

## Fluorinated Homopolymers and Block Co-polymers *via* Living Ring-opening Metathesis Polymerisation

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A series of fluorinated homopolymers and block co-polymers has been synthesised using the four-coordinate molybdenum ring-opening metathesis polymerisation (ROMP) initiators  $[\text{Mo}(\text{=CHR})(\text{=NAr})(\text{OR}')_2]$ , where  $\text{R} = \text{CMe}_2\text{Ph}$ ,  $\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-Pr}_2^i$  and  $\text{R}' = \text{CMe}_3$  or  $\text{CMe}(\text{CF}_3)_2$ .

In recent work, we have described the highly stereoregular and living ROMP of 2,3-bis(trifluoromethyl)bicyclo-[2.2.1]hepta-2,5-diene (**1**, Scheme 1) using well-defined four-coordinate initiators of the type  $\text{Mo}(\text{=CHR})(\text{=NAr})(\text{OR}')_2$  (see Scheme 1 for  $\text{R}$  and  $\text{R}'$ ).<sup>1,2</sup> Whereas the initiator bearing ancillary *tert*-butoxide ligands (Mo-I) affords a polymer with > 98% *trans* vinylene content, the hexafluoro-*tert*-butoxide initiator (Mo-II) results in a polymer with >98% *cis* vinylenes.<sup>3</sup> We have further shown that an equilibrating mixture of these two initiators provides a viable strategy for controlling the *cis/trans* vinylene content.<sup>3</sup>

Here, we report the synthesis of a series of novel fluorinated homopolymers and block copolymers derived from the norbornene and norbornadiene skeletons shown in Scheme 1. All of the polymerisations show characteristics of well-ordered living systems; *e.g.* (a) the persistence of propagating metal alkylidenes in the polymerisation mixtures (as observed

by <sup>1</sup>H NMR spectroscopy), (b) narrow molecular mass distributions of the resultant polymers (Table 1) and (c) the synthesis of diblock co-polymers (*vide infra*).

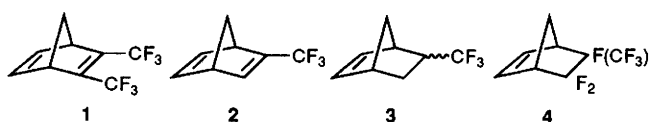
The metal alkylidene region of the <sup>1</sup>H NMR spectrum for the living polymer derived from the reaction of **2** with Mo-I is shown in Fig. 1(a), alongside the same region (b) for a sample of living poly**1**. The latter shows a propagating alkylidene doublet at 11.34 ppm whereas poly**2** gives two clusters of alkylidene resonances centred at 11.31 and 11.64 ppm in the ratio 3 : 1. The lower-intensity signal is attributed (on the basis of the similar chemical shift to the propagating alkylidene of poly**1**) to the alkylidene head group with the CF<sub>3</sub> substituent positioned at the  $\gamma$ -carbon. Its lower intensity relative to the signal to high frequency can be rationalised due to unfavourable steric interactions of the CF<sub>3</sub> substituent with the metal—ligand sphere. The absence of a residual signal due to the alkylidene of the initiator is indicative of a rate of initiation that is comparable or faster to the rate of propagation, a situation which is ideal for living polymerisation. This is supported by the very narrow molecular mass distributions found for the homopolymers of **1–4** and also the block co-polymers (Table 1).

The *cis/trans* vinylene content as a function of initiator is shown in Table 2. The *tert*-butoxide initiator Mo-I gives polymers with high *trans* vinylene content, whereas Mo-II

**Table 1** Gel-permeation chromatographic analyses on the homopolymers and block co-polymers synthesised using initiator Mo-I [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 10  $\mu\text{m}$  mixed columns, previously calibrated using commercially available polystyrene standards (Polymer Laboratories) in the molecular mass range 162 to  $1.03 \times 10^6$  (THF flow rate = 1 ml min<sup>-1</sup>)]

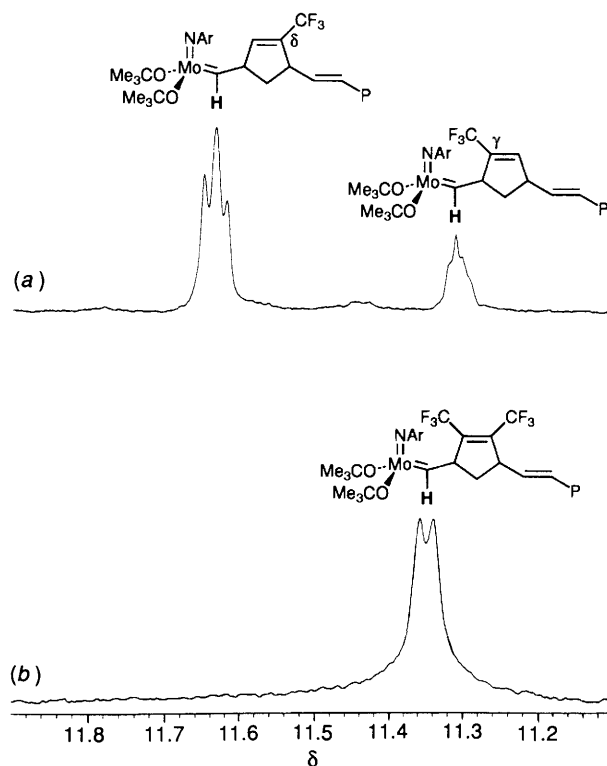
Monomer (equivalents)	$M_n$ (found)	$M_n$ (calc.) <sup>a</sup>	Polydispersity ( $M_w/M_n$ )
<b>1</b> (202)	46 090	27 130	1.05
<b>2</b> (50)	20 700	20 720	1.19
<b>3<sup>b</sup></b> (721)	105 400	11 6910	1.09
<b>4<sup>b</sup></b> (93)	41 020	20 100	1.03
<b>1</b> (64)- <b>b-2</b> (44)	29 010	21 650	1.12
<b>1</b> (164)- <b>b-3</b> (488)	145 200	116 600	1.08
<b>4</b> (63)- <b>b-1</b> (124)	79 780	41 900	1.07
<b>4</b> (91)- <b>b-3</b> (247)	97 760	59 670	1.08

<sup>a</sup> The discrepancies between measured and calculated  $M_n$  values are indicative of the different and variable solution behaviour of these polymers as compared to the polystyrene calibrant. <sup>b</sup> Monomers **3** and **4** were polymerised as their 'as made' *exolendo* racemates.



$\text{R}' = \text{CMe}_3$ , Mo-I  
 $\text{R}' = \text{CMe}(\text{CF}_3)_2$ , Mo-II

**Scheme 1**



**Fig. 1** 400 MHz <sup>1</sup>H NMR spectra (<sup>2</sup>H<sub>6</sub>benzene) of (a) Mo-I + 10 equivalents monomer **2**, (b) Mo-I + 10 equivalents monomer **1** (P = living polymer chain)

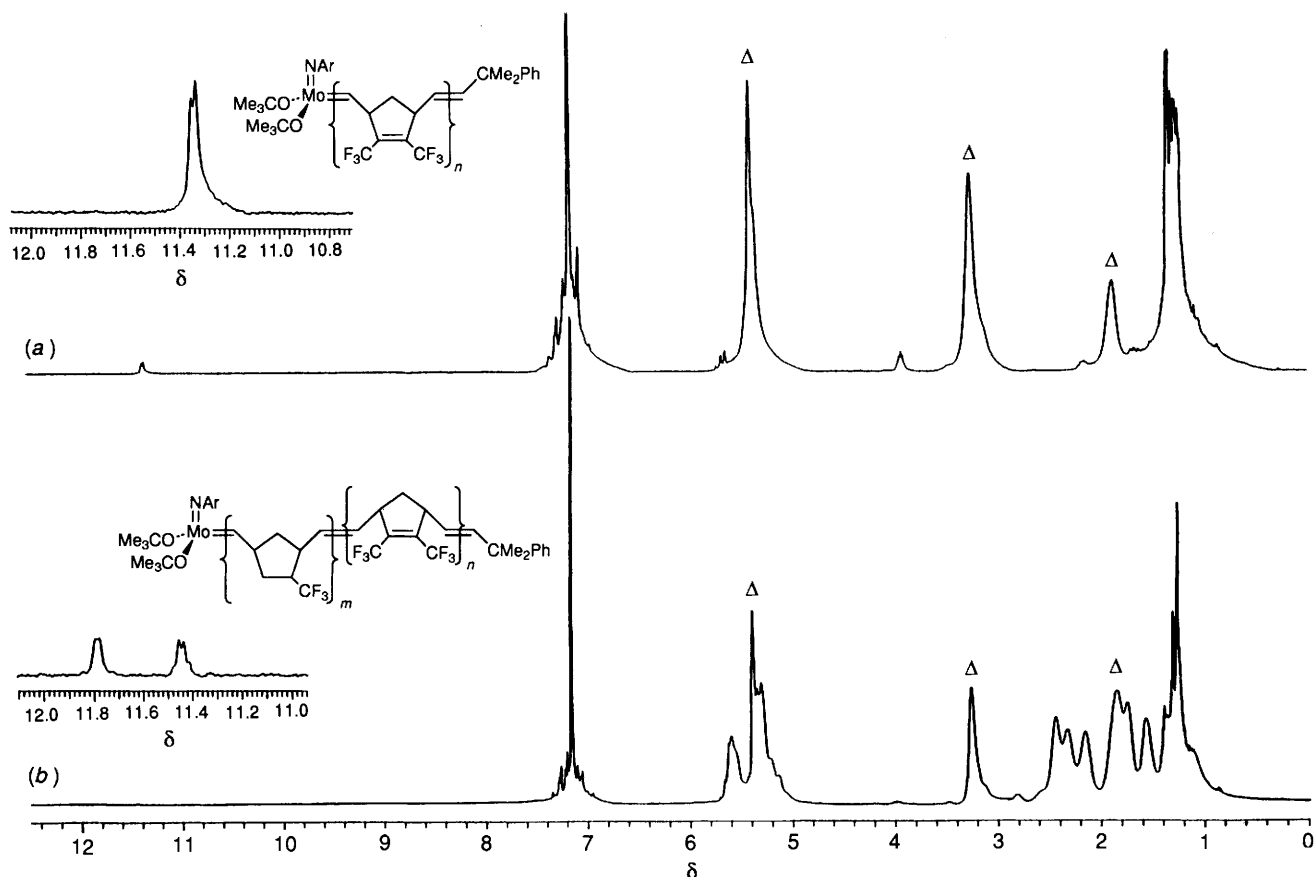


Fig. 2 400 MHz  $^1\text{H}$  NMR spectra of the living block copolymerisation of (a) monomer 1 and (b) monomer 3 by Mo-I

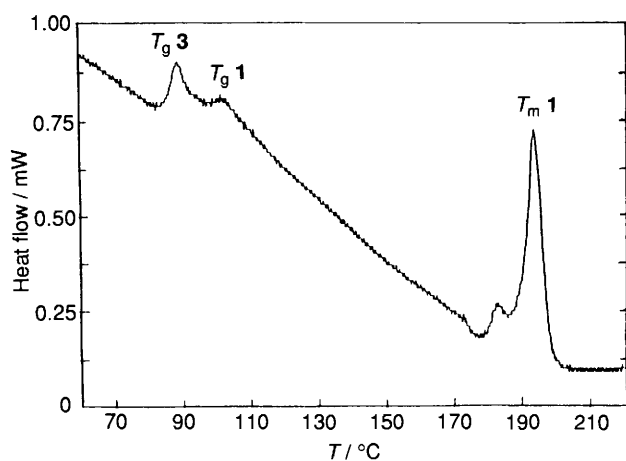


Fig. 3 DSC trace of block copoly 1-b-3

favours high *cis* vinylene linkages. Studies by Oskam and Schrock indicate that this selectivity is dependent upon the accessibility of *syn* or *anti* alkylidene rotamers on the timescale of propagation.<sup>4</sup>

Diblock co-polymers incorporating segments of the homopolymers 1–4 have been synthesised by sequential addition to the living molybdenum alkylidene chain ends and characterising data are collected in Table 1. As an example, the 400 MHz  $^1\text{H}$  NMR spectrum of the living diblock co-polymer obtained by addition of 1 to Mo-I followed by 3 is shown in Fig. 2(b). The propagating alkylidene resonance of living poly1 [Fig. 2(a)] is replaced by two new signals attributable to head and tail insertions of 3. The DSC trace of benzaldehyde-capped poly1-b-3 is shown in Fig. 3 and reveals two distinct glass-transition temperatures corresponding to those of the homopolymer segments and a multiple melting endotherm characteristic of poly1 (homopoly3 does not exhibit a melting endotherm).

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Table 2 *cis* and *trans* vinylene content as determined by  $^{13}\text{C}$  NMR spectroscopy

Monomer	Initiator	<i>trans</i> -Vinylene content (%)
2	I	90
	II	5
3	I	80
	II	10
4	I	99
	II	25

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