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Synthesis of Functionalized Iron N-Heterocyclic Carbene Complexes and their potential application as Flame Behavior Modifier in Cross Linked Epoxy Resins

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Keywords

Iron complexes, N-heterocyclic carbene, NHC, Cyclopentadienone, Epoxy resin, Flame behaviour modification, Flame retardant.

Abstract

The design of new flame retardants (FR) that avoid the use of halogen and phosphorus additives is challenging and urgent. Herein we report on the synthesis of bis-amino functionalized N-heterocyclic carbene cyclopentadienone iron complexes aimed at promoting the production of iron containing epoxy resins. Iron complexes are successfully employed to obtain high Tg thermosets with as low as 5% hardener content. Moreover the obtained resins display an impressive charring ability that paves the way to the application of such systems for material with improved flame behavior.

1. Introduction

A wide range of applications make use of epoxy resins (EP) due to their outstanding properties such as high tensile strength and modulus, excellent chemical and corrosion resistance, adhesion, and dielectric properties. While their use is spreading to an increasing number of fields, it should be also noted that epoxies suffer, as well renowned for plastic materials, from intrinsic high flammability[1, 2] that makes them inappropriate for application in critical areas where strict rule about flame behavior are issued. Since flammability is mainly a surface phenomenon, insertion of an outer layer can delay the flame without impacting on the substrate intrinsic properties,[3, 4] Nevertheless a more common method involves the addition of some specific additives known as flame retardants (FRs) to the bulk of the plastic.[5,6] This latter approach is suffering however of all the drawbacks involved with polymer mixing. In recent years, halogen and phosphorus containing FR have been withdrawn due to toxicity and bioaccumulation issues respectively.[7-10] Thus the design of new flame retardants that avoid the use of halogen and phosphorus additives appears urgent. As a potential alternative, organometallic complexes such as ferrocene-based co-monomers have been applied. In this context our group reported on the synthesis of functionalized ferrocenes as flame retardants.[11] Furthermore it has been demonstrated that ferrocene derivatives can catalyze the formation of char acting as smoke suppressors.[12-14] This behavior is likely to be further improved in the presence of aromatics.

Nevertheless, within the field of organometallic complexes only the ferrocene based materials cited above have been developed for such flame modification applications. Considering the previously described advantages and drawbacks, the development of novel organometallic iron based complexes able to act as resin hardener, thus entering in the main polymer backbone, still represents a challenge toward the production of new flame safer materials.

After getting involved for several years in functionalized ferrocene chemistry,[11, 15-19] our group has recently extended the research interests to cyclopentadienone iron complexes bearing N-heterocyclic carbene ligands.[20, 21] Since these complexes show similarity with ferrocenes in term of stability and electrochemistry, it follows that, in principle, they are good candidates to play a role as flame retardants.

With this objective in mind here we describe the design and the synthesis of bis-amino functionalized N-heterocyclic carbene (NHC) cyclopentadienone iron(0) complexes and their successful use as epoxy-based network promoters. Charring ability is also discussed as a parameter for the flame modification behavior of the hybrid epoxy resins obtained.

2. Experimental Section

2.1 Materials and methods. All reactions were carried out under a nitrogen atmosphere, using standard Schlenk techniques. Glassware was oven dried before use. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), toluene and acetonitrile (CH_3CN) were dried and distilled prior to use. Other solvents such as ethylacetate (EtOAc), methanol (MeOH), $CDCl_3$, Acetone-d_6 (Sigma Aldrich) were employed without further purification. Reagents HBF_4 (ether complex), KOH, NaOH, Na_2SO_4, trimethylamine-N-oxide and Ag_2O were used as received by Sigma Aldrich or Alfa Aesar. Compounds triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron and triscarbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one) iron,[20] 1-(3-BOC-aminopropyl)bromide[22] 1-(3-BOC-aminopropyl)-imidazole[23] were synthesized as previously reported.

Bisphenol A Diglycidyl Ether (DGEBA) with an epoxy equivalent weight (EEW) of 170 g/equivalent was purchased from Alfa Aesar. The commercial epoxy precursor ELANTAS Elan-tron ® EC 157 was kindly supplied by Elantas Europe srl.

The NMR spectra were recorded using Varian Inova 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz), Varian Mercury Plus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^{1}H, 599.7; ^{13}C, 150.8 MHz) spectrometers at 298 K; chemical shifts were referenced internally to residual solvent peaks. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum Two spectrophotometer. ESI-MS spectra were recorded on a Waters Micromass ZQ 4000 with samples dissolved in MeOH. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument.

The thermal behavior of the reacting mixtures was evaluated by Differential Scanning Calorimetry (DSC, Q2000 TA Instruments) and the measurements were carried out under nitrogen flow, heating the samples at a heating rate of 1°C/min from –50 to 280. After the first heating, the samples were quench cooled to 0°C and then heated again with a heating rate of 20°C/min from 0 to 260°C for T_g evaluation. Thermogravimetric (TGA) measurements were carried out using a TA Instrument SDT Q600 (heating rate 10°C/min) on 10–20 mg samples under nitrogen atmosphere (100 mL/min gas flow rate) from room temperature to 600°C.

2.2 Synthesis of 1,3-(BOC-aminopropyl) imidazolium bromide (1)

In a dried 100 mL Schlenk flask, 1-(3-BOC-aminopropyl)bromide (1.60 g, 6.72 mmol) 1-(3-BOC-aminopropyl)-imidazole (1,17 g, 5.19 mmol) were heated at 110 °C for 24h. At the end of the reaction the crude is dissolved in EtOAc (30 mL). Then the product was extracted washing twice with water (2x15 mL). The solvent was removed from the aqueous phase under vacuum to yield the product 1,3-(BOC-aminopropyl) imidazolium bromide (**1**), yield 70%.

^{1}H-NMR (DMSO-d_6): δ(ppm): 9.18 (s, 1H, CH), 7.78 (dd, 1H, CH), 6.97 (dd, 1H, CH), 4.15 (t, 4H, CH_2), 2.93 (t, 4H, CH_2), 1.90 (quint, 4H, CH_2), 1.37 (s, 18H, $CH_{3,\,Boc}$). FT-IR (CH_2Cl_2): $\nu_{(C=O)}$ 1705 cm^{-1}. ESI-MS: 383 m/z $[M]^+$. Anal. Calcd (%) for $C_{19}H_{35}BrN_4O_4$: C, 49.24; H, 7.61; N, 12.09. Found:

C, 49.09; H, 7.45; N, 11.86. Characterization is comparable with the literature, where **1** was obtained under different conditions.[24]

2.3 Synthesis of di-carbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one)(1,3-BOC-aminopropyl)ilidene)iron (2-BOC)

In a dried 100 mL Schlenk flask, 1,3-(BOC-aminopropyl) imidazolium bromide (**1**) (1.370 g, 2.69 mmol) and silver oxide (0.662 g, 2.86 mmol), triscarbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one) iron (0.996 g, 2.38 mmol) and trimethylamine-N-oxide (0.268 g, 3.57 mmol) were dissolved in CH_3CN (40 mL). The reaction mixture was stirred at room temperature and protected from light for 3 h, and then solvent was removed under reduced pressure. The solid was re-dissolved in toluene (60 mL) and left under reflux for 1 h. At the end of reaction time, solvent was removed under reduced pressure and the crude product was purified by column chromatography on neutral alumina using CH_2Cl_2/EtOAc (5:5) affording the titled complex as a yellow powder (55%).

^{1}H-NMR (399.9 MHz, 298 K, acetone-*d*$_6$): δ(ppm): 6.95 (s, 1H, CH), 6.81 (s, 1H, CH), 3.89 (4H, CH_2), 2.96 (4H, CH_2), 2.25 (m, 4H, CH_2), 1.87 (m, 4H, CH_2), 1.56 (4H, CH_2), 1.38 (s, 18H, CH_{3BOC}), 0.27 (s, 18H, CH_{3TMS}). ^{13}C-NMR (150.8 MHz, 298 K, acetone-*d*$_6$): δ(ppm): 217.23 (CO), 183.91 ($C_{q,carbene}$), 168.86 (C=O, $_{CpO}$), 156.21 (CO, $_{BOC}$), 124.61 (CH), 122.3 (CH), 104.21 ($C_{3,4}$, $C_{q,CpO}$), 79.3 ($C_{q,BOC}$), 72.11 ($C_{2,5}$, $C_{q,CpO}$), 67.20 (CH_2), 48.57 (CH_2), 32.00 (CH_2), 32.02 (CH_2), 28.63 (CH_3, $_{BOC}$), 24.71 (-CH_2), 22.58 (-CH_2), 0.20 (CH_3, $_{TMS}$). FT-IR (CH_2Cl_2): $\nu_{(CO)}$ 1989, 1926, $\nu_{(C=O)}$ 1709 cm^{-1}. ESI-MS: 773 m/z $[M+H]^+$. Anal. Calcd (%) for $C_{36}H_{60}FeN_4O_7Si_2$: C, 55.94; H, 7.82; N, 7.25. Found: C, 56.14; H, 7.96; N, 7.12.

2.4 Synthesis of di-carbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one)(1,3-aminopropyl)ilidene)iron (2)

In a dried 100 mL Schlenk flask, di-carbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one)(1,3-BOC-aminopropyl)ilidene)iron (**2-BOC**) (1.025 g, 1.33 mmol) was dissolved in

Et_2O (20 mL), then 8 equivalent of $HBF_4 \cdot Et_2O$ (0,724 mL, 5.32mmol) were added. The reaction mixture was stirred at room temperature and protected from light for 1 h. The solid precipitated was washed with Et_2O (3 x 20 mL) and then the residual solvent was removed under reduced pressure. The solid was re-dissolved in CH_2Cl_2 (40 mL) and washed with a basic water solution (KOH 2M, 2 x 20 mL). The organic phase was dried over Na_2SO_4 and then, after filtration, the solvent was removed under vacuum to yield (85%) di-carbonyl(1,3-di(trimethylsilyl)-(4,5-cyclohexyl)cyclopenta-3,5-dien-2-one)(1,3-aminopropyl)ilidene)iron (**2**) as a yellow solid.

^{1}H-NMR (399.9 MHz, 298 K, acetone-d_6): δ(ppm): 7.00 (s, 1H, CH), 6.85 (s, 1H, CH), 3.99 (4H, CH_2), 2.66 (4H, CH_2), 2.28 (m, 4H, CH_2), 1.84 (m, 4H, CH_2), 1.56 (4H, CH_2), 0.31 (s, 18H, CH_{3TMS}). ^{13}C NMR (150.8 MHz, 298 K, acetone-d_6): δ (ppm) 217.30 (CO), 184.7 (C_{carb}), 177.01 (C=O, $_{CpO}$), 124.50 (CH_{NHC}), 122.34 (CH_{NHC}), 104.35 ($C_{3,4}$, Cp), 71.22 ($C_{2,5}$, Cp), 49.62 (CH_2), 48.72 (CH_2), 32.87 (-NCH_2-), 31.72 (CH_2), 24.63 (-CH_2), 22.61 (-CH_2), 0.21 (CH_{3TMS}). FT-IR (CH_2Cl_2): $\nu_{(CO)}$ 2004, 1944. ESI-MS: 573 m/z $[M+H]^+$. Anal. Calcd (%) for $C_{26}H_{44}FeN_4O_3Si_2$: C, 54.53; H, 7.74; N, 9.78. Found: C, 55.01; H, 7.56; N, 9.72.

2.5 Synthesis of dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1,3-BOC-aminopropyl)-ilidene]iron (3-BOC)

In a dried 100 mL Schlenk flask, 1,3-(BOC-aminopropyl) imidazolium bromide (**1**) (0.500 g, 1.08 mmol) and silver oxide (0.300 g, 1.29 mmol), triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (0.631 g, 1.08 mmol) and trimethylamine-N-oxide (0.122 g, 1.62 mmol) were dissolved in CH_3CN (40 mL). The reaction mixture was stirred at room temperature and protected from light for 3 h, and then solvent was removed under reduced pressure. The solid was re-dissolved in toluene (60 mL) and left under reflux for 1 h. At the end of reaction time, solvent was removed under reduced pressure and the crude product was purified by column chromatography on neutral alumina using EtOAc/MeOH (9:1) and affording the titled complex **3-BOC** as a yellow powder (74%).

^{1}H-NMR (acetone-*d6*): δ(ppm): 7.82 (d, 4H, CH_{aryl}), 7.35 (s, 2H, CH, NHC), 7.15 (m, 10H, CH_{aryl}), 6.75 (d, 4H, CH_{aryl}), 4.20 (t, 2H, CH_2), 3.72 (s, 6H, CH_3O), 3.70 (t, 4H, CH_2), 3.32 (t, 4H, CH_2), 1.72 (quint, 4H, CH_2), 1.39 (s, 18H, $CH_{3(Boc)}$). ^{13}C-NMR (150.8 MHz, acetone-*d6*) δ(ppm): 218.01 (CO), 181.75 ($C_{q,carbene}$), 166.18 (C=O, $_{CpO}$), 159.88 (*C*OCH_3), 156.44 (CO, $_{Boc}$), 136.10-123.85 (CH_{NHC}, CH_{aryl} and C_{aryl}), 113.83 (CH_{aryl}), 100.41 ($C_{2,5}$, $C_{q,CpO}$), 80.51 ($C_{3,4}$, $C_{q,CpO}$), 78.51 ($C_{q,\ Boc}$), 67.16 (CH_2), 55.38 (OCH_3), 48.77 (CH_2), 31.86 (CH_2), 28.65 ($CH_{3,\ Boc}$). FT-IR (CH_2Cl_2): $\nu_{(CO)}$ 1988, 1933, $\nu_{(C=O)}$ 1706 cm^{-1}. ESI-MS: 939 m/z $[M+H]^+$, 961 m/z $[M+Na]^+$. Anal. Calcd (%) for $C_{52}H_{58}FeN_4O_9$: C, 66.52; H, 6.23; N, 5.97. Found: C, 66.34; H, 6.45; N, 5.86.

2.6 Synthesis of dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1,3-aminopropyl)-ilidene]iron (3)

In a dried 100 mL Schlenk flask, dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1,3-BOC-aminopropyl)-ilidene]iron (**3-BOC**) (0.500 g, 0.53 mmol) was dissolved in Et_2O (20 mL), then 8 equivalent of $HBF_4 \cdot Et_2O$ (0,577 mL, 4,24 mmol). The reaction mixture was stirred at room temperature and protected from light for 1 h. The solid precipitated was washed with Et_2O (3 x 20 mL) and then the residual solvent was removed under reduced pressure. The solid was re-dissolved in CH_2Cl_2 (40 mL) and washed with a basic water solution (KOH 2M, 2 x 20 mL). The organic phase was dried over Na_2SO_4 and then, after filtration the solvent was removed under vacuum to yield (88%) dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1,3-aminopropyl)-ilidene]iron (**3**) as a yellow solid.

^{1}H-NMR (acetone-*d6*): δ(ppm): 7.82 (d, 4H, CH_{aryl}), 7.32 (s, 2H, CH, NHC), 7.12 (m, 10H, CH_{aryl}), 6.75 (d, 4H, CH_{aryl}), 3.73 (s, 6H, CH_3O), 3.70 (t, 4H, CH_2), 2.74 (t, 4H, CH_2), 1.82 (quint, 4H, CH_2). ^{13}C-NMR (150.8 MHz, acetone-*d6*) δ(ppm): 218.17 (CO), 181.51 ($C_{q,\ carbene}$), 166.46 (C=O, $_{CpO}$), 159.83 (*C*OCH_3), 136.20-123.99 (CH_{aryl} and C_{aryl}), 113.78 (CH_{aryl}), 100.38 ($C_{2,5}$, $C_{q,CpO}$), 80.30 ($C_{3,4}$, $C_{q,\ CpO}$), 55.38 (OCH_3), 49.46 (CH_2), 48.68 (CH_2), 33.23 (CH_2). FT-IR (CH_2Cl_2): $\nu_{(CO)}$ 1995, 1938.

ESI-MS: 739 m/z $[M+H]^+$. Anal. Calcd (%) for $C_{42}H_{42}FeN_4O_5$: C, 68.29; H, 5.73; N, 7.59. Found: C, 68.09; H, 6.01; N, 7.54.

2.7 Formulations preparation

The epoxy precursor (DGEBA or Elan-tron ® EC 157) and the bis-amino functionalized iron complexes (**2** or **3**) were mixed in a vial at 40 or 50°C (DGEBA and Elan-tron ® EC 157, respectively) until complete homogenization. Then the mixtures were cooled to RT and used for the preparation of DSC samples. Different mixtures were produced and labelled according to the list reported in Table 1.

Table 1. Compositions of the different DGEBA/**2**, EC157/**2**, DGEBA/**3**, and EC157/**3** investigated thermoset formulations

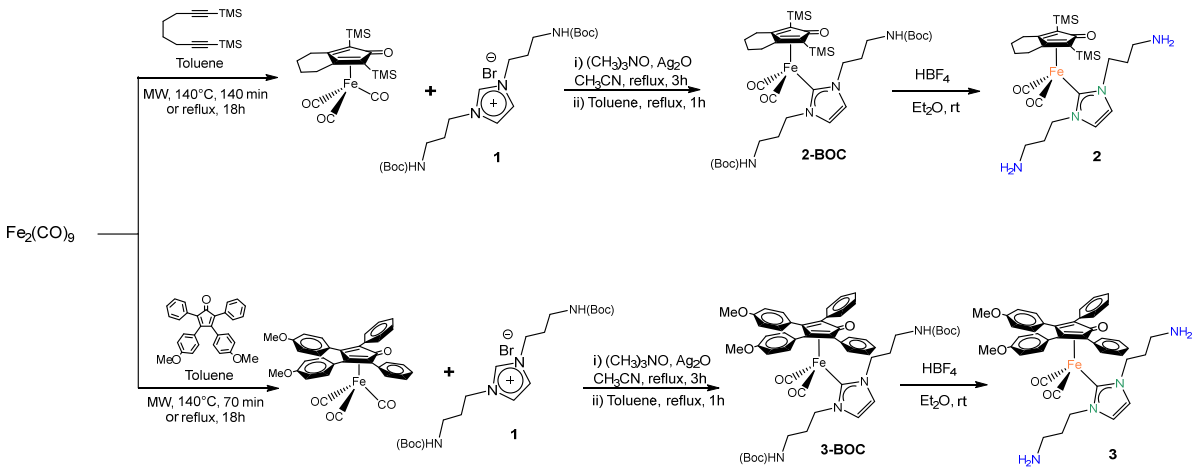
Sample	**Epoxy precursor**	**Hardener**	**Hardener/epoxy precursor**	**Iron (m/m%)**
DGEBA/**2**-5	DGEBA	**2**	5	0.98
DGEBA/**2**-7.5	DGEBA	**2**	7.5	1.47
DGEBA/**2**-10	DGEBA	**2**	10	1.96
EC157/**2**-5	Elan-tron ® EC 157	**2**	5	0.98
EC157/**2**-7.5	Elan-tron ® EC 157	**2**	7.5	1.47
EC157/**2**-10	Elan-tron ® EC 157	**2**	10	1.96
DGEBA/**3**-2.5	DGEBA	**3**	2.5	0.38
DGEBA/**3**-5	DGEBA	**3**	5	0.76
DGEBA/**3**-7.5	DGEBA	**3**	7.5	1.14
EC157/**3**-2.5	Elan-tron ® EC 157	**3**	2.5	0.38
EC157/**3**-5	Elan-tron ® EC 157	**3**	5	0.76
EC157/**3**-7.5	Elan-tron ® EC 157	**3**	7.5	1.14

3. Results and discussion

In order to design curing agents for epoxy resins a bis- or multi-amino ligand is required. In this frame, N-heterocyclic carbenes (NHCs) are good candidates for functionalization[25-35] because they are easy to prepare and tolerant, once coordinated to the metal, to functional groups.[36-40] Another class of ligands that can provide stability to the corresponding complexes are variously functionalized cyclopentadienones.[41-50] As above cited, our group has recently developed a straightforward synthetic procedure that combine NHC and cyclopentadienone as ligands in stable iron(0) complexes.[20,21] This latter pathway is here exploited in order to prepare bis-amino functionalized N-heterocyclic carbene iron complexes **2** and **3** designed to work as co-monomer and hardener in the synthesis of epoxy resins.

3.1 Synthesis of bis-amino functionalized iron complexes 2 and 3.

At a first stage the BOC protected bis-amino functionalized imidazolium salts 1,3-(BOC-aminopropyl) imidazolium bromide (**1**) was prepared by reacting 1-(3-BOC-aminopropyl)bromide and 1-(3-BOC-aminopropyl)-imidazole and heating at 110 °C for 24h in solvent free conditions (70% yield). NMR and ESI-MS characterization of **1** were superimposable with those reported for the same salt obtained with a different synthetic strategy.[24] The bis-amino functionalized iron complexes **2** and **3** has been then prepared under the conditions described in Scheme 1.



Scheme 1. Synthesis of bis-amino NHC iron complexes bearing different cyclopentadienone ligands **2** and **3**.

The one pot reaction between the two cyclopentadienone iron precursors and **1** leads to the BOC protected iron complexes **2-BOC** (Y = 55%) and **3-BOC** (Y = 74%), while the target bis-amino functionalized complexes **2** (Y = 85%) and **3** (Y = 88%) were obtained by deprotection of **2-BOC** and **3-BOC** with HBF_4, followed by neutralization of unreacted acid. Deprotection was monitored with IR spectroscopy by the disappearance of the C=O (BOC) stretching at 1709 cm^{-1} (**2-BOC**) and 1706 cm^{-1} (**3-BOC**).

All the synthesized compounds were characterized by means of FT-IR, ^{1}H and ^{13}C NMR spectroscopies, ESI-MS spectrometry and elemental analyses (see Experimental Section). In general NMR chemical shifts are in agreement with those reported for congener complexes.[20,21] In particular, complexes appear as yellow powders that are stable towards air and moisture while kept in the dark, both in the solid state and in most common organic solvents. ^{13}C NMR spectra show the diagnostic signal for the Fe-$C_{carbene}$ at 181-185 ppm, while the terminal CO stretching peaks around 1990-2000 and 1940-1930 cm^{-1} can be observed in the FT-IR spectra in CH_2Cl_2 solutions as expected.[20] The structures were further confirmed by ESI-MS analyses: **2-BOC** 773 m/z $[M+H^+]$, **2** 573 m/z $[M+H^+]$, **3-BOC** 939 m/z $[M+H^+]$, **3** 739 m/z $[M+H]^+$

3.2 Epoxy resin preparation

Commercially available epoxy hardeners are represented, for example, by 4,4′-methylene biscyclohexanamine (PACM) and diethyl toluene diamine (EPIKURE W) that are commonly used to obtain resins with high thermomechanical properties. By comparison, complexes **2** and **3** are by far more encumbered. In this frame, the investigation of the ability of complex **3**, i.e. the complex with the higher steric hindrance due to presence of a highly aromatic ligand on the metal, to react with di-epoxy functionalized moieties, is of particular interest in order to verify the suitability in the cross linking process for epoxy resin formation. Furthermore, as reported in literature, epoxy monomers and curing agents with higher aromaticity favor higher char yields[51] which, in turn, should result in better flame retardancy.[52, 53] Moreover, nitrogen containing FR were found to be competitive as

halogen-free flame retardants favoring inert N_2 evolution while burning.[5, 6] Finally, the actual incorporation of organometallic units into the polymer backbone would also avoid all the mixing issues of FRs additive with polymeric materials, allowing an intrinsic and time-stable formulation.

A preliminary screening of the reactivity of **3** was thus carried out in the presence of different amounts diglycidyl ether of bisphenol A (DGEBA, 5, 7.5 and 10%wt) labelled as DGEBA/**3**-2.5, DGEBA/**3**-5 and DGEBA/**3**-7.5. With the aim of establishing the occurrence of a curing process leading to a three-dimensional insoluble network, the analytical techniques available for the task are limited. Since in the present case the main purpose of the study is the preliminary assessment of the crosslinking occurrence and not a full and conclusive scheme of the reaction mechanism, a simple and reliable tool is required. Hence DSC measurements were carried out, since calorimetric investigation is able to provide some crucial information in a single test run for evaluating the reliability of the hardening system. Indeed, since epoxy opening reactions are highly exothermic owing to the strain release by the oxirane cycle's opening,[54] a DSC run can directly measure the overall rate of exothermic polymerization, as well as the temperature range required to trigger the process. Moreover, upon re-heating the same sample, it is also possible to obtain information on the glass transition temperature reached by the thermoset, a parameter that can be taken as an index for significant network formation. All the formulations were thus analyzed by DSC (Figure 1A) revealing a high-T exotherm accounting for cross-linking; in the II heating scan (Figure 1B) a glass transition (T_g) in the range 135-150°C is observed, as a symptom of resin formation (Table 2). It is worth noting that, by increasing the amount of hardener, the crosslinking reaction occurs at lower temperature, while the total cross-linking enthalpy (ΔH) increases (Table 2).

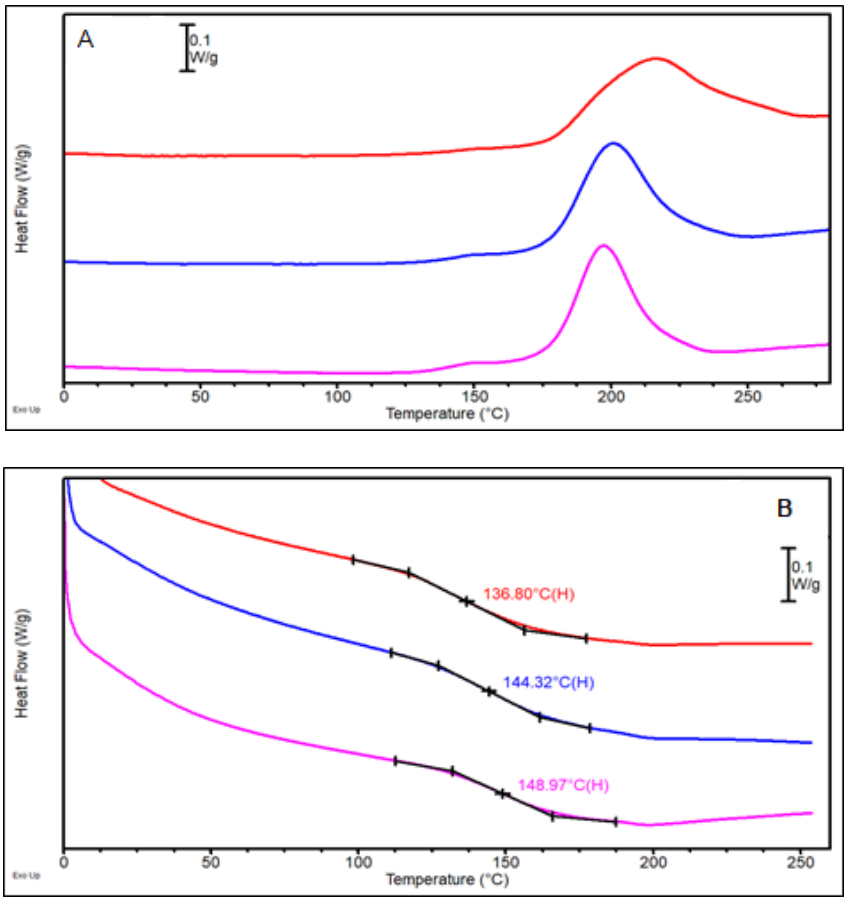


Figure 1. DSC thermograms in first (A) and second (B) heating scan of DGEBA/**3**-2.5 (—) DGEBA/**3**-5 (—) and DGEBA/**3**-7.5 (—).

Table 2. Data obtained by DSC isothermal runs applied at different DGEBA/**3** formulations

Sample	ΔH[a] (J/g)	$T_{r\ max}$[b]	T_g (°C)
DGEBA/**3**-2.5	420	214	137
DGEBA/**3**-5	437	200	144
DGEBA/**3**-7.5	460	197	149

[a] ΔH is the heat generated by the cross-linking reaction.
[b] $T_{r\ max}$ is the temperature corresponding to the maximum rate of the cross-linking reaction.

An analogous assessment carried out in the presence of 5, 7.5 and 10% of **2** was able to positively cross-link DGEBA though reaching slightly lower T_g (104°C, 105°C and 110°C respectively).[55] TGA curves (Figure 2) show, in addition to a high thermal stability of the resins with respect to the plain unreacted epoxy precursor, a significant char production in inert atmosphere (in the range of 20-30%

of the initial weight), that cannot be attributed to the DGEBA degradation pattern neither solely to the iron-related non-volatile residue. Such a behavior can be instead ascribed to the presence of the iron-based hardener which, as reported in literature[12-14] can catalyze the char formation. It is also worth to notice that the higher the iron content the higher the char produced upon resin degradation.

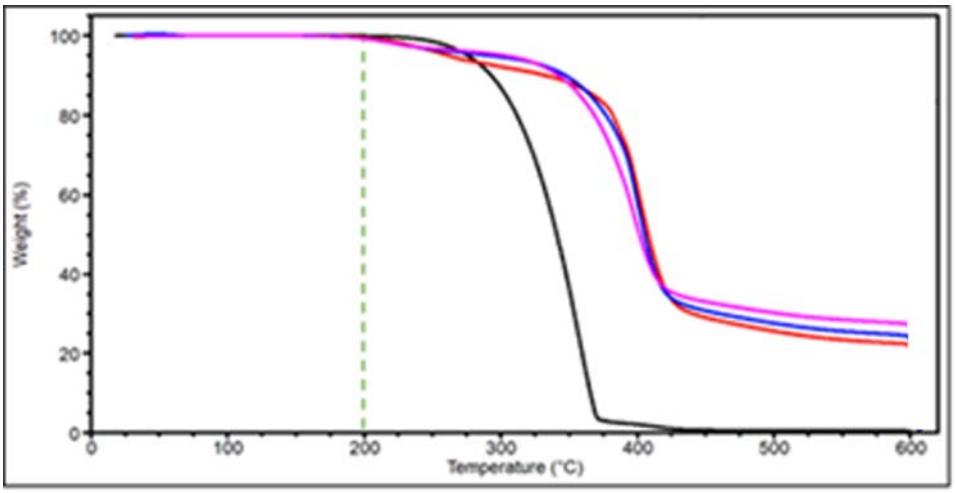


Figure 2. TGA thermograms in nitrogen atmosphere of plain DGEBA (—), DGEBA/**3**-2.5 (—), DGEBA/**3**-5 (—) and DGEBA/**3**-7.5 (—).

Given these preliminary results, hardener **3** was thus applied to cross-link a commercial epoxy precursor, Elan-tron® EC 157, intended for infusion applications. Depending on the hardener system used, technical datasheet reports the EC 157 epoxy precursor to be able to reach T_g as high as 80-130°C. In the present case formulations with 2.5, 5, and 7.5%wt of iron-based hardener **3**, namely EC157/**3**-2.5, EC157/**3**-5 and EC157/**3**-.7.5, were studied. Once again DSC analyses reveal exotherms at high temperature, while the T_g attained (around 90°C) were lower than DGEBA systems (Figure 3, Table 3), nonetheless confirming the thermoset formation.

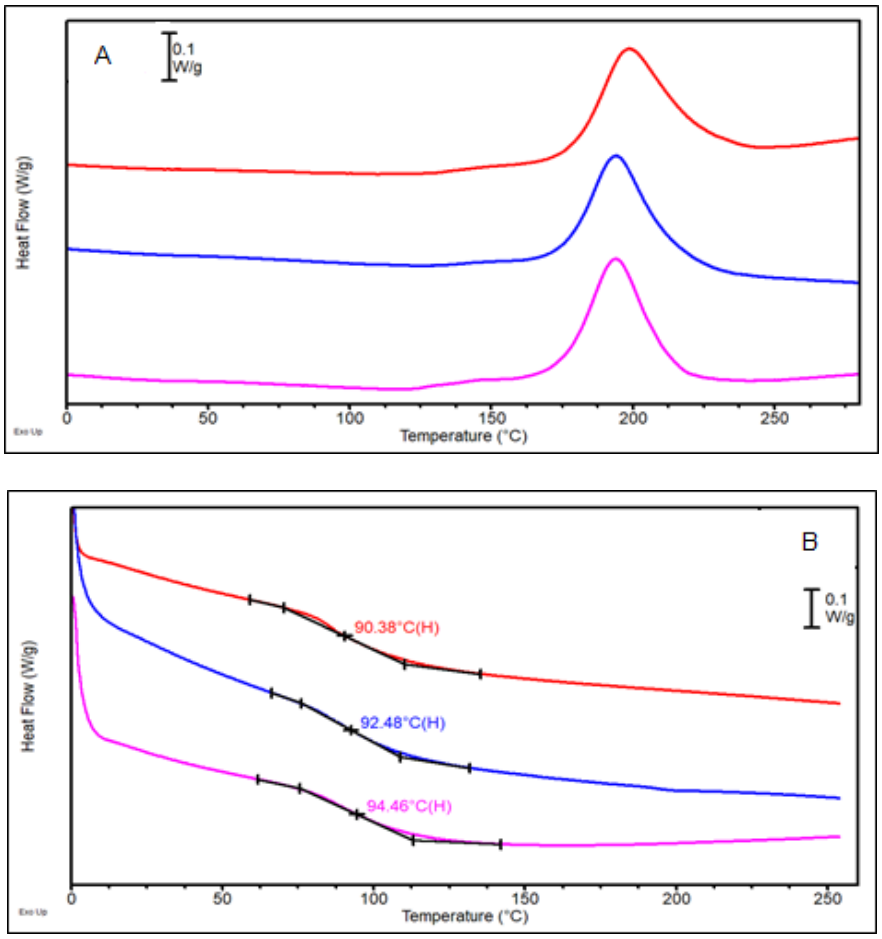


Figure 3. DSC thermograms in first (A) and second (B) heating scan for EC157/**3**-2.5 (—), EC157/**3**-5 (—) and EC157/**3**-7.5 (—).

Table 3. Data obtained by DSC isothermal runs applied at different EC157/**3** formulations

Sample	ΔH^a (J/g)	$T_{r\ max}{}^b$	T_g (°C)
EC157/**3**-2.5	420	198	90
EC157/**3**-5	441	194	93
EC157/**3**-7.5	455	194	94

[a] ΔH is the heat generated by the cross-linking reaction.
[b] $T_{r\ max}$ is the temperature corresponding to the maximum rate of the cross-linking reaction.

It is worth noting that by enhancing the amount of hardener, the reaction enthalpy increases and is also associated to a shift of the exotherm peak to lower temperatures (Table 3).

The resins formation was confirmed also by TGA analysis (Figure 4) showing a higher thermal stability with respect to the plain Elan-tron ® EC 157 precursor. The degradation pattern appears similar to those reported for DGEBA/**3** systems in Figure 2, with a residual char content around 25%wt, and a final solid residue after oxidation that well compares with the expected iron feed.

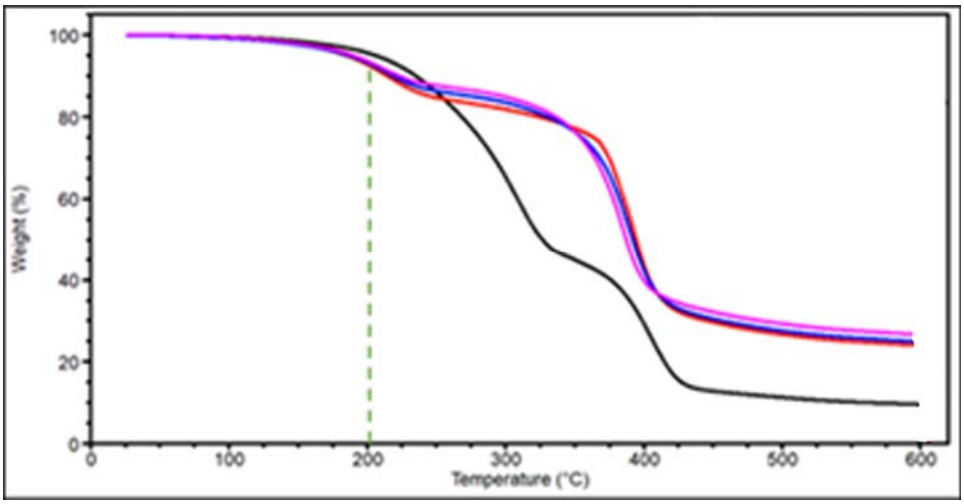


Figure 4. TGA thermograms of plain Elan-tron® EC 157 (—), EC157/**3**-2.5 (—), EC157/**3**-5 (—) and EC157/**3**-7.5 (—).

As reported above, the high char formation confirms the catalytic effect of iron. It is also worth to point out that the char content of EC157/**3** systems at 600°C is similar to that one of EC157/**2** formulations with the same hardener content.[55] Anyway, considering the higher molecular weight of **3** with respect of **2**, EC157/**3** formulations results in an iron content lower than EC157/**2** systems, as shown in Table 1 (See Experimental Section). Hence, the presence of aromatic moieties seems to promote the charring ability of the systems which, in turn, should result in better flame retardancy.

4. Conclusions

Properly designed bis-amino functionalized iron complexes **2** and **3** were prepared and employed as suitable curing agents for the preparation of novel hybrid epoxy resins. Cross linking properties have been demonstrated with both DGEBA and commercial pre-polymer Elan-tron® EC 157. Different formulations were tested and up to 10%wt of iron-based hardener with an iron content up to about

2%wt, could be achieve. All the formulations proved to be able to cross-link epoxy precursors with good results. Indeed fairly high glass transition temperatures were obtained, confirming that **2** and **3** act as efficient cross-linkers. Finally, the presence of iron lead to high charring ability which should result in good flame retardancy. In particular the presence of aromatic moieties in the functionalized iron complex **3** seems to further promote the char formation which can act as smoke suppressor and fire inhibitor via intumescent later formation, thus paving the way to the application of these materials as potential flame behaviour modifiers.

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Conflict of Interest

There are no conflict of interest to declare.

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