Synthesis of stereoblock copolymers *via* ligand exchange in living stereoselective ring opening metathesis polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

Joost Broeders,† W. James Feast, Vernon C. Gibson‡ and Ezat Khosravi*

Interdisciplinary Research Centre in Polymer Science and Technology, University of Durham, South Road, Durham, UK DH1 3LE

Poly{2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene} is synthesised as a stereoblock copolymer containing *cis*- and *trans*-vinylene blocks *via* ligand exchange in living stereoselective ring opening metathesis polymerisation initiated by a well defined Schrock type initiator.

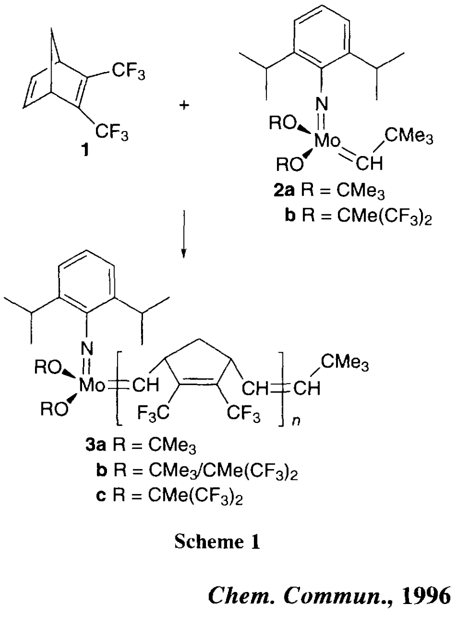
Rapid progress in understanding the correlations between molecular structure, conformation, supramolecular organisation and the chemical and physical properties of synthetic macromolecules, coupled to the continually improving capacity to model all these things theoretically,[1] puts heavy demands on available methods for the synthesis of macromolecules in a precisely controlled manner. In chain growth polymerisations a measure of control over the product polymer's molecular weight distribution can be obtained using polymerisation chemistries in which there are no spontaneous termination reactions.[2] Such systems are described as 'living' and examples of the genre are established for chain growth polymerisations using radicals,[3] anions,[4] cations[5] and well defined transition metal complexes,[6] as the chain carrying species. Some chain growth polymerisations are stereoselective and some give stereoregular polymers.[2,7,8] Living chain growth polymerisation allows the possibility of making block copolymers which in turn can allow control of supramolecular organisation *via* the phase separation of incompatible blocks.[9] Blocks derived from the same monomer but having different microstructures may be incompatible leading to the possibility of morphology control and hence bulk property control in a material derived from one monomer; such stereoblock copolymers have been prepared *via* anionic[10] and metallocene[11] methods and here we demonstrate that this is possible using ring opening metathesis polymerisation.

Previously we have demonstrated that in the polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene **1** initiated using the well defined Schrock complexes Mo(CH-t-Bu)(NAr)(OR)$_2$ all *trans* highly syndiotactic polymer is obtained when R = *tert*-butyl[7] (*i.e.* **2a** initiation, see Scheme 1) and all *cis*-polymer when R = hexafluoro-*tert*-butyl[12] (*i.e.* **2b** initition). Further, when a mixture of **2a** and **2b** is used to initiate this polymerisation the rate of alkoxy ligand exchange is faster than the propagation of the polymerisation and the distribution of *cis*- and *trans*-vinylenes in the polymer backbone is controlled by the relative proportion of the different alkoxy ligands in the polymerisation mixture.[12]

Here we report that the living polymer **3a** (Scheme 1), formed *via* initiation of the polymerisation of **1** with **2a**, undergoes ligand exchange with hexafluoro-*tert*-butanol to give a living chain end which initiates the polymerisation of **1** to give a stereoblock copolymer with *cis*- and *trans*-vinylene blocks.

All experiments were conducted under inert atmosphere conditions (dry box or vacuum line). In NMR tube scale trial experiments initiation of **1** (10 equiv.) with **2a** gave polymer **3a** with a living chain end characterised by a doublet in ^{1}H NMR (Varian VXR 400, C$_6$D$_6$ solution) at δ 11.34 arising from the alkylidene bound to molybdenum,[7] Fig. 1(*a*). The solution which gave the spectrum in Fig. 1(*a*) was freeze dried, the residue treated with a solution of dry hexafluoro-*tert*-butanol in dry C$_6$D$_6$ for 30 min, freeze dried and the residue redissolved in C$_6$D$_6$ before recording the spectrum Fig. 1(*b*). Three new alkylidene doublets appear in spectrum Fig. 1(*b*), on the basis of earlier work the weak signal at δ 12.42 can be assigned to the chain end alkylidene **3c** carrying two hexafluoro-*tert*-butoxy ligands.[12] It follows that the doublets at δ 11.86 and 11.92 must arise from the alkylidene of structure **3b** in which the molybdenum carries one *tert*-butoxy and one hexafluoro-*tert*-butoxy ligand and is therefore a chiral centre; since the tertiary carbon adjacent to the alkylidene is also chiral the alkylidene hydrogen may be located between centres of the same or different chirality giving rise to diastereoisomeric environments which occur at different chemical shifts and in different abundances. A further four repetitions of this reaction sequence gives the product **3c**, spectrum Fig. 1(*f*), in which all the alkoxy ligands are hexfluoro-*tert*-butyl; this was used to, initiate the polymerisation of **1** (15 equiv.). The resulting living stereoblock copolymer was terminated by addition of benzaldehyde (10 equiv.) to give a polymer which displayed all the signals associated with *cis*- (80%) and *trans*-vinylene sequences in blocks of poly{bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5 = diene}. The decreasing signal to noise observed in the spectra Fig. 1(*a*)–(*f*) together with the high *cis*-vinylene content of the final product indicates some destruction of living chain ends during this small scale series of experiments.

The process was repeated on a larger scale (2 × 100 equiv. of **1**) and with the addition of THF to improve polymer solubility to give a stereoblock copolymer having M$_n$ = 73 000 (Theoretical 46 000) and M$_n$/M$_w$ = 1.16 (Viscotek differential refractometer/viscometer, PLgel mixed column, THF, poly-



Scheme 1

styrene calibration). The relatively narrow polydispersity observed is as expected for the product of a well defined living polymerisation process. The measured molecular weights for samples of the all *trans* homopolymers have been shown to be significantly lower than the theoretical values (presumably indicating a somewhat collapsed coil in THF),[7] but the all *cis* homopolymer is insoluble in THF consequently it is not possible to predict the GPC behaviour of the *cis/trans* stereoblock copolymer. Differential Scanning Calorimetry (Perkin Elmer DSC7) revealed two transitions at *ca.* 95 and 145 °C as expected for the *trans*- and *cis*-blocks respectively.

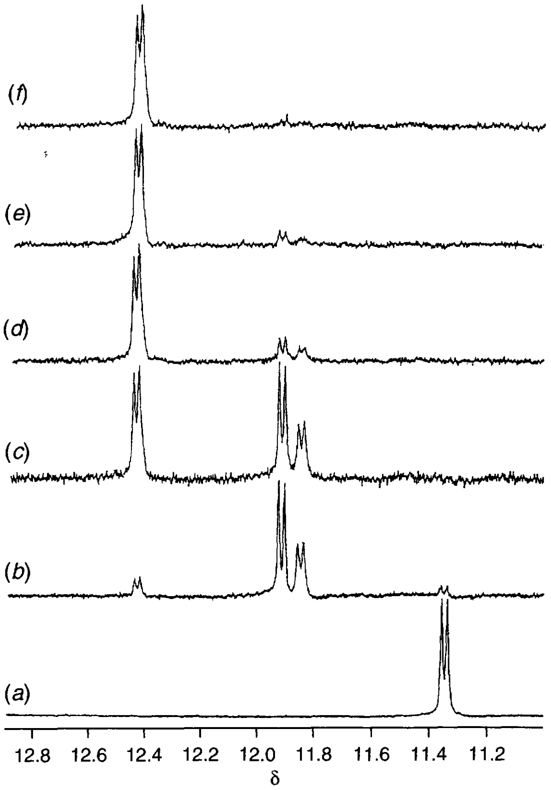


Fig. 1 ^{1}H NMR (400 MHz) spectra of the alkylidene region for the living polymerisation of **1** as a function of alkoxy ligand in initiator **2**

Taken together these data demonstrate the synthesis of a stereoblock copolymer *via* ligand exchange in living stereoselective ring opening metathesis polymerisation of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene.

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Footnotes

† Undergraduate visitor from the Technical University of Eindhoven, The Netherlands.

‡ *Present address*: Chemistry Department, Imperial College of Science, Technology and Medicine, South Kensington, London, UK SW7 2AY.

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