ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 5301–5303

www.rsc.org/chemcomm

COMMUNICATION

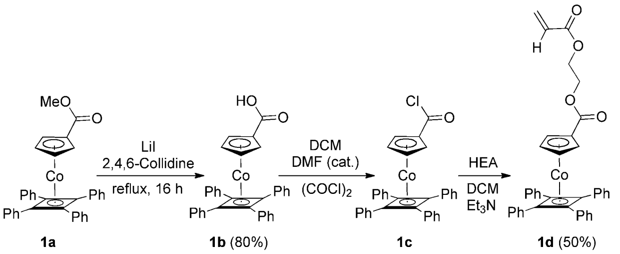
Side chain Co(I) polymers featuring acrylate functionalized neutral 18 electron CpCo(C_4R_4) (R = Ph, Me) units†

Preeti Chadha and Paul J. Ragogna*

Received 23rd February 2011, Accepted 17th March 2011
DOI: 10.1039/c1cc11076d

The synthesis of novel Co(I) polymers featuring CpCo(C_4R_4) units are reported. The cyclopentadienyl ring on the CpCo(C_4R_4) unit has been functionalized with acrylate or methacrylate groups. Acrylate derivatives of these compounds were found to polymerize giving rise to the first example of polymers containing neutral, 18 e cobaltoarenocenes in the side chain.

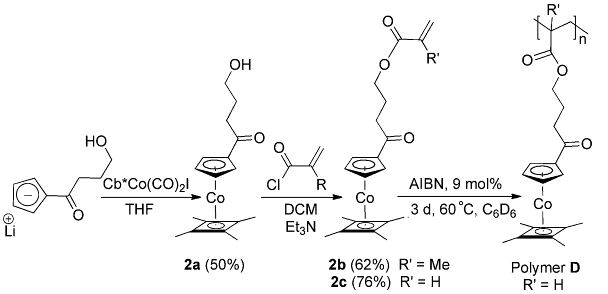
The field of metallopolymers has quickly matured over the last decade due to the emerging applications of these materials in various fields of science and technology.[1] Polyferrocenylsilanes (PFS) are by far the most broadly developed and well studied class of metallocene based polymers, which have found applications in areas such as ceramics,[2] photonic crystal displays,[3] nanolithography,[4] as well as precursors to electroactive, magnetic or catalytically active nanostructures.[5] The cobaltocenium cation ($CoCp_2^+$) is isoelectronic with ferrocene and three recent reports of cobaltocenium containing polymers have emerged, where one incorporates cobaltocenium in the main chain of the polymer[6] and the others incorporate it in the side chain.[7] Cyclopentadienyl-cobalt-cyclobutadiene (CpCoCb) is also isoelectronic with ferrocene and cobaltocenium and has different properties (*cf.* cobaltocenium) because it is electronically neutral (*e.g.* excellent solubility in many solvents). It also has the additional advantage that a wide variety of substituents can be incorporated on the cyclobutadiene ring, which in turn, greatly influence the properties of the CpCoCb framework.[8,9] Cobaltocenium, in comparison, is relatively difficult to functionalize. Polymers containing these Co(I) units have seen limited development wherein main chain Co(I) polymers have been primarily prepared by metallacycling polymerization (MCP)[10] of bisalkynes at a Co(I) centre. However, side chain Co(I) polymers utilizing the CpCoCb framework remain unreported. In this context, we have developed methacrylate and acrylate functionalized cobaltoarenocenes **1d**, **2b** and **2c** as the first representatives of this class of compounds and studied their polymerization behaviour.



Scheme 1 Synthesis of the acrylate appended monomer **1d**.†

The acrylate appended monomer **1d** was obtained in a moderate yield by the *in situ* conversion of carboxylic acid **1b** to the acid chloride **1c** and subsequent halide displacement with hydroxyethylacrylate (HEA) (Scheme 1). Compound **1b** was prepared from the hydrolysis of the ester **1a** following a literature procedure.[11] The phenyl substituted ($C_4R_4{=}C_4Ph_4$) acrylate monomer **1d** was comprehensively characterized using NMR spectroscopy, FT-IR spectroscopy, mass spectrometry and elemental analysis.†

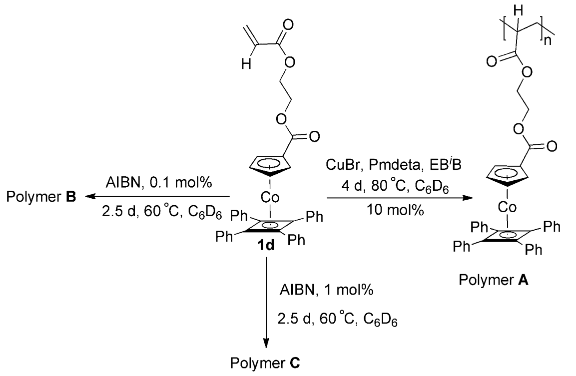
Synthesis of the methyl derivative of **1d** ($C_4R_4{=}C_4Me_4$) proved to be difficult since we were unable to hydrolyze the ester $Cb^*Co(C_5H_4CO_2Me)$[12] ($Cb^*{=}C_4Me_4$) into the corresponding carboxylic acid, partly due it's lower stability towards the comparatively harsh conditions required for the synthesis. An alternative approach was followed as to introduce the alcohol on the cyclopentadienyl ring prior to the installation of the Cb*Co unit (Scheme 2). Lithium(1-carboxy-propan-3-ol)cyclopentadiene was reacted with $Cb^*Co(CO)_2I$ to generate the alcohol appended species **2a** which was then treated with methacryloyl and acryloyl chloride to obtain **2b** and **2c**



Scheme 2 Synthesis of methyl substituted cyclobutadiene complexes **2a–2c**.

The University of Western Ontario, 1151 Richmond St., N6A 5B7, London, ON, Canada. E-mail: pragogna@uwo.ca; Fax: +1 519-661-3022; Tel: +1 519-661-2111 ext 87048

† Electronic supplementary information (ESI) available: Extensive experimental details for the synthesis of all compounds and full characterization data. CCDC 812213. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11076d



Scheme 3 Polymerization of monomer (**1d**) *via* ATRP and conventional free radical methods. Polymers **A–C** have the same general structure, but vary in the number of units (*n*).

(see ESI† for X-ray structural details) respectively, by simple halide displacement reaction.

Compounds **1d**, **2b** and **2c** were then subjected to polymerization conditions using two different methods: (a) atom transfer radical polymerization (ATRP); and (b) conventional free radical. The polymerization reactions were performed in J-Young NMR tubes in C_6D_6 to monitor the progress of the reaction by ^{1}H NMR spectroscopy. Copper(I) bromide (CuBr) was used as the catalyst, ethyl 2-bromoisobutyrate (EB^{i}B) as the initiator, and pentamethyldiethylenetriamine (Pmdeta) as the ligand. The first attempt was made with 1 mol% of the initiator (keeping the mol% of initiator : catalyst : ligand constant) and no polymerization was observed in all cases. Upon increasing to 10 mol%, the reaction was observed to 70% completion for **1d** (giving polymer **A**, Scheme 3) and only 10% for **2c** over a period of 4 d at 80 °C. Due to the low % conversion of the methyl substituted polymer by this method, no further investigations were pursued. Precipitation of green solids, likely resulting from the oxidation of CuBr was observed during the course of conversion, and accounts for the cessation of the reaction.

The conventional free radical method was also tested using azobisisobutyronitrile (AIBN). In the case of **1d**, polymerization proceeded with 1 mol% as well as 0.1 mol% AIBN. However, for **2c** 9 mol% AIBN was required to observe any polymerization. Over a period of 3 d at 60 °C, 90% completion was observed for the phenyl substituted polymers **B** and **C** (Scheme 3) and only 65% completion for methyl substituted polymer **D** (Scheme 2). It should be noted that no polymerization was observed in the case of **2b** under any of the above conditions. This could be due to the low reactivity of the methacrylate unit[13] in the present system or possible chain transfer processes involving the organometallic moiety. This is however, in contrast with the analogous ferrocene compounds reported by Tang *et al.* where the methacrylate species was found to be more reactive towards polymerization.[14]

All polymers **A–D** were found to be soluble in common organic solvents such as DCM, THF and benzene, allowing for their easy characterization by standard methods; and insoluble in *n*-pentane, Et_2O and H_2O. However, subtle differences were observed in the physical properties of the phenyl substituted polymers **A–C** which were insoluble in MeOH in contrast to polymer **D** which was soluble. The polymers were stored in open atmosphere and were found to be air and moisture stable for upto 30 d. Proton NMR spectra of the isolated polymer and monomer (Fig. 1 and 2), show the disappearance of the vinylic protons and a general broadening of the spectra. The appearance of broad peaks in the alkyl region (1.5–2.5 ppm) of the polymer correspond to the conversion of vinylic CH=CH$_2$ group into the internal CH–CH$_2$– fragment. The disappearance of the alkene peak at 1635 cm^{-1} in the FT-IR spectra of polymer **A** (Fig. S1, ESI†) gave corroborating evidence to polymer formation.

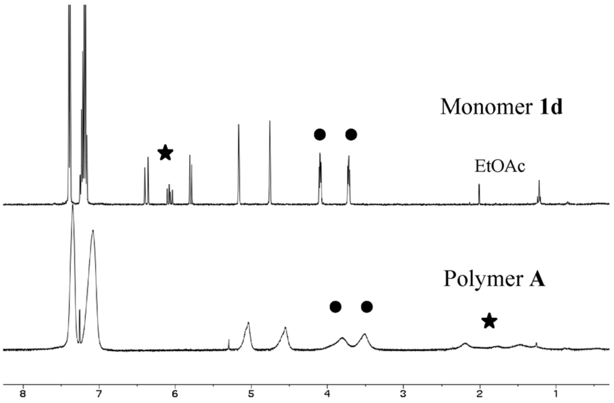


Fig. 1 Proton NMR spectra of monomer **1d** and polymer **A**. ★ denotes the vinylic protons and ● denotes the CH$_2$ protons in the linker.

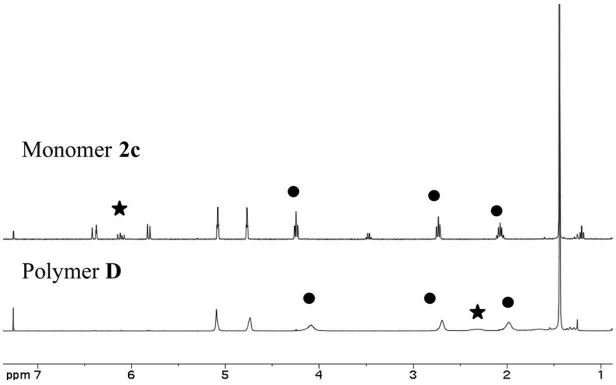


Fig. 2 Proton NMR spectra of monomer **2c** and polymer **D**. ★ denotes the vinylic protons and ● denotes the CH$_2$ protons in the linker.

Molecular weights and PDI's of the polymers were determined by size exclusion chromatography (SEC) (Table 1) which indicates both low molecular weight and low PDI for polymer **A** prepared by the ATRP method. Lower molecular weight for **A** results from the use of more initiator which was necessary, since a lower percentage resulted in sluggish reactivity. Polymers **B** and **C** exhibit higher molecular weights (less mol% of initiator used) and higher PDI values. The methyl substituted polymer **D** had a lower molecular weight due to the higher percentage of AIBN (9 mol%) that was required. The requirement of more AIBN may be speculated due to the short lifetime of the radical that is formed and propagates the chain during

Table 1 Summary of the molecular weights and PDI of polymers **A–D**

Polymer	Method	Mol%	PDI	M_n/g mol^{-1} ($\times10^3$)	n	% Yield (isolated)
A	ATRP	10%	1.15	3.6	6	60
B	AIBN	0.1%	2.09	30.5	49	70
C	AIBN	1.0%	1.90	26.1	42	70
D	AIBN	9.0%	1.31	10.6	28	50

n = average number of monomer units incorporated in the polymer based on M_n (absolute mol. wt.); Mol% = mol% of the initiator with respect to the monomer **1d** or **2c** respectively.

polymerization, however, further studies are required in this regard.

Thermogravimetric analysis (TGA) (Fig. S2, ESI†) of the polymers revealed that the phenyl substituted polymers **A–C** are stable upto 360 °C, whereas the methyl substituted polymer **D** was found to be thermally less stable (T_d = 235 °C) (Fig. S2, ESI†). This can be attributed to the lower thermal stability of the monomer **2c** (T_d = 214 °C) as compared to the phenyl substituted monomer **1d** (T_d = 367 °C).

Differential Scanning Calorimetry (DSC) of monomer **1d** (Fig. S3, ESI†) showed a melting endotherm and an exotherm for polymerization suggesting that the phenyl substituted monomer is thermally polymerizable. No melting or polymerization transition was observed in the DSC of monomer **2c**. Glass transition temperatures (T_g) of the polymers (Fig. S4, ESI†), were determined from the DSC measurements and were found to be in the range of 100 °C–130 °C for polymers **A–C**. Thermal analysis of polymer **D** revealed a much lower T_g at 43 °C. This can be attributed to increased flexibility of the methyl substituted polymer due to less steric bulk.

In summary, we have synthesized a series of functionalized $CpCo(C_4R_4)$ complexes bearing a methacrylate or acrylate moiety on the Cp ring. The acrylate-appended monomers (**1d** and **2c**) were found to polymerize using radical polymerization methods. These polymers represent the first example of the incorporation of such unique organometallic species into a poly(acrylate) architecture and furthermore, attains a 100% incorporation of the Co(I) subunit in the resulting material. The reactivity of the monomer was found to be influenced by the variation of substituents on the remotely located C_4R_4 ring (away from the polymerization site). The thermal properties of the polymer could also be varied by changing the R substituents. Future efforts aim at incorporating electron withdrawing R groups, studying their effects, standardizing living polymerization methods for these species, and developing Co(I) block copolymers and studying their self assembly.

We thank the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Canada Foundation for Innovation (CFI) and The University of Western Ontario for generous financial support. We also thank Ali Nazemi and Dr E. Gillies (UWO) for the GPC analysis of the polymers; Jacquelyn Price and Caleb Martin for X-ray data collection.

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