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Note

Synthesis of new ferrocene containing diamines and their use in epoxy resins

Michael E. Wright [a,*], James Laub [a], Phillip R. Stafford [a], William P. Norris [b]

[a] *Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, USA*
[b] *NAWCWD, Chemistry and Materials Research Branch, China Lake, CA 93555-6001, USA*

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Abstract

Treatment of 4,4-bis(ferrocenyl)heptane-1,7-diol (**1**) with benzenesulfonyl chloride afforded after workup and crystallization, 4,4-bis(ferrocenyl)-heptane-1,7-bis(benzenesulfonate) (**2**) in 67% isolated yield. Compound **2** was reacted with sodium 3-aminophenoxide or sodium 4-aminophenoxide in DMF to afford 1,7-bis(3-aminophenoxy)-4,4-bis(ferrocenyl)heptane (**3a**) (80%) and 1,7-bis(4-aminophenoxy)-4,4-bis(ferrocenyl)heptane (**3b**) (88%), respectively. Compounds **3a** and **3b** were copolymerized with methylenedianiline (MDA) and Epon® Resin 828 to afford fully cured epoxy resins. We found **3b** to cure faster than **3a** by DSC analysis. Samples of the cured resins with 20 mol% of **3a** and without ferrocene monomer were prepared with engineered defects (polypropylene letters 3 mm thick) and subjected to X-ray analysis. The samples containing ferrocene show good contrast of the defects under mild X-ray imaging conditions; whereas, non-ferrocene containing samples did not allow detection of the engineered defects. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ferrocene remains after 50 years since its discovery a molecule of intrigue and continued interest [1]. The sustained interest in ferrocene is in part due to the rich chemistry of the iron(II) center and the variety of synthetic methods available for functionalizing the cyclopentadienyl-ligands [2]. The ability to tailor the chemical reactivity and chemical behavior of ferrocene derivatives is enhanced by the inherent and sometimes outstanding air-, heat-, and photochemical-stability associated with the ferrocene building unit [3].

Our laboratory in recent years has contributed to the synthetic methods available for modifying the cyclopentadienyl-ligand via selective transmetalation of organostannane derivatives [4]. This chemistry was used to prepare a series of new and successful ferrocene based nonlinear optical polymers (NLOPs) [5]. We have continued with our interest in ferrocene containing polymers with a focus on the synthesis of bis(amino) functionalized monomers for use in the construction of ferrocene-modified epoxy- and polyimide-materials. The role of ferrocene in the materials is multifaceted [3], however, our initial goal was to utilize the ferrocene unit, with its additional electron density, to assist in the nondestructive imaging of composite materials using X-rays [6]. Herein we report on the synthesis of two new ferrocene bis(amino) monomers and their successful use as imaging agents in epoxy resins.

2. Results and discussion

2.1. Monomer synthesis

Starting from the readily accessible 4,4-bis(ferrocenyl)heptane-1,7-diol (**1**) [7] we prepared the 4,4-bis(ferrocenyl)-1,7-bis(benzenesulfonate)heptane complex **2** in very good yield. The reaction is carried out in the

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* Corresponding author. Fax: + 1-804-828-7507.
E-mail address: mewright@vcu.edu (M.E. Wright).

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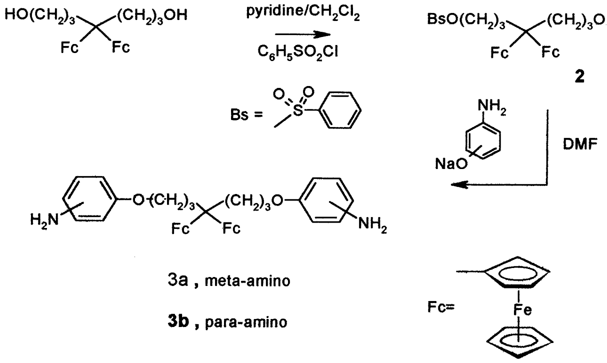

Scheme 1.

presence pyridine and the reaction time is critical for success. It is also interesting to note that when we prepared the tosyl-derivative, a crystalline product could not be obtained and this made purification difficult. This result led to the benzenesulfonate becoming the leaving group of choice.

Treatment of **2** with sodium salt of *m*-aminophenoxide or *p*-aminophenoxide resulted in a very efficient synthesis of the desired bis(amino) ferrocene monomers **3a** and **3b**, respectively (Scheme 1).

The new compounds **3a** and **3b** were fully characterized by NMR spectroscopy and elemental analysis. They were found to be air-stable and solid materials that were easily manipulated without the use of Schlenk techniques. They showed excellent solubility in common organic solvents such as dichloromethane. This is important because for solid diamines, like MDA and **3**, a carrier solvent is typically used to ensure a homogeneous epoxy mixture is formed. This solvent must then be removed prior to curing of the mixture; hence, a low boiling solvent like dichloromethane is attractive.

2.2. Epoxy resin synthesis

Monomers **3a** and **3b** were copolymerized with Epon® 828 (the bis(epoxide) or resin) and methylenedianiline (MDA). In each case, the mol-equivalents used of **3a** and **3b** directly reduced the amount of MDA used. This kept the resin and hardner in a one-to-one molar ratio regardless of the ferrocene doping levels. The resins were cured in air at 80 °C for several hours (typically 16 h). At all levels of doping the materials cured to tough glassy materials having similar properties as the ferrocene-free epoxies. At higher levels (~ 10 mol%) of doping the orange ferrocene color became more evident in the cured materials. At lower ferrocene loading levels the colors were very similar (a fairly dark amber color), and in fact, the ferrocene doped and cured materials (5 mol% or less) were less colored than the pure organic materials!

We studied the heats of polymerization for the ferrocene monomers using differential scanning calorimetry (DSC) on a Perkin–Elmer DSC-7. A sample of the mixture was placed in an open aluminum DSC pan, purged with nitrogen, and quickly ramped to 100 °C. The heat flow was then monitored as the polymerization proceeded. What is evident from the DSC data (Fig. 1) is that the curing of the *p*-amino monomer **3b** is faster. Based on the increased nucleophilicity of the *p*-isomer the faster cure time is not surprising.

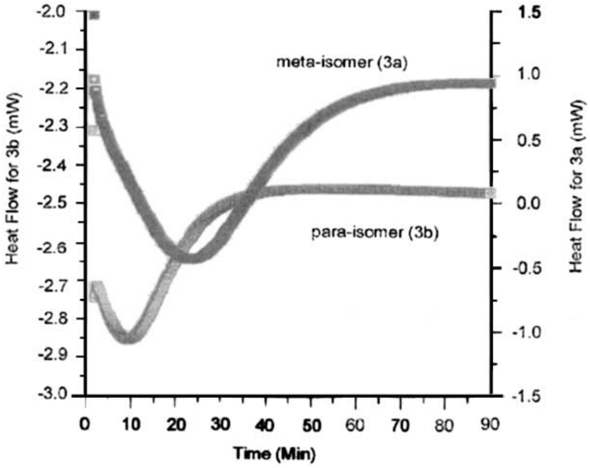

Fig. 1. Differential scanning calorimetry (DSC) plots for the thermal curing of imaging agents **3a** and **3b** with a loading level of 20 mol%. DSC samples were quickly ramped 100 °C and maintained at that temperature during the entire cure process. Samples were evaluated under an atmosphere of nitrogen. Exothermic is down and endothermic is up on the vertical scale.

One of the primary goals of this work was to make an epoxy material that would assist in detecting flaws in a composite material. With this in mind, we cured resins containing the ferrocene (20% monomer incorporation) and placed engineering defects within the resin. The defects were thin (3 mm) letters (i.e. Fc) of polypropylene that were suspended inside the resin sample. The resin was heated at 80 °C in a Pyrex vessel for 16 h to insure complete cure. The top sample in Fig. 2 was an epoxy mixture of Epon® 828 (bisphenol A/epichlorohydrin based resin, 100%) and MDA with no ferrocene. It also contained the polypropylene letters of ‘Fc’ in the resin sample. It is very clear from the X-ray image presented in Fig. 2 that the ferrocene-modified resin (bottom image) did indeed facilitate imaging of the engineered defects (i.e. the letters). In addition, the ferrocene agent helped in showing air bubble defects within the cured resin. The ring on the perimeter of the images is the side of the Pyrex sample holder. Areas that are dark in Fig. 2 represent a higher degree of X-ray transmission through the sample.

We found that the intensity of the X-ray source was important. Although we did not quantify this term, it was found that the lower setting of X-ray intensity used in a typical hospital mammogram facility was ideal for imaging the materials used in this study. At higher levels of X-ray intensity (e.g. typical of bone X-rays) the image contrast for the ferrocene system was washed out or greatly diminished. These results illustrate how the ferrocene-imaging agent changes the behavior of the bulk material relative to a pure organic epoxy resin in a way that appears quite useful.

3. Concluding remarks

We have presented a facile synthesis of two new ferrocene bis(amino) complexes and their use as effective monomers in the copolymerization with MDA and Epon® resin 828. The *p*-isomer (**3b**) cures somewhat faster; however, both ferrocene monomers produce completely cured and tough epoxy glasses. The ferrocene epoxy resins show the ability to enhance imaging of defects at selected levels of X-ray intensity. The additional electron-density supplied by the iron atoms in ferrocene may not only assist in imaging technology but may also serve a useful roll in differentiating and tracking the flow of resin in certain curing processes. This may prove especially useful in composite building techniques (such as resin transfer molding, RTM) where the resin flow within a mold is difficult to characterize. This would be useful in optimizing mold designs that could lead to successful and defect-free composite parts.

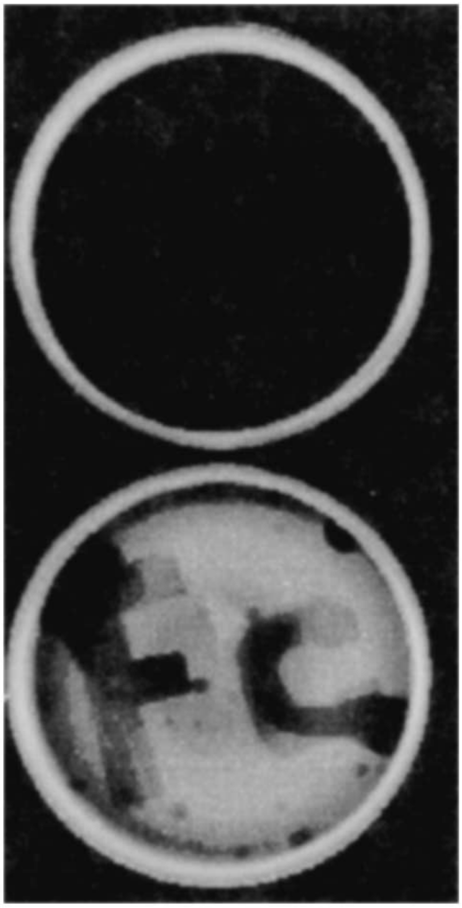

Fig. 2. X-ray 'photograph' taken of two fully cured epoxy resin samples that contain no imaging agent (top) and 20% of the ferrocene-imaging agent **3a** (bottom). In both samples polypropylene letters (Fc) were suspended in the cured resin.

4. Experimental

4.1. General methods

All manipulations of compounds and solvents were carried out using standard Schlenk techniques unless otherwise stated. Tetrahydrofuran (THF), CH_2Cl_2, and Et_3N were purified by distillation under nitrogen from standard drying agents. ^{1}H- (300 MHz) and ^{13}C-NMR (75 MHz) measurements were performed using a Varian Oxford instrument. NMR chemical shifts are reported versus Me_4Si in ^{1}H-NMR spectra and assigning the $CDCl_3$ resonance at 77.0 ppm in ^{13}C-NMR spectra. The Epon 828 resin was generously supplied by Shell Oil Co. The methylenedianiline (MDA), sodium ethoxide, benzenesulfonyl chloride, and aminophenols were purchased from Aldrich Chemical Co. and used as received. Elemental analyses were performed at Atlantic Microlab Inc., Norcross, Georgia.

*4.2. Preparation of compound **2***

A flask was charged with compound **1** (10.0 g, 20 mmol), CH_2Cl_2 (100 ml), and Py (9.8 g, 120 mmol). With stirring benzenesulfonyl chloride (7.5 g, 42 mmol) was added dropwise to the reaction mixture. The mixture was allowed to react with stirring over a period of 4 h upon which the solution became homogeneous. The reaction mixture was diluted with HCl (3 N, 100 ml) and the organic layer separated and washed with water (100 ml), and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and crude product crystallized from MeCN (100 ml $\Rightarrow$ reduce volume to induce crystal growth). The yellow crystals of **2** were collected on a glass-frit, washed with MeCN (-100 ml), and dried at 70 °C under reduced pressure (10.5 g, 67%, m.p. 168–170 °C). ^{1}H-NMR ($CDCl_3$): $\delta = 7.98$–7.88 (m, 2H), 7.69–7.53 (m, 3H), 4.09 (brs, 4H, Cp), 3.98 (brs, 7H, Cp and CH_2O), 1.95–1.70 (m, 4H, CH_2s). ^{13}C-NMR ($CDCl_3$): $\delta = 136.3$ (*ipso*-$ArSO_3$), 133.7 (ArCH), 129.3 (ArCH), 127.7 (ArCH), 98.3 (*ipso*-C_5H_4), 71.4 (CH_2O), 69.0 (Cp), 66.8, 66.5 (C_5H_4), 38.4 ($\mathit{C}Fc_2$), 34.7, 24.5 (CH_2s). Anal. Found: C, 60.21; H, 5.06; Fe, 14.50; S, 8.21. Calc. for $C_{39}H_{40}Fe_2O_6S_2$: C, 60.01; H, 5.17; Fe, 14.31; S, 8.22%.

*4.3. Preparation of compound **3a***

A THF (50 ml) solution of *m*-aminophenol (2.10 g, 19.2 mmol) was treated with sodium ethoxide (1.09 g, 16 mmol) and allowed to react for 15 min with stirring. Compound **2** (5.00 g, 6.41 mmol) was added directly to the reaction vessel in small portions and the mixture was diluted with DMF (30 ml). The resulting mixture was heated to 60 °C for 30 min, the heating bath removed, and then allowed to react for an additional 1 h. The mixture was diluted with benzene–ether (200 ml, 1:1, v/v) and the organic layer washed with aqueous K_2CO_3, water (2 × 100 ml), brine, and then dried over anhydrous K_2CO_3. The solvents were removed under reduced pressure and crude product purified by column chromatography on silica gel (gradient elution: $CHCl_3 \Rightarrow$ 2% MeOH in $CHCl_3$) to afford compound **3a** as an orange solid (3.50 g, 80%). ^{1}H-NMR ($CDCl_3$): $\delta = 7.06$ (apparent t, $J = 8.3$ Hz, 1H), 6.40–6.25 (m, 3H), 4.11 (s, 4H, Cp), 4.04 (s, 5H, Cp), 3.91 (t, $J = 5.8$ Hz, 2H, CH_2O), 3.5–3.1 (brs, 2H, NH_2), 2.15–1.95 (m, 4H, CH_2s). ^{13}C-NMR ($CDCl_3$): $\delta = 160.2$ (ArC1), 147.7 (ArC3), 130.0 (ArC5), 107.7 (ArC4), 104.5 (ArC6), 101.7 (ArC2), 99.2 (*ipso*-Cp), 68.7 (Cp), 68.3 (CH_2O), 66.6, 66.4 (C_5H_4s), 38.7 (CH_2), 35.2 (*C*Fc_2), 24.7 (CH_2). Anal. Found: C, 68.55; H, 6.10; N, 3.94. Calc. for $C_{39}H_{42}Fe_2N_2O_2$: C, 68.64; H, 6.20; N, 4.10%.

*4.4. Preparation of compound **3b***

Compound **3b** was prepared in a manner similar to **3a** utilizing *p*-aminophenol (3.56 g, 32.6 mmol), sodium ethoxide (1.85 g, 27.2 mmol), and compound **2** (8.52 g, 10.9 mmol) and isolated as an orange solid (6.54 g, 88%). ^{1}H-NMR ($CDCl_3$): $\delta = 6.77$ (d, $J = 8.8$ Hz, 2H), 6.64 (d, $J = 8.8$ Hz, 2H), 4.10 (s, 5H, Cp), 4.03 (s, 4H, Cp), 3.92 (t, $J = 6.1$ Hz, 2H, CH_2O), 3.6–3.2 (brs, 2 H, NH_2), 2.12–1.95 (m, 4H, CH_2s). ^{13}C-NMR ($CDCl_3$): $\delta = 152.4$ (ArC1), 139.9 (ArC4), 116.5 (ArC2,6), 115.8 (ArC3,5), 99.4 (*ipso*-Cp), 69.3 (CH_2O), 68.8 (Cp), 66.8, 66.4 (C_5H_4s), 38.8 (CH_2), 35.4 (*C*Fc_2), 24.9 (CH_2). Anal. Found: C, 68.33; H, 6.44; N, 3.99. Calc. for $C_{39}H_{42}Fe_2N_2O_2$: C, 68.64; H, 6.20; N, 4.10%.

4.5. DSC analysis of the curing reaction

Samples were prepared by combining Epon® Resin 828 (cas #25068-38-6), MDA, and a CH_2Cl_2 solution of the appropriate ferrocene monomer. The mixture was subjected to reduced pressure (~0.3 mm) for several minutes at ambient temperature and then placed in an aluminum DSC pan (no lid). The sample was placed in the DSC, allowed to purge for ~2 min under nitrogen, and then heated quickly (200 °C min^{-1}) to 100 °C and maintained at that temperature for the duration of the experiment.

4.6. X-ray analysis sample preparation

Samples were prepared by mixing Epon 828, MDA, and a CH_2Cl_2 solution of either **3a** or **3b**. The mol-equivalents wt of Epon 828 is 340 g mol^{-1} and is used to determine the needed amounts of diamine. The mol ratio of bis(epoxide) to diamine used was always 1:1. Hence in a typical experiment to prepare a 20 mol% ferrocene resin was as follows: Epon 828 (3 g, 8.8 mmol), MDA (1.40 g, 7.1 mmol), and a CH_2Cl_2 (1 ml) solution of **3a** (1.16 g, 1.7 mmol) were combined and mixed thoroughly. The sample was placed under reduced pressure for a few minutes and then transferred to a curing oven maintained at 80 °C for ~16 h. Samples that contained engineered defects had them placed in the samples after treatment under reduced pressure.

Acknowledgements

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References

[1] (a) T.J. Kealy, P.L. Pauson, Nature 168 (1951) 1039;
(b) For a general review of ferrocene chemistry see: M. Rosenblum, Chemistry of the Iron Group Metallocenes, Wiley, New York, 1965;
(c) W.E. Watts, Organomet. Chem. Rev. 2 (1967) 231;
(d) A. Tagni, T. Hayashi, Ferrocenes-Homogenous Catalysis, Organic Synthesis, Materials Science, VCH, New York, 1995.

[2] For example see: E.W. Neuse, J.R. Woodhouse, G. Montaudo, C. Puglisi, Appl. Organomet. Chem. 2 (1988) 53;
(b) J.E. Sheats, C.E. Carraher, C.U. Pittman Jr. (Eds.), Metal Containing Polymer Systems, Plenum, New York, 1985.

[3] (a) J.W. Harwood, Industrial Applications of Organometallic Compounds, Reinhold, New York, 1963;
(b) J.C. Johnson Jr., Metallocene Technology, Noyes Data Corporation, Park Ridge, NJ, 1973.

[4] M.E. Wright, Organometallics 9 (1990) 853.

[5] (a) M.E. Wright, E.G. Toplikar, R.F. Kubin, M.D. Seltzer, Macromolecules 25 (1992) 1838;
(b) M.E. Wright, E.G. Toplikar, Macromolecules 25 (1992) 6050;
(c) M.E. Wright, M.S. Sigman, Macromolecules 25 (1992) 6055.

[6] J.M. Winter, R.E. Green Jr., A.M. Waters, W.H. Green, Res. Nondestructive Eval. 11 (1999) 199 (and references cited therein).

[7] W.P. Norris, J. Org. Chem. 43 (1978) 2200.