Solid state polymerization of the unsymmetrical [1]ferrocenophane Fe(η-C_5H_4)$_2$SiMePh; synthesis of the first stereoregular organometallic polymer

John Rasburn, Daniel A. Foucher, William F. Reynolds, Ian Manners*† and G. Julius Vancso*‡

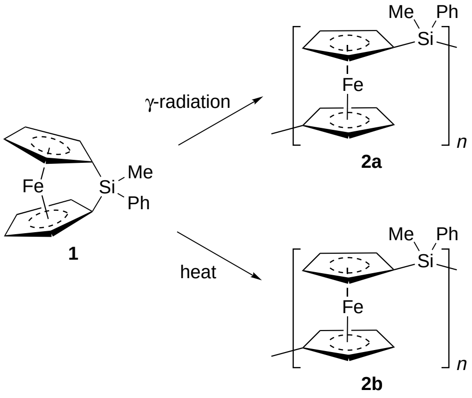
Department of Chemistry, University of Toronto, 80 St. George St., Toronto, Ontario M5S 3H6, Canada

Solid state polymerization of the [1]ferrocenophane Fe(η-C_5H_4)$_2$SiMePh yields a stereoregular poly(ferrocenylmethylphenylsilane), the first example of a stereoregular organometallic polymer.

Although stereoregular organic polymers (*e.g.* isotactic or syndiotactic polypropylene) are well studied materials of considerable industrial importance, stereoregular inorganic polymers are virtually unknown.[1] A rare recent report describes the preparation of poly(methylphenylsilane) [SiMePh]$_n$ using a chiral dehydrocoupling catalyst.[2] In this case the tacticity was not deduced unequivocally, but a syndiotactic microstructure was tentatively proposed on the basis of NMR data. Here, we report the first synthesis of a stereoregular organometallic polymer using the technique of solid-state polymerisation.

Owing to the possibility of accessing processable materials with novel electronic and optical properties, the synthesis and study of inorganic and organometallic polymers has attracted increasing recent interest.[3] Significant among these are the poly(ferrocenylsilanes), unusual polymers with a main-chain comprising alternating ferrocene and organosilane units.[4] A common method of polymerisation involves thermal ring-opening polymerization (ROP) of strained, silicon-bridged [1]ferrocenophanes to give high molecular mass materials (M_w = 10^5–10^6 Da).[5–10] More recently, anionic and transition metal catalyzed ROP has also been reported.[11] However, by analogy with the well known case of the topotactic polymerisation of trioxane and tetroxane to produce polyoxymethylene,[12–14] strained [1]ferrocenophanes would also seem to be excellent candidates for topotactic or solid-state polymerisation. Indeed, recently we showed that the symmetrically substituted [1]ferrocenophane Fe(η-C_5H_4)$_2$SiMe$_2$ yielded a high-molecular-weight poly(ferrocenyldimethylsilane) [Fe(η-C_5H_4)$_2$SiMe$_2$]$_n$ with properties similar to the thermally ring-opened materials on ^{60}Co γ-irradiation of symmetrically-substituted monomer crystals.[15] Nevertheless, important issues such as whether the reaction was topotactic remained open.

To gain further insight, we have investigated the use of an unsymmetrically-substituted [1]ferrocenophane monomer, Fe(η-C_5H_4)$_2$SiMePh **1**.[16] The resulting microstructure can be examined by solution NMR and hence represents an alternative approach to reliance on X-ray scattering methods, although not as detailed. In the reaction scheme (Scheme 1) **2a** refers to the solid-state polymerised polymer, to be compared with **2b**, the thermally ring-opened material.



Scheme 1

For our study, large maroon single-crystals of **1** were synthesised as described previously,[10] purified by repeated high-vacuum sublimations, and then sealed (0.65 g) in a Pyrex tube. The crystal structure of this monomer is well established.[16] The tube was then irradiated *via* placement close to a ^{60}C γ-ray source at 25 °C at 0.71 MRad for 24 h (for a total dosage of 17 MRad). On removal from the source, the temperature was measured to be 38 °C, well below the melting temperature of the crystals.[10,16] Any post-irradiation heat-treatment was avoided. The tube was then returned to the N$_2$ atmosphere and the contents extracted with an excess of hexanes to remove unreacted monomer and oligomeric species. The product **2a** was obtained as 0.30 g (46%) of yellow–orange platelets on which the original superstructure of the monomer crystals could be vaguely discerned. The platelets could be teased apart into fibrils. For solution NMR analysis, the product was purified by reprecipitation from THF into chilled *n*-propanol to give a pale yellow powder (M_w was determined to be 90 000 Da with a polydispersity of 1.4 by gel permeation chromatography *vs.* polystyrene standards). The thermally ring-opened polymer **2b** was synthesised as described previously.[10]

Wide-angle X-ray analysis of **2a** revealed three main scattering peaks at d = 7.81, 5.69 and 4.26 Å, all rather broad and suggestive of small and imperfect crystallites. By contrast, samples of **2b** give broad and featureless amorphous halos characteristic for this amorphous polymer. This suggested a different and more regular stereochemistry for **2a** compared to **2b**. Moreover, conspicuous differences in the ^{1}H and ^{13}C NMR spectra were evident when the solid state polymerized material **2a** was compared with the thermally generated product **2b**. In both the ^{1}H and the ^{13}C NMR spectra the methyl resonance of **2a** was a singlet. This implies stereoregularity when compared to the three observed resonances for **2b** where the approximate 1 : 2 : 1 intensity ratio can be assigned to mm (or rr), mr/rm, and rr (or mm) triads for an atactic polymer [see Fig. 1(*b*) *cf.* 1(*d*) and 2(*c*) *cf.* 2(*f*), respectively].[17] Similarly, the observed ^{1}H NMR resonances for the cyclopentadienyl group for **2a** [shown in Fig. 1(*a*)] constitute a subspectrum of that of **2b** [Fig. 1(*c*)]. Interestingly, the *ipso*-carbon atoms in the cyclopentadienyl groups show tetrad resolution with six ^{13}C NMR resonances in Fig. 2(*e*). In striking contrast, only one of the tetrad sequences is present in **2a** [Fig. 2(*b*)].[17,18]

The actual tacticity of **2a** (syndiotactic or isotactic) has not yet been definitively elucidated. The assignment is not straightforward, particularly as there is negligible *J*-coupling across the iron centres, and therefore some interpretation of the chemical shifts or dipolar couplings in terms of likely rotational isomeric states is required.[17,18] However, we tentatively assign a syndiotactic architecture. Thus, for the melt polymerized polymer **2b** although atactic triads (mr/rm) clearly predominate, syndiotactic triads (mm§) would be expected to be slightly more favoured than isotactic triads (rr§) based on steric arguments. This suggests the assignment of the ^{1}H NMR resonances at δ 0.772 in Fig. 1(*d*) and the ^{13}C NMR resonance at δ −3.17 in Fig. 2(*f*) to syndiotactic (mm) triads. Consideration of Fig. 1(*b*) *cf.* 1(*d*) and 2(*c*) *cf.* 2(*f*) shows that the ^{1}H and ^{13}C NMR resonances assigned to the methyl groups of **2a** correspond to these resonances of **2b** which we tentatively assign to syndiotactic triads.

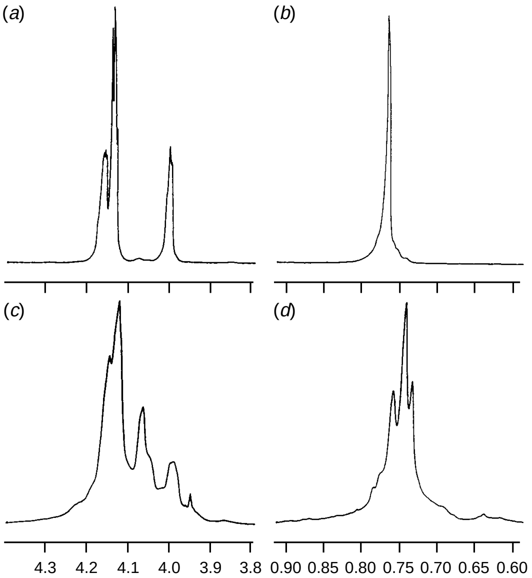


Fig. 1 ^{1}H NMR spectra (300 MHz, C_6D_6, 20 °C) of **2a** [(*a*), (*b*)] and **2b** [(*c*), (*d*)]. Spectra (*a*) and (*c*) compare cyclopentadienyl resonances, and (*b*) and (*d*) methyl resonances.

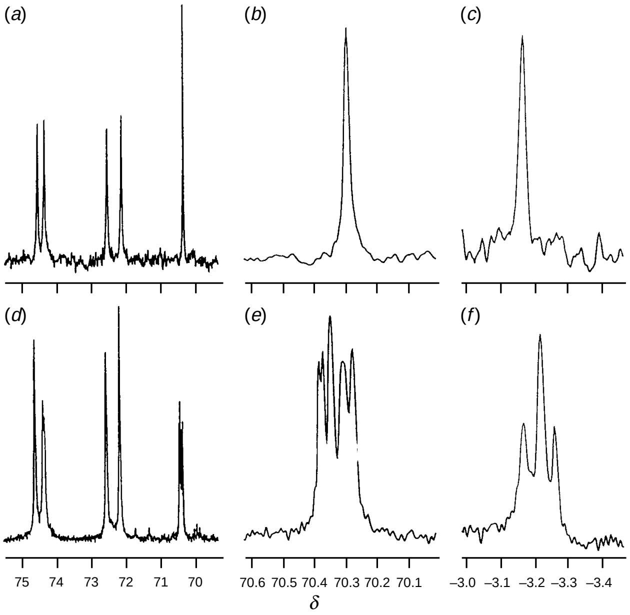


Fig. 2 Quantitative ^{13}C NMR spectra (75 MHz, C_6D_6, 20 °C) of **2a** [(*a*)–(*c*)] and **2b** [(*d*)–(*f*)]. Spectra (*a*) and (*d*) show resonances for cyclopentadienyl carbons, (*b*) and (*e*) show resonances for *ipso* cyclopentadienyl carbons, and (*c*) and (*f*) show resonances for methyl carbons.

Further work is aimed at definitively determining the stereochemistry of **2a** (isotactic or syndiotactic) as well as obtaining further insight into the kinetics and topotaxis of this novel solid-state reaction.

The authors would like to thank Dr J. K. Pudelski for provision of the thermally polymerised polymer sample. G. J. V. and I. M. are grateful to the Natural Science and Engineering Research Council (NSERC) and Institute for Chemical Sciences and Technology (ICST) for funding this research. I. M. also thanks NSERC for an E. W. R. Steacie Fellowship (1997–99), the Alfred P. Sloan Foundation for a Fellowship (1994–98), and the University of Toronto for a McLean Fellowship (1997–2003).

Notes and References

† E-mail: imanners@alchemy.chem.utoronto.ca

‡ Present address: University of Twente, Department of Chemical Technology, Drienerlo Laan 5, NL 7522 NB Enschede, The Netherlands.

§ For an isotactic poly(ferrocenylsilane) (*i.e.* a chain comprising repeat units of identical stereochemistry) inspection of the asymmetric center by Newman projections from within a given dyad indicates that both have the same handedness and hence isotactic dyads are r and syndiotactic dyads are m, in contrast to the situation with vinyl and silane polymers.

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Received in Bath, UK, 5th February 1998; 8/01042K