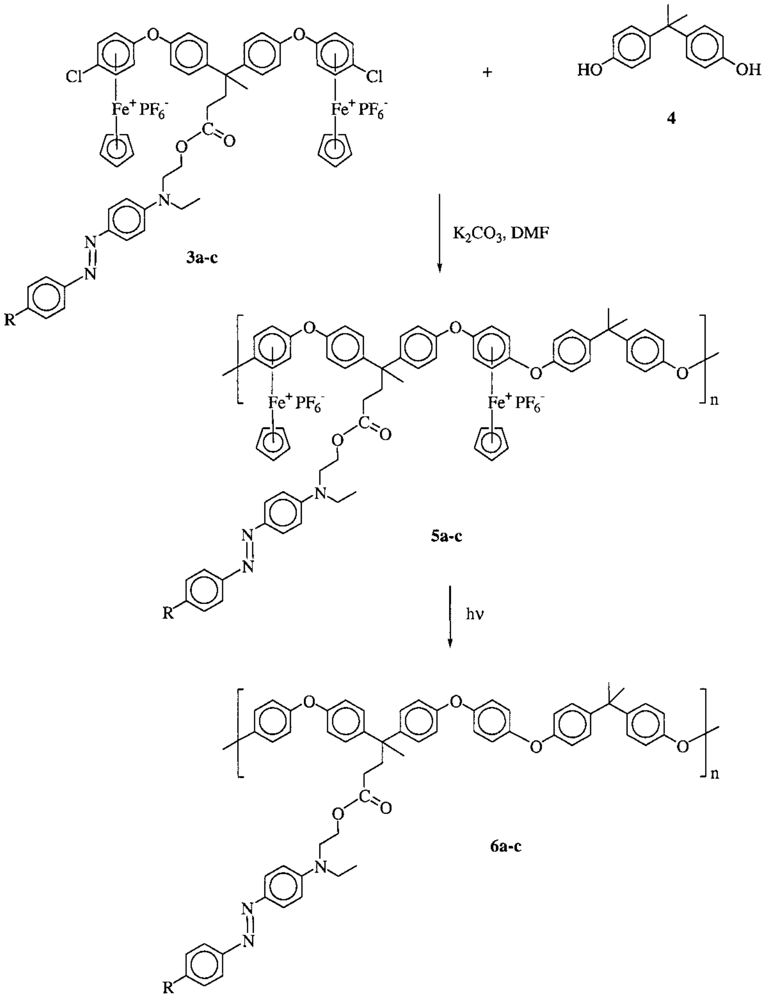
Aromatic Polymers with Azobenzene Side Chains

We have recently reported the synthesis of a bimetallic complex containing a pendent carboxylic acid group.[9] These organoiron complexes were reacted through the carboxylic acid groups with a number of azo-containing compounds functionalized with hydroxyl groups to produce azobenzene-functionalized complexes.[29] Scheme 1 shows the reaction of complex **1** with the azo chromophores **2a-c** in the presence of dicyclohexylcarbodiimide (DCC) and *N,N*-dimethylamino pyridine (DMAP). Complexes **3a-c** were isolated in good yields as orange to red solids. As the R group on the azobenzene moieties became more electron-withdrawing, there was a concurrent increase in the red shifts that these complexes experienced. For example, the λ_{max} values for the dyes increased from 421 to 452 to 491 nm in DMF, when the R groups changed from H, to $COCH_3$ to NO_2.



Scheme 1

Polymerization of complexes **3a-c** was achieved in the presence of potassium carbonate in DMF using a number of different dinucleophiles. Scheme 2 shows the reaction of monomers **3a-c** with bisphenol A (**4**). Polymerization reactions were carried out at 60 °C for a period of 18 hours. The resulting aromatic polyethers (**5a-c**) were isolated in good yields and were soluble in common polar organic solvents. In order to determine the molecular weights of polymers **5a-c**, it was first necessary to remove the cyclopentadienyliron cations pendent to their backbones due to interactions between these polar groups and GPC columns. Photolytic demetallation of polymers **5a-c** produced polymers **6a-c**.



Scheme 2

The weight average molecular weights of polymers **6a-c** were estimated to range from 8,600 to 11,500 with polydispersities ranging from 1.2 to 2.0. From these values, the molecular weights of the corresponding organoiron polymers were estimated to range from 13,400 to 18,200. Differential scanning calorimetry showed that the glass transition temperatures (T_g) of polymers **5a-c** ranged from 167 to 173 °C, while the T_g values of polymers **6a-c** ranged from 111 to 123 °C. Following the photolytic demetallation reactions, NMR, IR and visible spectroscopic investigations of the organic polyethers **6a-c** verified that the azobenzene chromophores were still present in the polymer side chains. Figure 1 shows the visible spectra of polymers **6a**, **6b** and **6c** with R = H, $COCH_3$ and NO_2. The λ_{max} values for these polymers were measured to be 417, 452 and 489 nm, respectively, and it was found that there were not significant shifts in the λ_{max} values of these polymers in comparison to their organoiron analogs or their corresponding monomers.

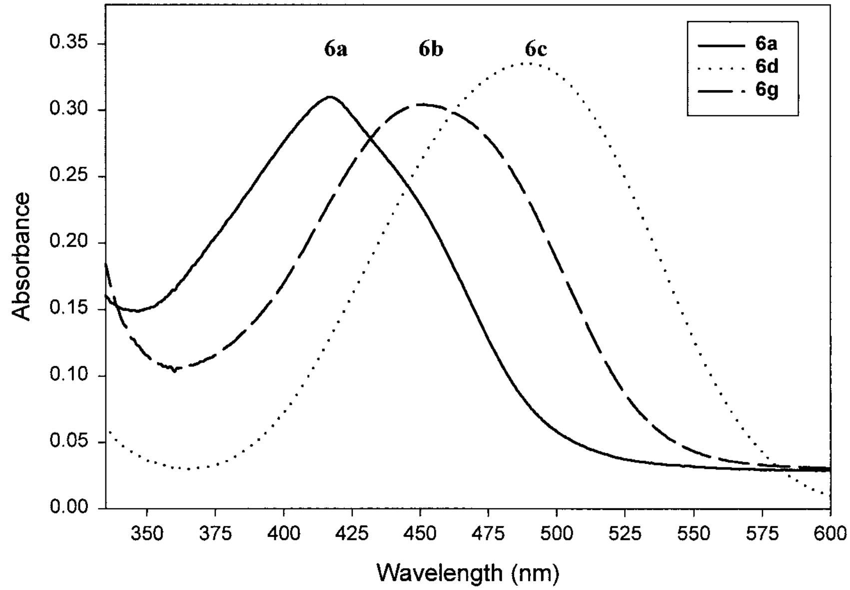
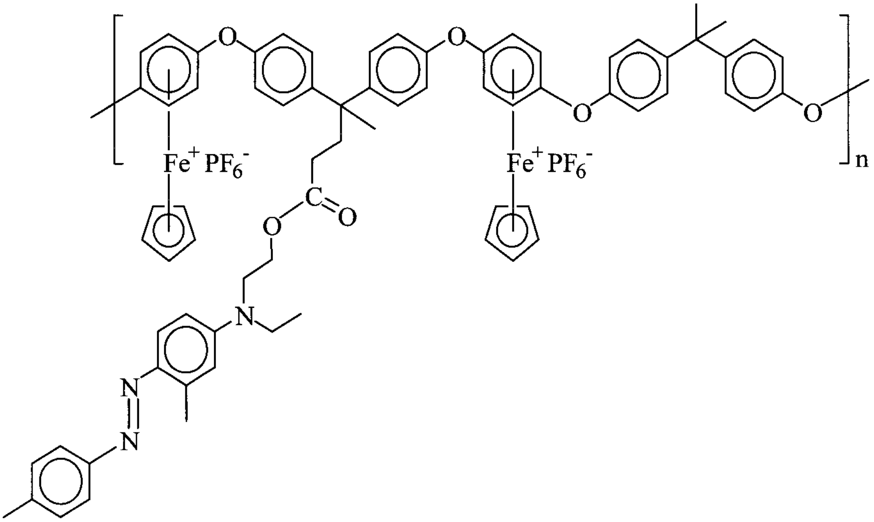


Figure 1. Visible spectra of organic polymers **6a-c** in ethanol (Reproduced with permission from *Macromolecules* **2002**, *35*, 8929-8932. Copyright 2002 Am. Chem. Soc.).

Polymer 7 was also synthesized using our previously described procedure.[29] The visible spectrum of polymer 7 showed a λ_{max} value at 422 nm in DMF. Upon acidification of the solution with HCl, the spectrum showed a bathochromic shift to 534 nm.



7

While it was found that irradiation of the polymers in acetonitrile solutions removed the cyclopentadienyliron moieties pendent to the polymer backbones, irradiation of the organic polymers in the presence of hydrogen peroxide resulted in their discoloration.[29] The photobleaching reactions were followed using UV-Vis spectroscopy. Figure 2 shows the absorption spectra of polymer **6c** in the presence of excess hydrogen peroxide following different irradiation times. It can be seen that the absorption of the polymer decreased as the length of time increased, and after 90 minutes of photolysis, the polymer solution was colorless.

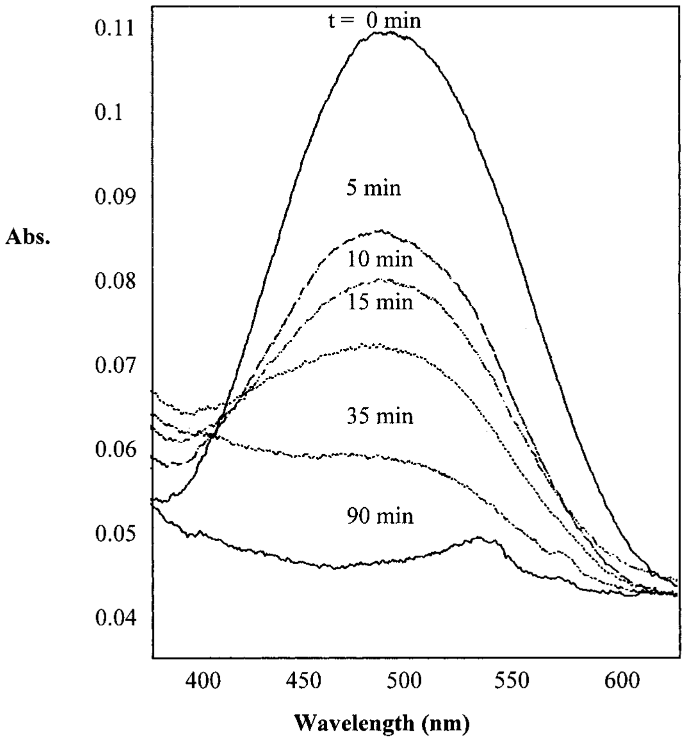
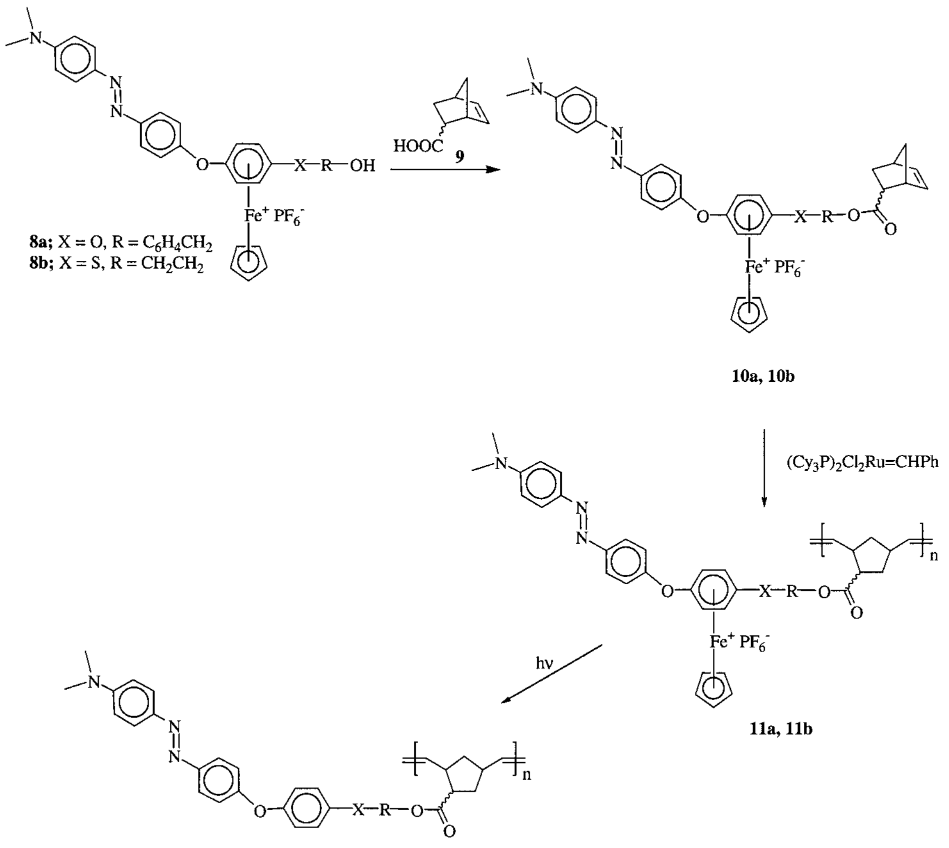


Figure 2. Absorption spectra following irradiation of a H_2O_2 solution of **6c** with a 300 nm light source.

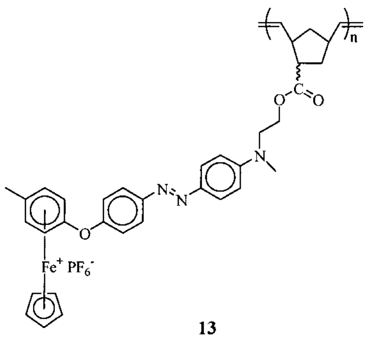
Polynorbornenes with Azobenzene Side Chains

We have also been interested in synthesizing azobenzene-substituted polymers by ring-opening metathesis polymerization of substituted norbornene monomers.[30] The synthesis of these monomers was accomplished via the reaction of azobenzene-substituted arene complexes containing terminal hydroxyl groups with 5-norbornene-2-carboxylic acid. These organoiron monomers were subjected to ROMP using the Grubbs catalyst in dichloromethane. Scheme 3 shows the synthesis of some of the ether and thioether complexes substituted with azobenzene chromophores that we have examined.



Scheme 3

All of the polynorbornenes were orange solids that had λ_{max} values between 420 and 430 nm in DMF. Figure 3 shows the visible spectrum of the organoiron polynorbornene **13** in DMF and DMF/HCl solutions. Protonation of the azo groups by the addition of HCl to these solutions caused a red shift of about 90 nm.[30]



13

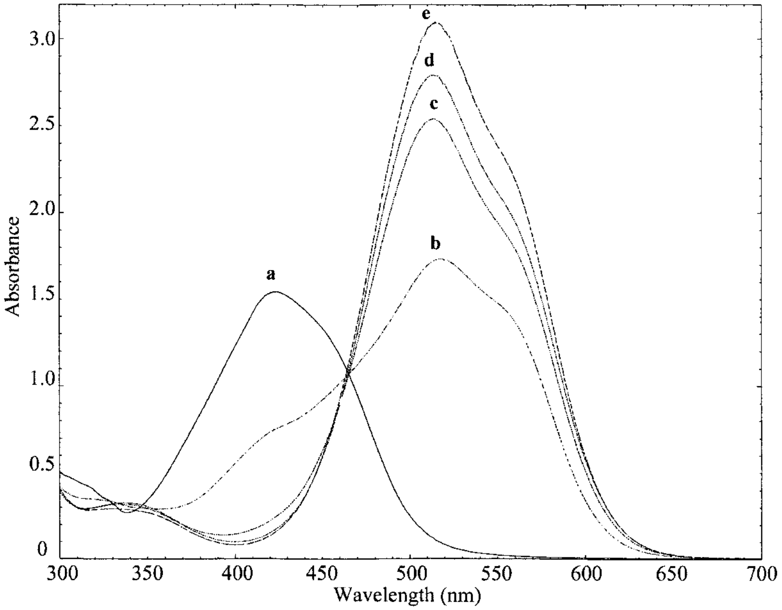


Figure 3. UV-Vis spectra of **13** in) DMF, b) DMF/10% HCl, c) DMF/30% HCl, d) DMF/50% HCl and e) DMF/100% HCl. (Reproduced from, “A New Class of Cationic Organoiron Polynorbornenes Containing Azo Dyes”, A.S. Abd-El-Aziz, R.M. Okasha, T.H. Afifi, E.K. Todd, *Macromol. Chem. Phys.*, **204**, 555 (2003) Copyright, © [2003] Wiley Periodicals, Inc.).

It was found that the cationic iron centers pendent to the side chains of these polynorbornenes underwent reversible reduction processes between –1.2 and –1.4 V versus Ag/AgCl. The cyclic voltammogram of polymer **11a** obtained in propylene carbonate containing tetrabutylammonium perchlorate (0.1 M) as the supporting electrolyte is shown in Figure 4. The cathodic and anodic peak potentials were measured at –1.4 and –1.1 V, respectively, and the half wave potential was calculated to be –1.25 V.

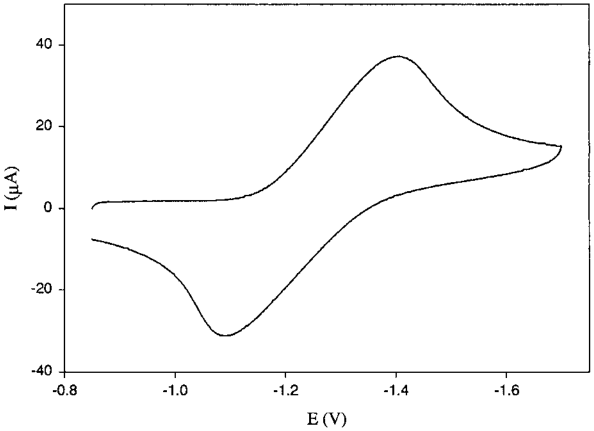


Figure 4. Cyclic voltammogram of 0.002 M polymer **11a** obtained in propylene carbonate at -40 °C using a scan rate of 0.5 V/s.

The thermal properties of the polynorbornenes were analyzed using thermogravimetric analysis and differentials scanning calorimetry. The metallated polymers underwent weight losses starting between 225 and 231 °C, which were assigned to degradation of the cyclopentadienyliron moieties and to partial decomposition of the polymer side chains. Second weight losses that began between 400 and 450 °C were caused by decomposition of the polymer backbones. Polynorbornenes with cationic cyclopentadienyliron moieties pendent to their side chains had T_g values that were much higher than their organic counterparts. For example, the organoiron polymer **11a** had a T_g at 178 °C, while its organic analog **12a** had a T_g at 99 °C. This large difference in glass transition temperatures was attributed to the bulkiness and polarity of the cyclopentadienyliron cations.

Conclusions

A number of different classes of cyclopentadienyliron-coordinated polymers functionalized with azobenzene moieties have been synthesized. These polymers were prepared either via metal-mediated nucleophilic aromatic substitution reactions of chloroarene complexes or via ring-opening metathesis polymerization of organoiron norbornenes. The colors of these organoiron polymers could be tuned by changing the functional groups on the azobenzene chromophores. Photolytic demetallation reactions allowed for the isolation of the corresponding organic polymers. These polymers could be bleached through irradiation in the presence of hydrogen peroxide.

Acknowledgements

Financial support provided by the Natural Sciences and Research Council of Canada (NSERC) and Manitoba Hydro are gratefully acknowledged. R.M.O. would also like to thank the Department of Chemistry, University of Manitoba.

[1] A. S. Abd-El-Aziz, *Macromol. Rapid Commun.* **2002**, *23*, 995.
[2] A. S. Abd-El-Aziz, *Coord. Chem. Rev.* **2002**, *233-234*, 177.
[3] R. D. A. Hudson, *J. Organomet. Chem.* **2001**, *637-639*, 47.
[4] P. Nguyen, P. Gomez-Elipe, I. Manners, *Chem. Rev.* **1999**, *99*, 1515.
[5] A. S. Abd-El-Aziz, S. Bernardin, *Coord. Chem. Rev.* **2000**, *203*, 219.
[6] A.S. Abd-El-Aziz, C.R. de Denus, E.K. Todd, S.A. Bernardin, *Macromolecules* **2000**, *13*, 5000.
[7] A. S. Abd-El-Aziz, L. May, A. L. Edel, *Macromol. Rapid Commun.* **2000**, *21*, 598.
[8] A. S. Abd-El-Aziz, A. L. Edel, L. May, K. M. Epp, H. M. Hutton, *Can. J. Chem.* **1999**, *77*, 1797.
[9] A. S. Abd-El-Aziz, L. J. May, J. A. Hurd, R. M. Okasha, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2716.
[10] A. S. Abd-El-Aziz, R. M. Okasha, J. Hurd, E. K. Todd, *Polym. Mater. Sci. Eng.* **2002**, *86(1)*, 91.
[11] A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, J. DiMartino, *J. Inorg. Organomet. Polym.* **2000**, *10*, 265.
[12] A. S. Abd-El-Aziz, E. K. Todd, *Polym. Mater. Sci. Eng.* **2002**, *86(1)*, 103.
[13] A. S. Abd-El-Aziz, E. K. Todd, G. Z. Ma, *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1216.
[14] A. S. Abd-El-Aziz, E. K. Todd, R. M. Okasha, T. E. Wood, *Macromol. Rapid Commun.* **2002**, *23*, 743.
[15] A. S. Abd-El-Aziz, C. R. de Denus, K. M. Epp, S. Smith, R. J. Jaeger, D. T. Pierce, *Can. J. Chem.* **1996**, *74*, 650.
[16] A. S. Abd-El-Aziz, T. C. Corkery, E. K. Todd, T. H. Afifi, G. Z. Ma *J. Inorg. Organomet. Polym.* In press.
[17] A. Natansohn, P. Rochon, *Chem. Rev.* **2002**, *102*, 4139.
[18] M. Hasegawa, T. Ikawa, M. Tsuchimori, O. Watanabe, *J. Appl. Polym. Sci.* **2002**, *86*, 17.
[19] L. A. Howe, G. D. Jaycox, *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 2827.
[20] K. Huang, H. Qiu, M. Wan, *Macromolecules* **2002**, *35*, 8653.
[21] S. H. Kang, H.-D. Shin, C. H. Oh, D. H. Choi, K. H. Park, *Bull. Korean Chem. Soc.* **2002**, *23*, 957.
[22] P. Uznanski, J. Pecherz, *J. Appl. Polym. Sci.* **2002**, *86*, 1456.
[23] C. Samyn, T. Verbiest, A. Persoons, *Macromol. Rapid Commun.* **2000**, *21*, 1.
[24] G. Iftime, F. L. Labarthet, A. Natansohn, P. Rochon, K. Murti, *Chem. Mater.* **2002**, *14*, 168.
[25] G. H. Kim, C. D. Keunm S. J. Kim, L. S. Park, *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3715.
[26] K. Tawa, K. Kamada, K. Kiyohara, K. Ohta, D. Yasumatsu, Z. Sekkat, S. Kawata, *Macromolecules* **2001**, *34*, 8232.
[27] L. Wu, X. Tuo, H. Cheng, Z. Chen, X. Wang, *Macromolecules* **2001**, *34*, 8005.
[28] X.-H. Liu, D. W. Bruce, I. Manners, *Chem. Commun.* **1997**, 289.
[29] A. S. Abd-El-Aziz, T. H Afifi, W. R. Budakowski, K. J. Friesen, E. K. Todd, *Macromolecules* **2002**, *35*, 8929.
[30] A. S. Abd-El-Aziz, R. M. Okasha, T. H. Afifi, E. K. Todd, *Macromol. Chem. Phys.* **2003**, 204, 555.