A Remarkable Ancillary Ligand Effect in Living Ring-opening Metathesis Polymerisation

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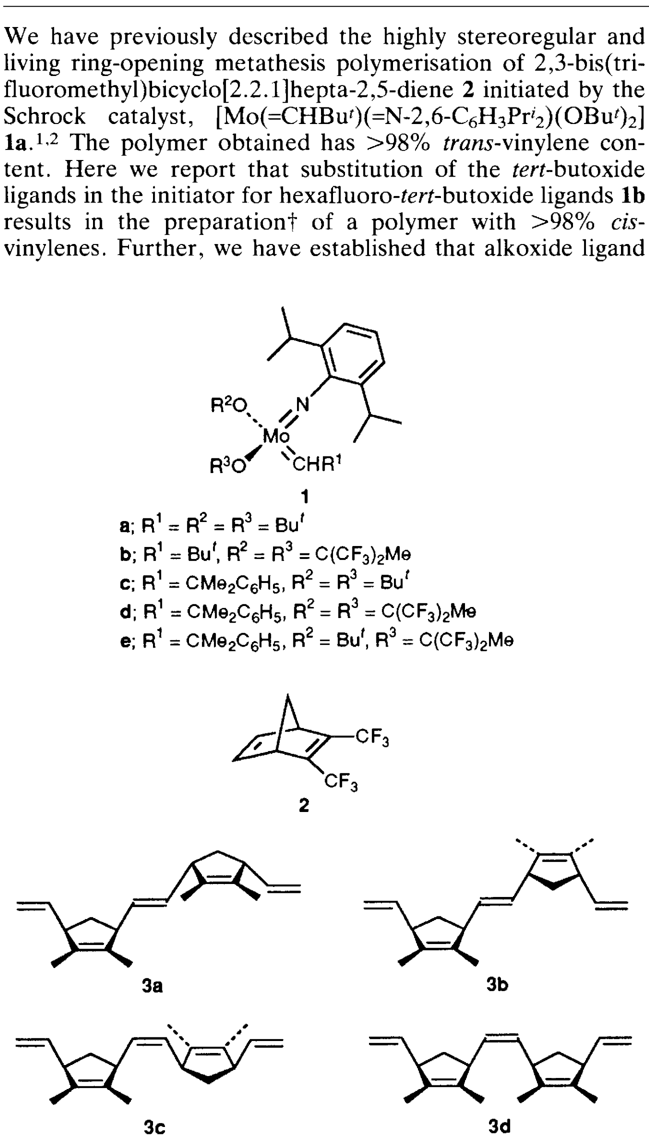
The microstructure of poly {3,5-[1,2-bis(trifluoromethyl)cyclopentenylene]vinylene} obtained *via* living ring-opening metathesis polymerisation initiated by Schrock catalysts, $[\mathrm{Mo(=CHR^1)(=NAr)(OR^2)_2}]$, is a sensitive function of the alkoxide ligands.

We have previously described the highly stereoregular and living ring-opening metathesis polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene **2** initiated by the Schrock catalyst, $[\mathrm{Mo(=CHBu^{t})(=N\text{-}2,6\text{-}C_6H_3Pr^{i}_2)(OBu^{t})_2}]$ **1a**.[1,2] The polymer obtained has >98% *trans*-vinylene content. Here we report that substitution of the *tert*-butoxide ligands in the initiator for hexafluoro-*tert*-butoxide ligands **1b** results in the preparation† of a polymer with >98% *cis*-vinylenes. Further, we have established that alkoxide ligand exchange is rapid compared with the rate of propagation and that this may be exploited to prepare polymers with a predetermined *cis–trans*-vinylene content.



a; $R^1 = R^2 = R^3 = Bu^t$
b; $R^1 = Bu^t$, $R^2 = R^3 = C(CF_3)_2Me$
c; $R^1 = CMe_2C_6H_5$, $R^2 = R^3 = Bu^t$
d; $R^1 = CMe_2C_6H_5$, $R^2 = R^3 = C(CF_3)_2Me$
e; $R^1 = CMe_2C_6H_5$, $R^2 = Bu^t$, $R^3 = C(CF_3)_2Me$

3a = *trans*-syndiotactic; **3b** = *trans*-isotactic;
3c = *cis*-syndiotactic; **3d** = *cis*-isotactic

Scheme 1

Scheme 1 shows the catalyst and monomer structures and the possible assembly modes for poly{3,5[1,2-bis(trifluoromethyl)cyclopentenylene]vinylene} **3**. When **1a** or **1c** is used as the initiator the chain microstructure is **3a** and/or **3b**[2] and the 100 MHz ^{13}C NMR spectrum of this product is shown in Fig. 1(*a*). When **1b** or **1d** is employed the resultant polymer gives the spectrum shown in Fig. 1(*b*) which is indicative of a material with >98% *cis*-vinylenes. The multiplicity of the methylene carbon signal (two resonances, at δ 38.33 and 37.54) indicates that this polymer is not 100% tactic, *i.e.* neither solely **3c** nor **3d**.

These polymerisations show all the characteristics of well-ordered living systems with narrow molecular mass distributions and progressive increases in molecular mass with increasing monomer to initiator ratios, Table 1.

Fig. 2 shows the alkylidene region of the ^1H NMR spectrum of a 1 : 1 mixture of **1c** and **1d** in $[^2H_6]$benzene, together with the assignments of the three signals. The same equilibrium mixture is observed when the mixed ligand species **1e**, crystallised selectively from toluene, is dissolved in $[^2H_8]$tolu-

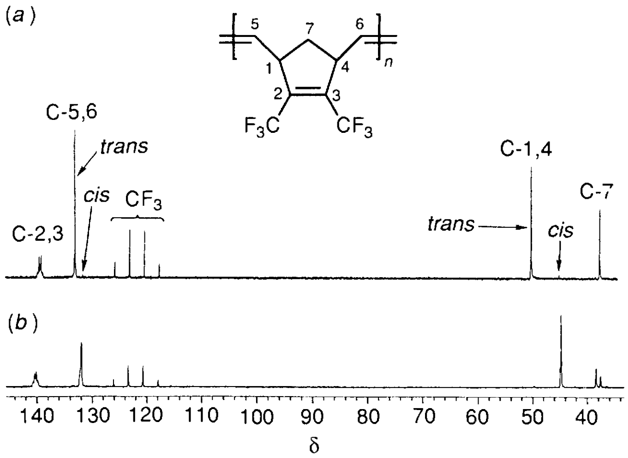


Fig. 1 The 100 MHz ^{13}C NMR spectra $[(CD_3)_2CO]$ of **3** initiated by (*a*) **1a**; (*b*) **1b**

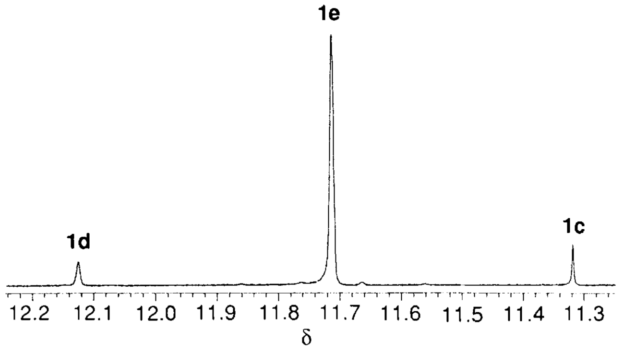


Fig. 2 The 400 MHz ^1H NMR spectrum (C_6D_6) of the alkylidene region for a 1 : 1 mixture of **1c** and **1d**

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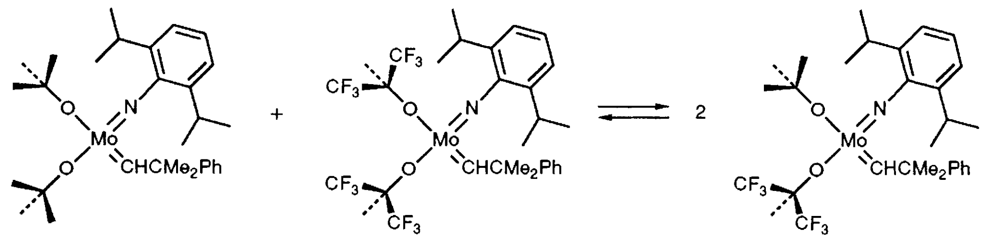
† The general procedure is analogous to that adopted for the synthesis of *trans*-2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (see ref. 2). Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (1.11 g, 4.87 mmol) in trifluorotoluene (1.2 ml) was added dropwise to a rapidly stirred solution of $[\mathrm{Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}C_6H_3Pr^{i}_2)\{OCMe(CF_3)_2\}_2}]$(0.008 g, 1.05×10^{-2} mmol in 1.2 ml of trifluorotoluene; 464 equivalents of monomer). No colour change was apparent, but within 3 min the mixture became extremely viscous and turned noticeably cloudy. In order to maintain a homogeneous solution, an additional 4 ml of trifluorotoluene were added and stirring was continued for 24 h. The polymerisation was then terminated by addition of benzaldehyde (50 µl) accompanied by stirring for a further 60 min. The polymer was isolated by precipitation from hexane. Yield 0.88 g, 79%.



Scheme 2

Table 1 Gel permeation chromatographic analysis on high-*cis*-poly{3,5-[1,2-bis(trifluoromethyl)cyclopentenylene]vinylene}[a]

Molar ratio of monomer to initiator	M_n found	M_n calculated	Polydispersity (M_n/M_w)
51	11200	11700	1.06
200	45700	45600	1.10

[a] Traces recorded on 0.1–0.3% m/v samples using a Viscotek differential refractometer fitted with a Knauer HPLC pump 64 and two PLgel 10μ mixed columns, previously calibrated using commercially available polystyrene standards (Polymer Laboratories) in the molecular mass range 1206–1.03 × 10^6 (tetrahydrofuran flow rate = 1 ml min^{-1}).

ene at −80 °C (spectrum obtained immediately after thawing),[3] indicating that the ligand exchange process shown in Scheme 2 is very rapid. By contrast, the rate of polymer formation (propagation) is much slower; for example, 200 equivalents of monomer (at a concentration of 6 × 10^{-1} mol dm^{-3}) takes 24 h to be completely consumed. These observations indicated the potential for controlling *cis–trans* vinylene content through a mixed, rapidly equilibrating, initiator system.

The *cis–trans*-vinylene content of **3** as a function of the composition of the initiator mixture is shown in Fig. 3, which demonstrates the degree of microstructural control accessible by this strategy.

The high-*trans*-polymer displays an unusually high relaxed dielectric constant[4] and is potentially interesting in relation to pyro- and piezo-electric devices. An understanding of the structure–property relationships in such materials is dependent on access to a range of samples with well-defined and different microstructures. This work establishes a control strategy for *cis–trans*-vinylene content. Relaxed dielectric constant measurements lead to the conclusion that all the materials described here have a predominantly syndiotactic structure.[5]

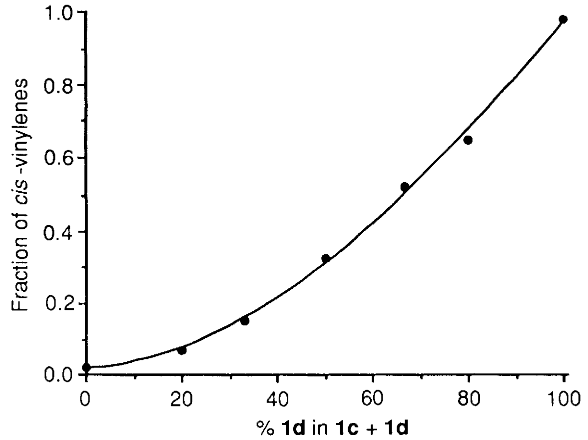


Fig. 3 Variation of *cis*- and *trans*-content with different initiating mixtures of **1c** and **1d**

The SERC is gratefully acknowledged for a studentship (to E. L. M.). V. C. G. is the recipient of a BP Chemicals Young University Lecturer Award and an Edward Frankland Fellowship of the Royal Society of Chemistry. We also express our gratitude to Professor R. R. Schrock and Professor K. J. Ivin for helpful discussions, and Professor I. M. Ward, Dr G. R. Davies, Dr H. V. St. A. Hubbard and S. C. Wellings of the IRC at Leeds University for helpful discussions and the dielectric measurements.

Received, 13th April 1992; Com. 2/01906J

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