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Ring-opening metathesis polymerization of 7-methylbicyclo[2.2.1]hepta-2,5-diene initiated by well-defined molybdenum and ruthenium carbene complexes

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Abstract

Polymers of 7-methylnorbornadiene (7-MNBD) have been prepared by ring-opening metathesis polymerization (ROMP) using $Mo(=CHCMe_2Ph)(=NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(OR)_2$ [**1**, OR = $OCMe(CF_3)_2$; **2**, OR = $OCMe_3$], $Mo(=CHCMe_3)(=NC_6H_3\text{-}2,6\text{-}i\text{-}Pr_2)(OR)_2$ (**2′**) and $Ru(=CHPh)Cl_2(PCy_3)_2$ (**3**) as initiators in CD_2Cl_2. The structures of the polymers were investigated by ^{1}H- and ^{13}C-NMR spectroscopy. In all cases the ROMP was very fast and the initial product was essentially a polymer of *anti* units, linked by 88% *cis* double bonds for initiation by **1**, 68% for **2** or **2′**, and 17% for **3**. The tacticities of the polymers varied from atactic using **1** as initiator to fully tactic (*t*/*m* and *c*/*r*) using **2** or **2′** as initiator. Values of k_p/k_i were derived from the proportion of initiator consumed and the initial ratio of monomer to initiator: $k_p/k_i = 550$ for **1**, 1100 for **2**, 64 for **2′**, and 61 for **3**. Two kinds of secondary reaction were observed: the first gave rise to a second set of ^{13}C-NMR peaks (10–20% of the intensity of the main peaks), and the second, observed only with **1**, was characterised by sudden gelation of the reaction mixture some time after the monomer had been consumed, and was followed by a marked fall in the intensity of the main ^{13}C-NMR peaks. These effects are attributed to secondary intra- and inter-molecular metathesis reactions, respectively. The high-*trans* polymer could be fully hydrogenated, but the high-*cis* polymer could only be partially hydrogenated.

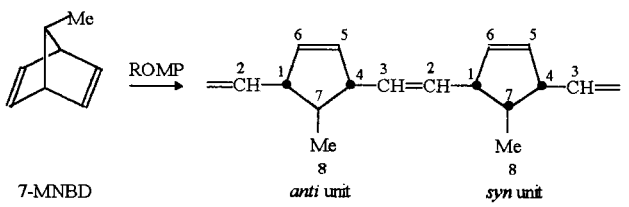
Keywords: 7-Methylnorbornadiene; 7-Methylbicyclo[2.2.1]hepta-2,5-diene; Molybdenum carbene complexes; Ruthenium carbene complex; Ring-opening; Metathesis; Polymerization; Cross-linking; Hydrogenation

1. Introduction

The ring-opening metathesis polymerization (ROMP) of cyclic olefins is known to proceed via metal carbene and metallacyclobutane complexes as chain carriers [1]. An initiating metal carbene complex (I) adds monomer (M) to yield the first propagating species (P) (initiation rate constant k_i) which then adds further monomer (propagation rate constant k_p) to yield a polymer chain which in some cases remains living after all the monomer has been consumed.

The ROMP of 7-substituted norbornadienes gives polymers whose chains have three distinct structural features: (i) *syn* and *anti* units may be present depending on which double bond in the monomer is opened, Eq. (1), (ii) the double bonds linking the cyclopentene rings may be *cis* or *trans*, and (iii) adjacent rings may have an *m* or *r* relationship.

(1)



Previous work using old-style catalysts to polymerize 7-MNBD gave polymers containing largely *anti* units, with *cis* contents between 97% ($OsCl_3$ as catalyst) and 20% ($MoCl_5/Me_4Sn/Et_2O$ as catalyst). Variable tacticity was also observed [2]. We now report the structure of the polymers formed by the ROMP of this monomer using the well-defined metal carbene complexes **1**, **2**, **2′**

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and **3** as initiators (see Abstract). In another paper we will describe the ROMP of 7-*t*-butoxybicyclo[2.2.1]hepta-2,5-diene with these initiators.

2. Results and discussion

For all four initiators the ROMP was so fast that polymerization was complete by the time the first spectrum could be taken (a few minutes). The initial product in each case was a polymer consisting almost entirely of *anti* units but with various *cis* contents. The formation of a small proportion of a secondary product was observed after the monomer had all been consumed and, in the case of **1**, there was clear evidence for the occurrence of a secondary cross-linking reaction. The spectrum of the product obtained with **2** or **2′** was much simpler than that obtained with **1** or **3** and will be described first.

2.1. ROMP initiated by *2* and *2′*

On mixing the initiator and monomer solutions there was immediate polymerization causing the solvent to boil briefly (40°C) and the solution to become highly viscous. More solvent was added in the glove box to reduce the viscosity and allow the solution to be transferred to the NMR tube.

The ^{13}C-NMR spectrum of the resulting living polymer using **2** as initiator is shown in Fig. 1. Comparison with previously reported spectra [2] showed that the polymer contained only *anti* units, and 68% *cis* double bonds ($\sigma_c = 0.68$). The spectrum is much simpler than those previously reported, indicating a high degree of tacticity in the present case. The fine structure for C-5,6, C-2,3, C-1,4 and C-7 is largely attributable to *cc*/*ct* or *tt*/*tc* splitting. (The first and second italic letters denote the configuration of the nearest and next nearest double bond, respectively). The detailed assignments are listed in Table 1. The carbons represented by *ct* and *tc* are necessarily equal in number and may be assigned to the two inner peaks for C-5,6 and the two outer peaks for C-2,3. The fraction of *cis* double bonds σ_c estimated from various parts of the spectra are in good agreement, supporting the assignments: 0.67 (C-5,6), 0.72 (C-2,3), 0.66 (C-1,4), 0.67 (C-7), average 0.68; also 0.69 (H-1,4), see later. The ratios r_t (= *tt*/*tc*) were also in reasonable agreement: 1.7 (C-5,6), 2.1 (C-2,3), 1.7 (C-7), 1.4 (C-1,4), average 1.7, as were the ratios r_c (= *cc*/*ct*): 4.6 (C-5,6), 6.9 (C-2,3), 4.5 (C-7), average 5.4, and indicating a blocky *cis*/*trans* distribution of double bonds as commonly found in high-*cis* polymers made by ROMP [1].

The C-7 *tt* and *tc* signals show additional fine structure which, by analogy with the spectra of the related polymers of 7-methylnorbornene [3], is attributed to tacticity splitting (*m*/*r*) of the *trans* component(s). The fact that the C-7 *cc* signal is not split could be due either to the absence of *m*/*r* splitting or to the absence of one type of dyad. The latter is more likely since there are no signs of splitting for *cis* resonances in any other part of the spectrum. Again by analogy with the spectra of the polymers of 7-methylnorbornene [3] we conclude that the *cis*-centred dyads are highly syndiotactic (*r*) while the *trans*-centred dyads are mainly isotactic (*m*). It is estimated from the C-7 *tt* fine structure (Table 1) that 82% of the *trans*-centred dyads are isotactic, $(\sigma_m)_t = 0.82$.

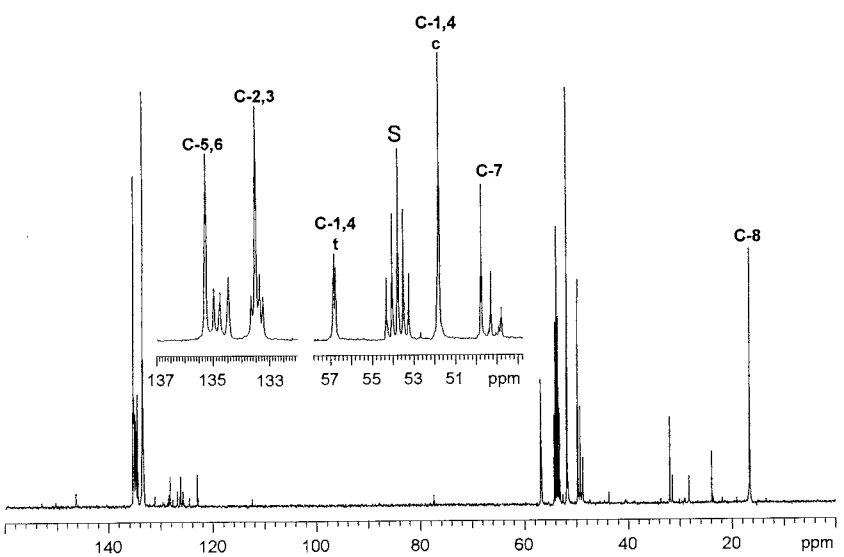


Fig. 1. 100 MHz ^{13}C-{^{1}H}-NMR spectrum of the living polymer formed by the ROMP of 7-MNBD using **2** as initiator in CD_2Cl_2 (S); $[M]_o = 1.41$ M, $[I]_o = 0.0342$ M. For line positions and assignments see Table 1. Most of the unmarked peaks are due to carbons in the ligands around the metal in the initiator and propagating species.

Table 1
^{13}C-NMR shifts [a] and assignments in the living ring-opened polymer of 7-MNBD initiated by **2** in CD_2Cl_2, containing anti units. Shifts are relative to the central solvent peak, δ 53.80

Line position (ppm)	Assignment	Line position (ppm)	Assignment
135.29	C-5,6 *cc*	49.77	C-7 *cc*
134.99	*ct*	49.42	c_rt_r
134.77	*tc*	49.35 [b]	c_mt_r
134.48	*tt*	49.31	c_rt_m
		49.25 [b]	c_mt_m
133.67	C-2,3 *ct*	49.04	t_rt_r
133.53	*cc*	48.92	t_mt_r
133.37	*tt*	48.81	t_mt_m
133.25	*tc*		
		16.63	C-8 c_rc_r and *t*
56.88	C-1,4 *tt*		
56.78	*tc*		
51.89	*ct*		
51.82	*cc*		

[a] There is a systematic difference of 0.36 ± 0.05 ppm between the present and previously reported values [2] determined in $CDCl_3$.
[b] Not visible in Fig. 1 (tactic polymer) but visible in Fig. 8 (slightly tactic polymer).

After 24 h a secondary reaction resulted in the appearance of new peaks in the ^{13}C-NMR spectrum at δ 13.45, 14.8, 38.87, 44.04, and 55.40 with an overall intensity of the order of 10–15% of that ascribed to the *anti* units. The origin of these peaks will be discussed later.

The ^{1}H-NMR spectrum of the same living polymer as in Fig. 1 is shown in Fig. 2. The positions and assignments for the main lines are listed in Table 2. The carbene proton for initiator (I) appears as a singlet at δ 11.257, and for the propagating species (P) as a doublet

Table 2
^{1}H-NMR shifts and assignments in the living ring-opened polymer of 7-MNBD initiated by **2** in CD_2Cl_2, containing *anti* units. Shifts are relative to the residual solvent proton signal, δ 5.35

Line position (ppm)	Assignment	Line position (ppm)	Assignment
5.665	H-5,6 *tc*	3.291	H-1,4 *c*
5.642	*tt*	2.833	*t*
5.602	*cc*		
sh	*ct*	1.580	H-7
5.414	H-2,3 *t*	1.094 (d)	H-8
5.283	*c*	($J = 6.4$ Hz)	

at δ 11.429 ($J = 6.8$ Hz). The intensities show that 25.2% of initiator was consumed in this experiment, and knowing $[M]_o/[I]_o = 41.4$ one may calculate $k_p/k_i = 1100$ from the integrated rate equations [4]. In the upfield region spin-coupling is only resolved for H-8 ($J = 6.4$ Hz). With **2′** the efficiency of initiation was higher than with **2**, 77.5% of the initiator being consumed for $[M]_o/[I]_o = 46.1$, giving $k_p/k_i = 64$. Since k_p must be the same for initiation by **2** and **2′** the replacement of Ph by Me in the carbene ligand evidently favours k_i by a factor of 17. The spectrum confirmed that the microstructure of the polymer produced by **2′** was essentially the same as that produced by **2**.

2.2. Hydrogenation of the polymer made from 7-MNBD/**2**

The polymer whose spectrum is shown in Fig. 1 was hydrogenated after termination with pivaldehyde and gave the ^{13}C-NMR spectrum in Fig. 3. It is immediately evident from the olefinic region that hydrogenation was

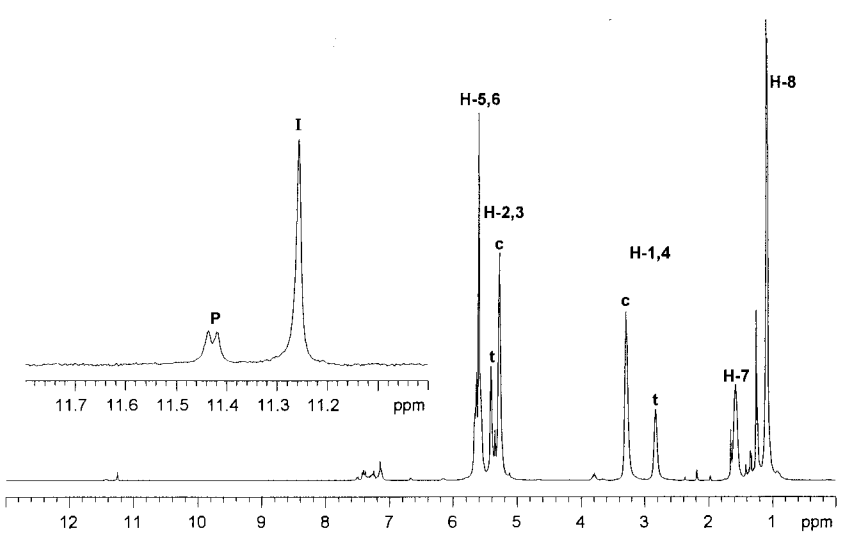
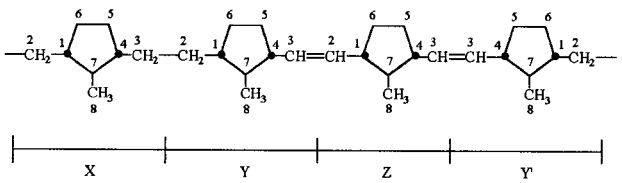


Fig. 2. 400 MHz ^{1}H-NMR spectrum of the same living polymer as in Fig. 1. For line positions (relative to the residual protons in the solvent, δ 5.35) and assignments see Table 2. Most of the unmarked peaks are due to protons in the ligands around the metal in the initiator and propagating species.

complete for C-5,6, but not for C-2,3, which were only 57% hydrogenated (as calculated from the C-8 intensities). Further attempts to carry the hydrogenation to completion were unsuccessful, but Fig. 3 can still provide some useful information.

Three types of unit, X, Y (≡Y′) and Z, are present in the product; see **4**. The C-8 intensities indicate the presence of 36% X, 20.5% each of Y and Y′, and 23% Z units. X and Z correspond to units of hydrogenated and unhydrogenated polymers of 7-methylnorbornene for which the chemical shifts are known [3]. The carbons in these units will be designated by letter and number, e.g. X2 for the carbon at the extreme left.



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Trans Z1,4 signals, if present, would be expected at δ 51.49 (*r*) and 51.26 (*m*), but are clearly absent, showing that all the original 32% *trans* C-2,3 double bonds have been hydrogenated. Of the original C-2,3 double bonds 41%, all *cis*, remain unhydrogenated. The comparative difficulty of hydrogenating *cis* double bonds in ring-opened polymers of norbornene derivatives has been attributed elsewhere to steric hindrance by the adjacent five-membered rings [5].

The fine structure in the olefinic region (four peaks) is likely to be a compositional rather than a tacticity effect. In a YZ (≡ZY′) dyad Y3 and Z2 will give rise to two equally intense peaks while YY' dyads (connected at C-3) and ZZ dyads will each give one peak if there is no *m*/*r* splitting. On the basis of the known proportions of X, Y and Z units, and assuming a statistical distribution of units in the chain, the relative intensities of the four olefinic lines should be ZY′ 25%, ZZ 28%, YY′ 22%, YZ 25%, which is reasonably consistent with the observed pattern. The lines that do not correspond to carbon atoms in either X or Z units are, by elimination, assigned to Y units. The positions and assignments of all the lines are given in Table 3.

The distinction between X, Y and Z units is particularly clear in the C-8 resonances. The intensities of the three X8 lines indicate that the fraction of *m* dyads is about 0.48. This is consistent with the fact that of the original C-2,3 double bonds, 32% *trans* (82% *m*) and 27% *cis* (~ 100% *r*) were hydrogenated. It may also be seen that the central *mr* line is weaker than it would be for a statistical distribution of *m* and *r* dyads showing that the distribution is somewhat stereoblocky. This is again as expected because of the correlations *c*/*r* and *t*/*m* and the known blocky distribution of *cis* and *trans* double bonds in the original polymer (see above). For Y8 there are only two lines, indicating that the chemical shift is sensitive to the structure only on the saturated side of the triad. The intensity ratio is about 1:2. If this is a tacticity effect and the line order is the same as for X triads (*r* upfield from *m*) one must conclude that *r* dyads are preferred in XY and/or Y′Y dyads. This may indicate that *cis* double bonds adjacent to hydrogenated *trans* double bonds are hydrogenated more easily than those adjacent to *cis* double bonds. However, the splitting of the Y8 resonance could also be a compositional effect, i.e. XY and Y′Y may give individual lines.

A further conclusion from Fig. 3 is that there are no *syn* units present, either fully hydrogenated, which would have given peaks at δ 6.9–7.2 (C-8), 28.2 (C-5,6)

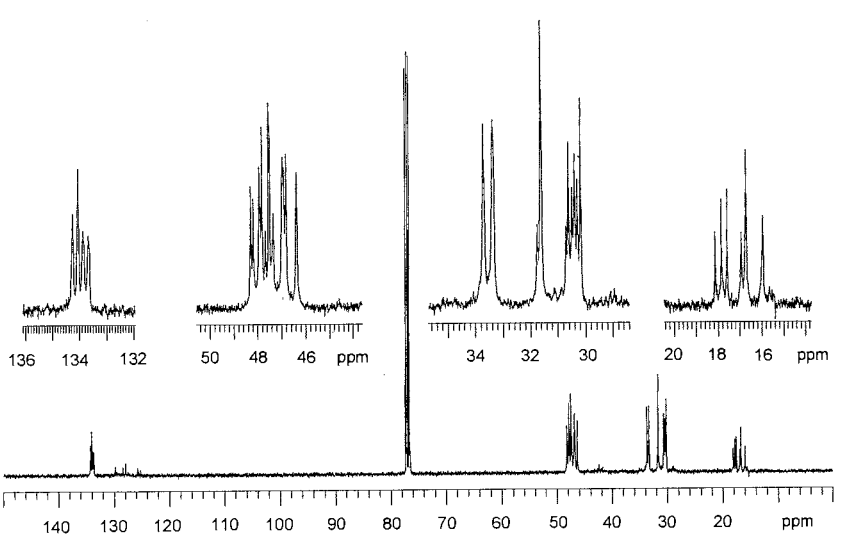


Fig. 3. 100 MHz ^{13}C-{^{1}H}-NMR spectrum of the partially hydrogenated polymer of 7-MNBD derived from the polymer whose spectrum is shown in Fig. 1. Solvent $CDCl_3$. For line positions and assignments see Table 3.

Table 3
^{13}C-NMR shifts and assignments in the partially hydrogenated polymer of 7-MNBD initiated by **1**, based on the published values [3] in brackets [a]; solvent $CDCl_3$ (δ 77.00). X, Y and Z; see **4**.

Line position (ppm)	Assignment		
	X	Y	Z
134.26			ZY′2 *c*
134.07 (134.25)			ZZ2,3 *c*
133.88		YY′3 *c*	
133.68		YZ3 *c*	
48.32 (48.66)	X1,4 *mm*		
48.20 (48.57)	X1,4 *mr*		
47.96 (48.38)			Z7 *cc*/*rr*
(48.31)	X1,4 *rm*		
47.84 (48.22)	X1,4 *rr*		
47.69		Y1 *m*	
47.55		Y7 *c*	
47.36	Y1 *r*		
46.98 (47.20)	X7		
46.82		Y4 *c*	
46.40 (46.69)			Z1,4 *c*
33.73 (33.88)	X2,3 *m*		
		Y2 *m*	
33.40 (33.58)	X2,3 *r*		
		Y2 *r*	
31.78		Y5 *c*	
(31.98)			Z5,6 *c*/*r*
31.64		Y5 *c*	
30.72		Y6 *c*/*m*	
30.64 (30.90)	X5,6 *mm*		
30.51 (30.80)	X5,6 *mr*		
30.42		Y6 *c*/*r*	
30.32 (30.59)	X5,6 *rm*		
30.20 (30.50)	X5,6 *rr*		
18.17 (18.37)	X8 *mm*		
17.88 (18.12)	X8 *mr*		
17.61 (17.87)	X8 *rr*		
16.96		Y8 *mr*? [b]	
16.73		Y8 *rr*? [b]	
15.97 (16.29)			Z8 *cc*/*rr*

[a] There is a systematic difference of 0.27 ± 0.07 ppm between the present and previous values.
[b] See text.

and 37.4–38.4 (C-7), or partially hydrogenated, which would have given peaks corresponding to those seen in the spectrum of the polymer of *syn*-7-methylnorbornene [2,6]. This confirms the absence of *syn* units in the precursor.

2.3. ROMP initiated by **1**

The ^{13}C-NMR spectrum of the initially formed polymer is shown in Fig. 4. Extremely weak peaks due to carbons in *syn* units, marked 's', may just be seen at the positions reported in the literature (δ 131, 47.5, 41, 13) [2]. There are also some peaks of moderate intensity marked 'x' in positions similar to those observed for the secondary product using **2** as initiator (see above). The main peaks marked 'a' are in the same regions as those in Fig. 1 and may be assigned to carbons in *anti* units. The fine structure in these regions shows (i) that the *cis* content is higher ($\sigma_c = 0.88$) than for the polymer whose spectrum is shown in Fig. 1, as may be seen particularly from the C-1,4 and C-7 regions; and (ii) that the polymer is atactic, as may be seen from the C-1,4 *cis* region where there are now three peaks in the ratio 1:2:1 at δ 52.03 (*mm*), 51.93 (*mr*) and 51.82 (*rr*) instead of the single peak in Fig. 1 at δ 51.82 (*rr*); also from the C-8 region where there are again three peaks in the ratio 1:2:1 at δ 17.27 (*mm*), 16.95 (*mr*) and 16.65 (*rr*) instead of one at 16.63 (*rr*). Again the C-5,6 fine structure, consisting of four peaks ($\sim$1:1:1:1), must also be due to tacticity splitting: δ 135.30 (*rr*), 135.16 (*rm*), 135.07 (*mr*), 134.93 (*mm*), whereas that in Fig. 1 was due solely to *c*/*t* splitting; only the 135.30 (*rr*) peak is common to both spectra. The C-2,3 signal consists of two 1:2:1 triplets, indicating partial resolution of the eight tactic tetrads.

When the ^{13}C-NMR spectrum was taken at intervals after the monomer had all reacted it was found that the 'a' peaks declined in height and broadened with time while the 'x' peaks remained relatively unaffected; see, for example, the spectrum taken after 17.9 h, Fig. 5. A plot of the area under the peaks in the 12–18 ppm region relative to that under the solvent peaks is shown in Fig. 6. It was also observed that the reaction mixture, while remaining fluid immediately after consumption of monomer, became a stiff gel overnight.

In a further experiment three identical reaction mixtures were prepared, one being terminated with benzaldehyde immediately after consumption of monomer (5 min). The second was terminated when the magnetic stirrer suddenly ceased to turn (44 min), while the third was terminated some time after gelation had occurred (109 min). In the first case the ^{13}C-NMR spectrum showed the very weak 's' peaks, but only traces of the 'x' peaks proving that these must arise from a secondary reaction of the living polymer. In the third case more solvent was added and a soluble fraction removed. Its spectrum showed that it did not contain the species responsible for the 'x' peaks; instead this species remained in the gel. In the second case, terminated at the gel point, the C-8 'a' peaks were still sharp and well resolved and about seven times stronger than the adjacent 'x' peaks, as expected from Fig. 6.

The most likely explanation of these observations is that there are two independent secondary metathesis reactions of the living polymer: (i) an intermolecular reaction involving the double bond in the cyclopentene rings of the initially formed linear polymer, leading first to a branched polymer and then, at the gel point, to a highly cross-linked polymer; (ii) an intramolecular back-biting reaction leading to cyclic oligomers giving rise to the 'x' peaks. Unsuccessful attempts were made

by GC-MS to detect the presence of cyclic oligomers in the products of reaction terminated at the gel point. The failure to extract soluble secondary products after gelation had occurred suggests that the cyclic species, if formed, are trapped, either physically or chemically, within the cross-linked polymer but retain sufficient mobility to give sharp peaks in the ^{13}C-NMR spectrum. The intensity pattern for C-8 in the 'x' signals (1:2:1) is the same as for C-8 in the 'a' units, but with a splitting of 0.48 ppm instead of 0.305 ppm. This is consistent with a mixture of stereoisomeric cyclic oligomers of a particular ring size, formed by a back-biting metathesis but, if so, it is surprising that such species do not become involved in the cross-linking process. The nature of the species giving rise to the 'x' peaks is therefore uncertain.

As a further test a ^{1}H–^{13}C correlation spectrum (HSQC) was determined using a reaction mixture which had been allowed to stand for several hours so that the 'a' signals had fallen to a height comparable to that of the 'x' signals; see Fig. 7. This shows that for every 'a' signal there is a corresponding 'x' signal as would be expected if the latter correspond to a cyclic oligomer formed by a back-biting reaction of the linear polymer. The line positions are summarized in Table 4.

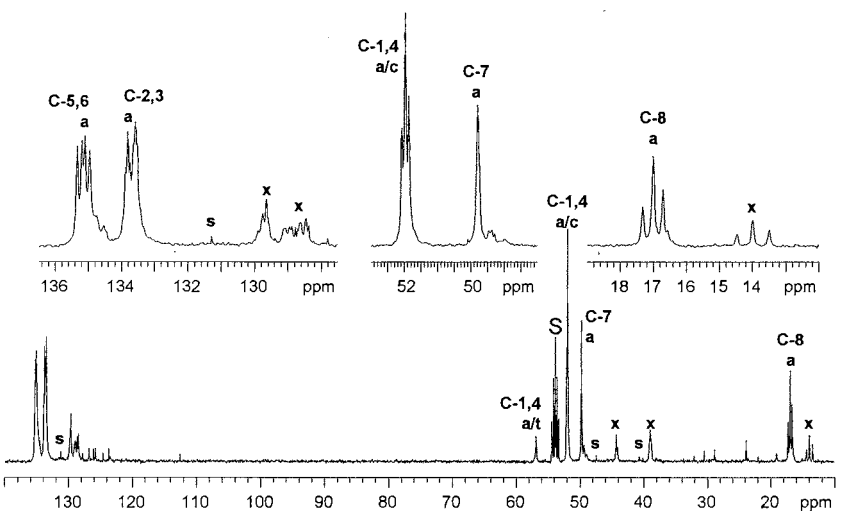


Fig. 4. 100 MHz ^{13}C-{^{1}H}-NMR spectrum of the living polymer formed by the ROMP of 7-MNBD using **1** as initiator in CD_2Cl_2 (S), after 1.4 h (mid-point of the pulsing period); $[M]_o = 1.00$ M, $[I]_o = 0.0177$ M. Peaks marked 'a', 's' and 'x' are from carbons in *anti* units, *syn* units, and an unidentified species respectively. Most of the unmarked peaks are due to carbons in the ligands around the metal in the initiator and propagating species.

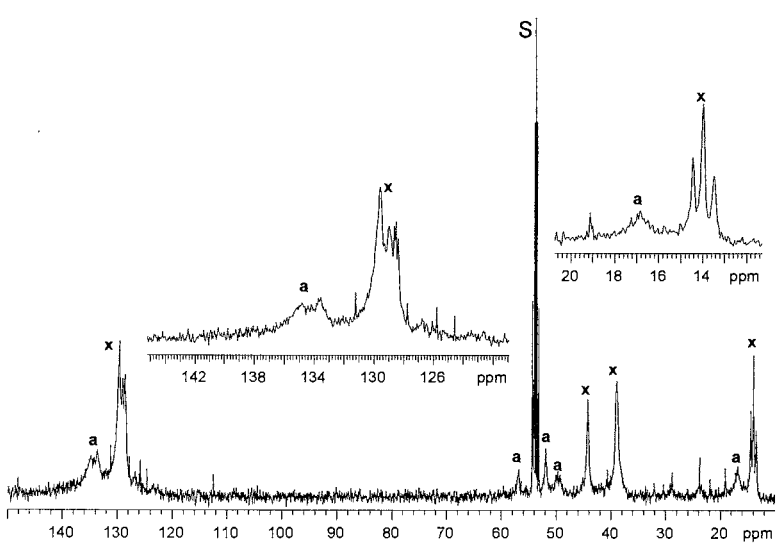


Fig. 5. As for Fig. 4 but after 17.9 h.

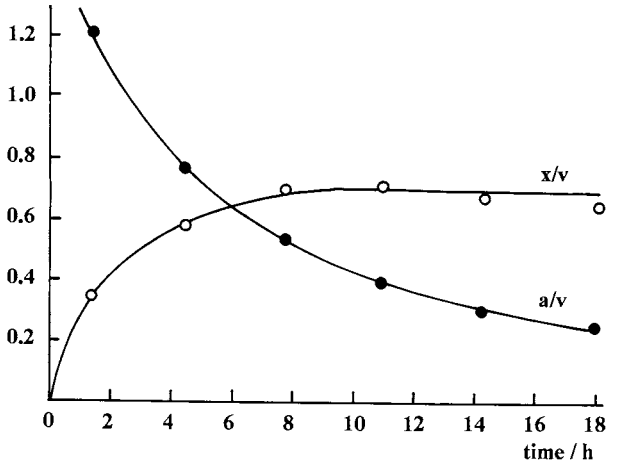


Fig. 6. Plot of the areas under the methyl carbon peaks 'a' and 'x' relative to the area under the solvent peaks 'v' as a function of time for the living system illustrated in Figs. 4 and 5.

In another experiment polymer made with **2** as initiator and terminated with benzaldehyde was recovered by precipitation in methanol, thoroughly dried in vacuum, redissolved in CD_2Cl_2 and mixed with 18 mg **1** in CD_2Cl_2. The initial ^{13}C-NMR spectrum (61 min) was well resolved but showed the presence of some of the peaks listed in Table 4. After 4 h the original 'a' peaks had fallen to a level comparable with the 'x' peaks at 13.55 (C-8), 38.87 (C-1,4 c), 44.0 (C-1,4 t), 44.5 (C-7), 128.84, 129.61 (C-2,3 and C-5,6), showing that initiator **1** is capable of bringing about the cross-linking reaction of a dead polymer made with initiator **2**. The 'x' peaks were, however, fewer in number than those listed in Table 4 which accords with the fact that the new species is being formed from a tactic rather than an atactic polymer.

Table 4
Chemical shifts for the carbons giving the signals 'x' in Figs. 5 and 7

Line position (ppm)	Assignment	Line position (ppm)	Assignment
129.6-128.4	C-2,3 C-5,6	5.8-5.7	H-2,3 H-5,6
44.28	C-7	1.6	H-7
44.07	C-1,4 *t*		
39.08 38.99 38.89 38.72	C-1,4 *c* [a]	2.9	H-1,4 *c*
14.41 13.95 13.45	C-8	0.9	H-8

[a] The corresponding *trans* peak is expected at about 44 ppm, but being weak, is concealed by the strong C-7 peak.

The carbene proton spectrum of the propagating species in the reaction mixture corresponding to Fig. 4 was an ill-defined multiplet, δ 12.5–12.4, with the initiator singlet at δ 12.20. The intensities showed that 20–40% of initiator was consumed when $[M]_o/[I]_o$ was in the range 15–53, leading to $k_p/k_i = 550 \pm 100$ (average of three values).

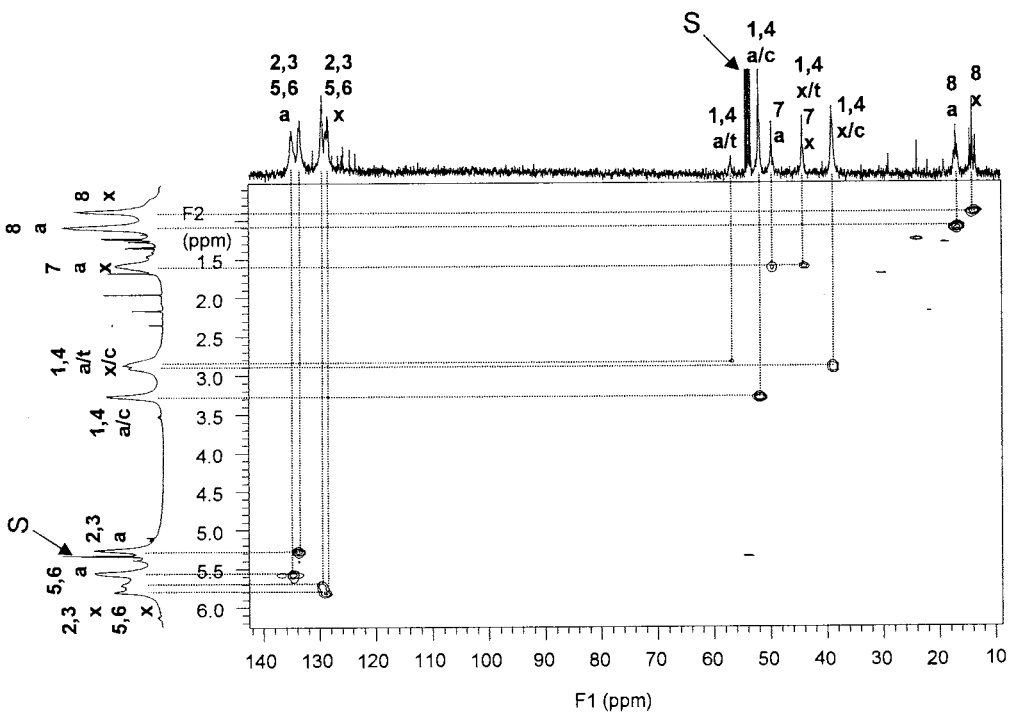


Fig. 7. ^{1}H-^{13}C correlation spectrum (HSQC) of the polymer formed in the reaction mixture of 7-MNBD/**1**/CD_2Cl_2 after 7.5 h. See Tables 1, 2 and 4 for line positions.

2.4. ROMP initiated by **3**

The ^{13}C-NMR spectrum of the reaction mixture taken 4.9 h after mixing, Fig. 8, showed that the polymer consisted essentially of *anti* units (peaks marked 'a') connected by 83% *trans* double bonds as determined from the C-7 resonance, with only the very slightest sign of *syn* units (peaks marked 's'). Some peaks of intermediate size, marked 'y', having about 20% of the intensity of the *anti* peaks, are also present. Some, but not all, of these are in similar positions to those of the 'x' peaks in Figs. 4 and 5 (see below). The four peaks in the region 26–33 ppm are due to carbons in the PCy_3 ligands. These, together with some of the phenyl peaks in the 124–130 ppm region, disappear when the polymer is terminated with ethyl vinyl ether, precipitated in methanol, dried in vacuum and redissolved, leaving a small signal due to PhCH= end groups.

Three features of the spectrum relating to the *anti* units are worthy of note. First, the C-7 signal (49.8–48.8 ppm) contains three lines for *tt* triads, in the same positions as those in Fig. 1, Table 1, already assigned to *rr*, *mr*, and *mm*, but in intensity ratio 29:53:18. The *trans*-centred dyads are thus slightly *r*-biased, $(\sigma_r)_t = 0.55$. Second, the C-1,4 *trans* signal ($\sim$57 ppm) also consists of three lines, compared with two lines in the tactic polymer (*tt* and *tc*); Fig. 1, Table 1. This may be interpreted in terms of an *m*/*r* splitting (0.04 ppm) with respect to the nearer double bond, superimposed on the *tt*/*tc* splitting (0.10 ppm). The additional downfield line at δ 56.94 then corresponds to t_rt, the central line (δ 56.86) to t_mt and t_rc (unresolved) and the upfield line (δ 56.80) to t_mc. Third, the C-1,4 *cis* resonance in Fig. 8 is complex compared with the single line for the tactic polymer, Fig. 1, indicating that both *m* and *r* *cis*-centred dyads are present. Furthermore the C-7 *ct* resonance consists of four lines, assigned to c_rt_r, c_mt_r, c_rt_m, c_mt_m (Table 1), the intensities of which give $(\sigma_r)_t = 0.55$, in agreement with the value from the *tt* peaks, and $(\sigma_r)_c = 0.62$; the overall fraction of *r* dyads is then $\sigma_r = 0.83 \times 0.55 + 0.17 \times 0.62 = 0.56$. This conclusion is supported by the ^{13}C-NMR spectrum of the fully hydrogenated polymer, Fig. 9, which, when compared with published spectra of the hydrogenated polymers of 7-methylnorbornene [3], shows it (i) to be atactic with a slight *r* bias ($\sigma_r = 0.53$ (C-1,4), 0.55 (C-5,6), 0.53 (C-8); average 0.54); (ii) not to be stereoblocky; and (iii) to contain a negligible proportion of *syn* units. The spectrum in Fig. 9 also contains a set of smaller peaks 'z' which clearly derive from the hydrogenated counterpart of the species responsible for the peaks 'y' in Fig. 8. The hydrogenated by-product was thus not removed during the work-up of the main hydrogenated polymer, showing it to be insoluble in methanol and probably not of particularly low molecular weight. The hydrogenated polymer, when analysed by GPC, gave only a single broad peak with no sign of a low-molecular-weight component: $M_w/M_n = 3.35$, $M_w = 29800$, $M_n = 8900$ (based on polystyrene calibration), corresponding

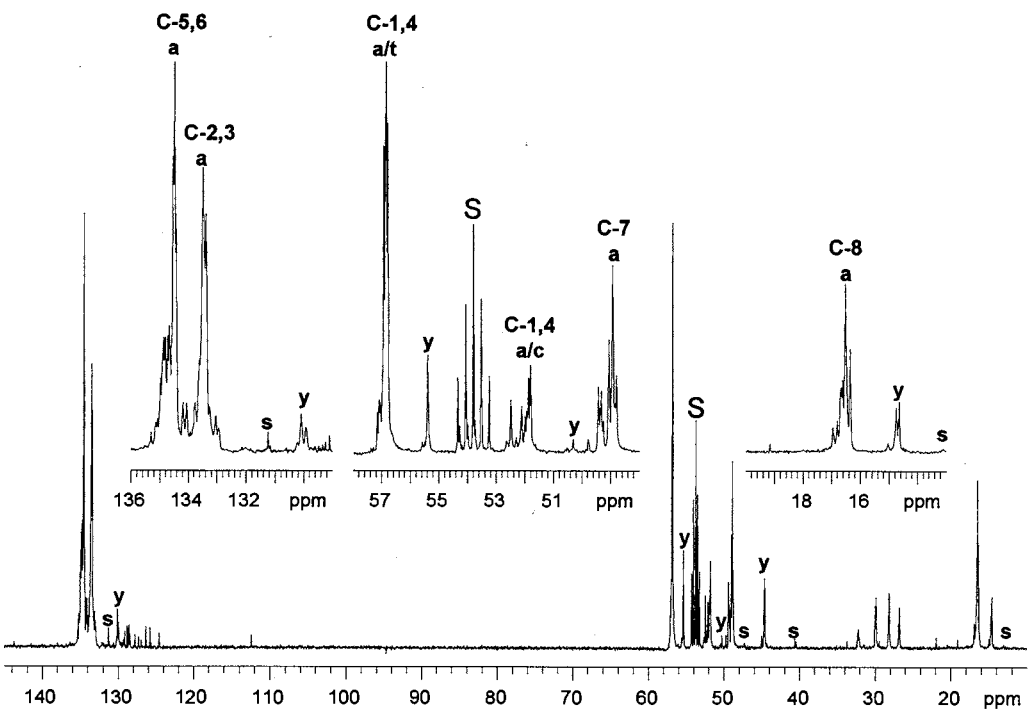


Fig. 8. 100 MHz ^{13}C-{^{1}H}-NMR spectrum of the living polymer formed by the ROMP of 7-MNBD using **3** as initiator in CD_2Cl_2 (S), after 4.9 h (mid-point of the pulsing period); $[M]_o = 1.06$ M, $[I]_o = 0.0191$ M.

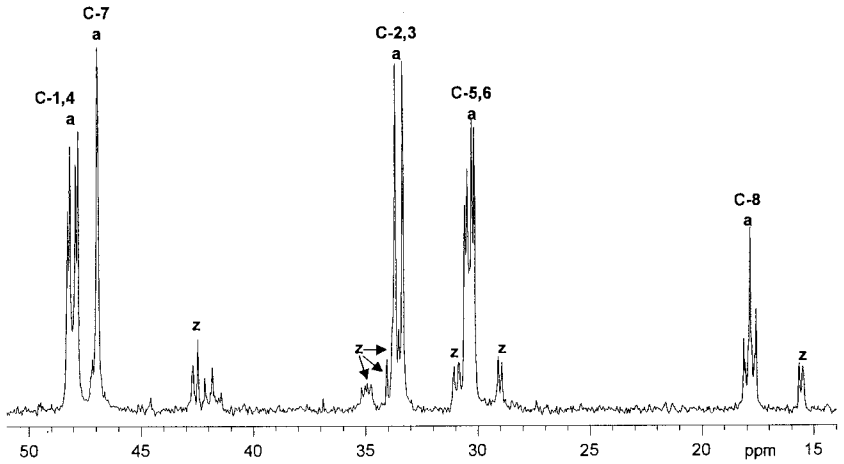


Fig. 9. 100 MHz ^{13}C-{^{1}H}-NMR spectrum of a polymer of 7-MNBD prepared using **3** as initiator, which had been terminated with ethyl vinyl ether and then fully hydrogenated. Solvent $CDCl_3$. Peaks marked 'a' are due to carbons in the hydrogenated *anti* units. Peaks marked 'z' are due to carbons in the hydrogenated secondary product.

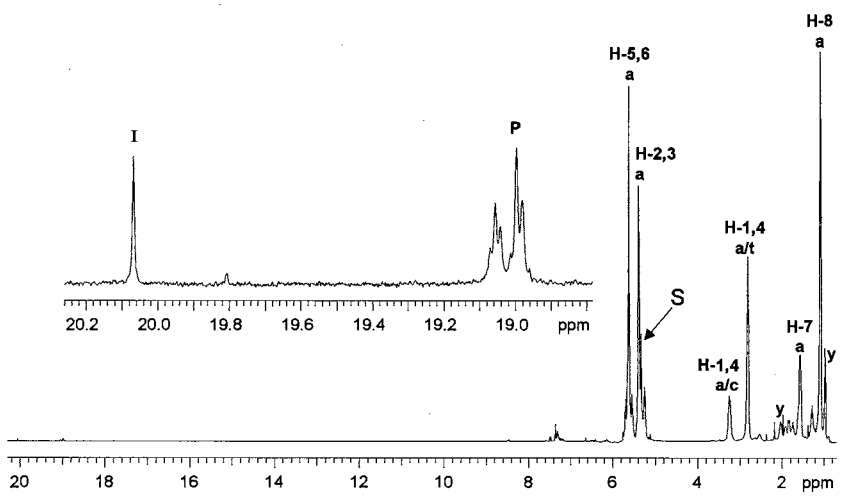


Fig. 10. 400 MHz ^{1}H-NMR spectrum of the same living polymer as in Fig. 8.

to $DP_n = 81$ which is of the expected order of magnitude (see below). Nor could any cyclic oligomers be detected by GC-MS.

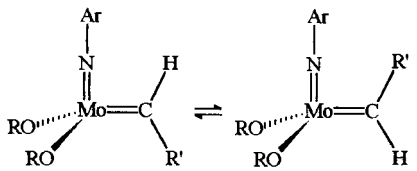
The ^{1}H-NMR spectrum of the original reaction mixture (Fig. 8) taken at 3.3 h is shown in Fig. 10. The H-1,4 signals give $\sigma_c = 0.25$, somewhat higher than the value of 0.17 derived from the C-7 peaks. The discrepancy is probably due to the variable contribution of the secondary products to the peaks used in these calculations. The carbene proton signal of the propagating species appears to consist of two partially resolved quartets 0.061 ppm (24.4 Hz) apart. This splitting is too large to be due to $H_\alpha H_\beta$ or PH coupling and is probably due to sensitivity to the *cis* or *trans* configuration of the nearest C-2,3 double bond in the chain, enhanced by the bulk of the PCy_3 ligands. The origin of the quartet splittings is not clear. $H_\alpha H_\beta$ coupling will give rise to a doublet splitting of about 6 Hz but, while PH coupling is common enough in ruthenium carbene complexes bearing PPh_3 ligands [7–11], it is not normally observed in complexes that bear PCy_3 ligands [9,10,12]. The additional splitting may therefore be due to m/r sensitivity. Further work is needed to clarify this question. The carbene proton intensities showed that 82% of initiator was consumed when $[M]_o/[I]_o = 55.6$, giving $k_p/k_i = 61$, and a predicted DP_n of 68 (see above).

3. General discussion

The results for the four systems are summarized in Table 5. The features of particular interest are first, the high *cis* content with **1** as initiator, second, the formation of highly tactic polymers with **2** and **2′** as initiators, third, the secondary cross-linking of the polymer chains

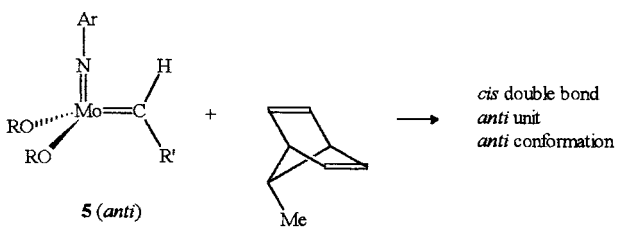
when **1** is the initiator, and fourth, the nature of the secondary products.

The molybdenum initiators have tetrahedral symmetry about the metal centre and, in solution, are known to exist in *syn* and *anti* conformations **5** and **6** (R′ = CMe_2Ph for **1** and **2**) [13,14].



5 (*anti*) **6** (*syn*)

The equilibrium strongly favours the *syn* conformation for both **1**, OR = $OCMe(CF_3)_2$, (K = 1450 at 25°C in toluene), and **2**, OR = $OCMe_3$ ($K = 1200$ at 0°C in toluene), but the *anti* conformation is much more reactive than the *syn*. We shall assume the same to be true of the propagating species when R′ is the polymer chain. When a *cis* double bond is formed in a propagation step at the *exo* face of the monomer, the conformation of the metal carbene complex immediately formed is the same as the starting conformation. Therefore when the rate of conversion of *syn* to *anti* conformation is low compared with the rate of propagation, as it is likely to be for initiation by **1** ($k \sim 5 \times 10^{-5}$ s^{-1} for the initiator [13]), the reaction will proceed readily via the *anti* conformation only if mainly *cis* double bonds are formed. If a *trans* double bond is formed the chain growth will effectively stop until such time as the newly formed *syn* conformation has been converted to the *anti* conformation. The preferred mode of addition using initiator **1** is thus that shown in Eq. (2).



(2)

Table 5
Summary of results on the ROMP of 7-MNBD using metal carbene complexes as initiators

Initiator	Polymer (*anti* units) [a]			k_p/k_i
	σ_c	$(\sigma_r)_c$	$(\sigma_m)_t$	
1	0.88	~0.5	~0.5	550
2	0.68	~1.00	0.82	1100
2′	0.68	~1.00	0.82	64
3	0.17	0.62	0.45	61

[a] Secondary cross-linking reactions occur with **1** only. Other secondary reactions occur in all cases

With **2** as initiator the interconversion of *syn* and *anti* conformations of the propagating species is expected to be much faster ($k \sim 1$ s^{-1} for the initiator [13]) and the formation of a *trans* double bond is likely to be less restrictive on the course of reaction and indeed a higher *trans* content is observed.

The configuration of a unit formed in a given type of propagation step, such as Eq. (2), depends on which of the two CNO faces is approached by the monomer. If there is no preference then the two configurations have equal probability of formation and successive units will have an equal probability of being *m* or *r* dyads, i.e. the polymer formed will be atactic. This is the case for the ROMP initiated by **1**. However, in the case of polymer made with **2** there is a strong tactic bias which means that there must be a different probability of reaction at the two CNO faces, i.e. that there is another factor, not shown in **5**, that makes the two faces non-equivalent. This could be the generation of chirality at the metal centre in the previous propagation step, with relatively slow relaxation to the achiral form **5**, or there may be an influence of the nearest chiral centre within the polymer chain R′. It has been shown [15] that where the metal centre is chiral and the chirality is preserved between propagation steps a *cis* double bond will be associated with an *r* dyad, and a *trans* double bond with an *m* dyad as tends to be the case with the polymers made using **2** or **2′**. However, the fact that $(\sigma_r)_c$ is not exactly equal to $(\sigma_m)_t$, either for polymer made with **2** or for that made with **3**, shows that another factor must be involved. As discussed elsewhere [16] there may be a tendency for the previously formed double bond to remain coordinated to the metal centre, especially when this has a *cis* configuration, so that **5c** may be kinetically distinct from **5t**, resulting in $(\sigma_r)_c \neq (\sigma_m)_t$.

The observation of a sharp gel point with **1** as initiator must mean that there is secondary metathesis involving the double bonds in the cyclopentene units of the polymer chain, leading to branching and cross-linking. This is unusual but not without precedent [17], but only occurs with the extremely active initiator **1** in the present case.The differences in the ^{13}C fine structure for C-8, C-7 and C-1,4 of the secondary products formed with the various initiators may be due to the different *cis* content and tacticity of the precursors and therefore of the secondary products. The rise in concentration of species 'x' (Fig. 6) with a half-life of about 1.5 h to a steady value after 10 h is such as one would expect of a slow secondary back-biting metathesis reaction at the living chain ends, leading to an equilibrium concentration of cyclic oligomers. The favoured ring size may depend on the c/t and m/r ratios and so affect the fine structure. The 88% *cis* atactic precursor (initiator **1**) gives rise to the secondary product with C-8 'x' peaks at

δ 14.41, 13.95 and 13.45, while the 17% *cis* slightly tactic precursor (initiator **3**) gives rise to the secondary product with C-8 'y' peaks at δ 14.76 and 14.67. The 67% *cis* tactic precursor (initiator **2**) on the other hand gives rise to the secondary product with a main peak at δ 13.45, assigned to a c_rc_r triad, and a lesser peak at δ 14.8 assigned to a t_mt_m triad. The absence of a third peak (c_rt_m) may be due partly to the fact that the precursor is c/t blocky and partly to a stereoselective effect in the secondary reaction. The C-1,4 signals show a much greater difference. The C-1,4 'x' *cis* signals are clustered around δ 38.6 while the expected weak *trans* signal is presumably concealed by the C-7 peak at δ 44.1. The C-1,4 'y' *trans* peak on the other hand appears at δ 55.39 with a small 'y' *cis* peak visible at δ 50.3. It would thus appear that there is a significant difference between the compounds responsible for the 'x' and 'y' peaks, other than c/t or m/r isomerism. For the intermediate case of the 67% *cis* tactic precursor (initiator **2**) the secondary product shows peaks in both the 'x' and 'y' positions. In spite of the circumstantial evidence for the production of cyclic oligomers we were unable to separate and characterise them and further work is required to achieve a proper identification of the secondary products.

4. Experimental

4.1. Materials

7-MNBD was prepared from norbornadiene via 7-*t*-butoxybicyclo[2.2.1]hepta-2,5-diene as described in the literature [18]. Before use it was passed through a short alumina column. The solvents, CD_2Cl_2 and $CDCl_3$, were stirred over P_2O_5 and vacuum distilled. The initiators were prepared by published methods [9,19,20]. Benzaldehyde (Aldrich) and pivaldehyde (Aldrich) were used as supplied. Ethyl vinyl ether (Aldrich) was passed through a short column of alumina before use.

4.2. Polymerization procedure

Solutions of monomer and initiator were prepared and mixed with the aid of a magnetic stirrer at ambient temperature (about 20°C) in a glove box (Braun) under an atmosphere of dry oxygen-free nitrogen. NMR tubes were filled with reaction mixture in the glove box and sealed either by means of a Young's valve or with a plastic cap wound with Parafilm. In a typical experiment a solution of about 100 mg of monomer (M) in 0.4 ml CD_2Cl_2 was mixed with a stirred solution of about 15 mg initiator in 0.4 ml CD_2Cl_2. The fraction of residual initiator was determined from the integrals of the carbene proton signals for the initiator and propagating species (see text for line positions appropriate to individual initiators). The living ends were terminated where necessary by the addition of one drop of benzaldehyde (Mo systems) or one drop of ethyl vinyl ether (Ru system).

4.3. Hydrogenation

About 100 mg of polymer were heated in xylene with 2 g *p*-toluenesulfonhydrazide at 120–130°C for 1–2 h and the hydrogenated product recovered by precipitation in methanol.

4.4. NMR instrumentation

NMR spectra were generally recorded at ambient temperature on a Varian VXR-400S operating at 399.96 MHz for ^1H, or 100.57 MHz for ^{13}C with continuous proton decoupling. Chemical shifts based on TMS were determined by reference to the central solvent peaks (see Tables). Heteronuclear single-quantum correlation (HSQC) spectra were recorded at ambient temperature on a Varian Inova-500, operating at 499.78 MHz for ^1H and 125.68 MHz for ^{13}C, using pulsed field-gradient coherence-pathway selection.

Note added in proof

We have confirmed that with **3** as initiator in $CDCl_3$ the positions of the lines in the carbene proton signal of the propagating species (P in Fig. 10) are independent of NMR operating frequency (250–500 MHz). None of the fine structure (triplet 19.024, 19.008, 18.996 and quartet 18.965, 18.949, 18.935, 18.915 ppm) is therefore due to spin coupling and can only be due to c/t and/or m/r isomerism.

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