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Poly(2,5-(3,4-bis(methoxymethyl)furanylene)vinylene)s prepared by aqueous ring opening metathesis polymerisation

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SUMMARY

Poly(2,5-(3,4-bis(methoxymethyl)furanylene)vinylene)s of various microstructures, prepared by aqueous Ring Opening Metathesis Polymerisation (ROMP) of *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicylo[2.2.1]hept-2-ene, were characterised by high field NMR.

INTRODUCTION

Recent publications have described the polymerisation of *exo,exo*-5,6-bis(methoxymethyl)-7-oxabicyclo- -[2.2.1]hept-2-ene (I) by aqueous ROMP using the trichlorides of ruthenium, iridium and osmium as the precursors to the initiating and chain propagating species (1,2,3). The resulting polymers were found to contain respectively 60%, 90% and 75% of *trans* vinylenes in the backbone(3,4). This paper describes a detailed analysis of the high field NMR of these polymers carried out in order to obtain a greater understanding of the polymer microstructures.

EXPERIMENTAL

Polymer synthesis:

A schematic representation of the ROMP of monomer **I** to yield polymer **II** is outlined in Figure 1., which also records the numbering system employed.

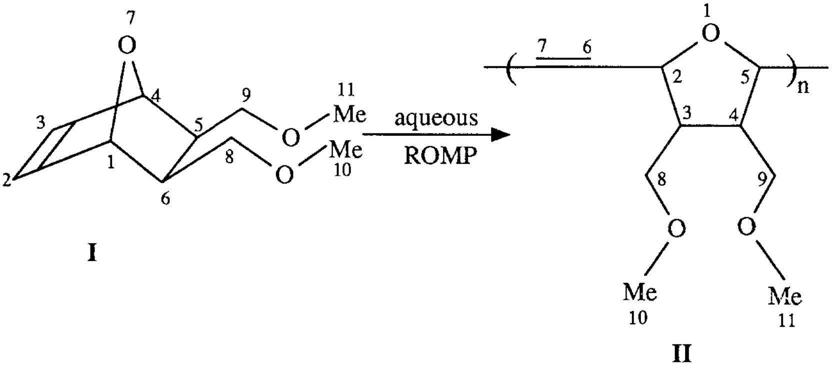

Figure 1: Aqueous ROMP of monomer **I** to yield polymer **II**.

The preparation and isolation of these polymers is reported elsewhere (3). Three samples of different microstructures and molecular weights were obtained using $RuCl_3.3H_2O$, $OsCl_3.3H_2O$, and $IrCl_3.3H_2O$ as the precursors to the initiating and chain propagating species (Table 1).

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TABLE 1: Polymers **II** prepared using transition metal chlorides as the precursors to the initiating and chain propagating species, σ^c is the fraction of cis vinylenes.

	Compound used as the precursor to the initiating and chain propagating species		
	$RuCl_3.3H_2O$	$OsCl_3.3H_2O$	$IrCl_3.3H_2O$
Mn σ^c	150K 0.40	5K 0.25	20K 0.10

Polymer characterisation:

The NMR spectra of the polymers were recorded in $(CD_3)_2CO$ using a Varian VXR-400-s NMR spectrometer, operating at 399.952 MHz for ^1H NMR, and 100.577 MHz for ^{13}C NMR.

RESULTS AND DISCUSSION

General considerations:

The microstructural analysis of poly(norbornene)s has been discussed in detail(4), and the analysis established can be applied directly to these heterocyclic analogues. Monomer **I** is symmetrical and therefore cannot give rise to HH, TT or HT addition modes; nevertheless, there are several different ways in which the repeat unit can be incorporated into the polymer chain. The double bonds may be *cis* or *trans*, and the allylic methines on either side of the double bonds are chiral and may have opposite chirality, giving meso- or m-dyads and isotactic polymer, or the same chirality giving racemic- or r-dyads and syndiotactic polymer. Thus, there are four possible homopolymer microstructures and a variety of other microstructures determined by *cis/trans* and meso/racemic dyad sequence effects. The stereochemical constraints in the monomer carried over into the polymer result in *syn* relationships between the pairs of methoxymethyls and vinylic-allylic C-C bonds, and an *anti* relationship between the methoxymethyls and vinylic-allylic bonds.

For convenience, **II-Ru**, **II-Os**, and **II-Ir** refer to the ROMP polymer prepared using $RuCl_3.3H_2O$, $OsCl_3.3H_2O$, and $IrCl_3.3H_2O$ as the precursors to the initiating and chain propagating species respectively.

^1H NMR of polymer II:

The ^1H NMR spectra are shown in Figure 2 and their assignments, which follow in a straight forward way from the shifts and integrations, are recorded in Table 2.

The ^1H NMR spectra of polymers **II-Ru**, **II-Os**, and **II-Ir** contain the resonances of the vinylic protons at positions 6 and 7, 5.72 ppm (*trans*) and 5.52 ppm (*cis*) (Figure 2). Integration of this region demonstrates that all the polymers **II** have predominantly *trans* double bonds, σ^c= 0.4 for **II-Ru**, 0.25 for **II-Os**, and 0.1 for **II-Ir** (3). The allylic protons on positions 2 and 5 resonate at 4.20 ppm (adjacent to *trans*) and 4.54 ppm (adjacent to *cis*). In the case of **II-Ru** (Figure 2a) there is an additional signal at 4.63 ppm due to a *cis*-allylic proton, Grubbs and Novak reported similar data but did not record the lower field *cis*-allylic signal (2). In this work we have found the inclusion of the lower field signal necessary to balance the proton integration, so it is assumed to be real, and may possibly arise from sequence effects. The spectra of both **II-Os** (Figure 2b) and **II-Ir** (Figure 2c) contain only the higher field *cis*-allylic resonance at 4.54 ppm.

The rest of the ^1H NMR can be readily interpreted; the methine protons on positions 3 and 4 resonate as a broad singlet at 2.29 ppm; methyl protons on positions 10 and 11 as a narrow singlet at 3.29 ppm; methine protons on positions 8 and 9 as a close pair at 3.46 ppm and 3.41 ppm. Additional resonances are observed at 2.95 ppm in the

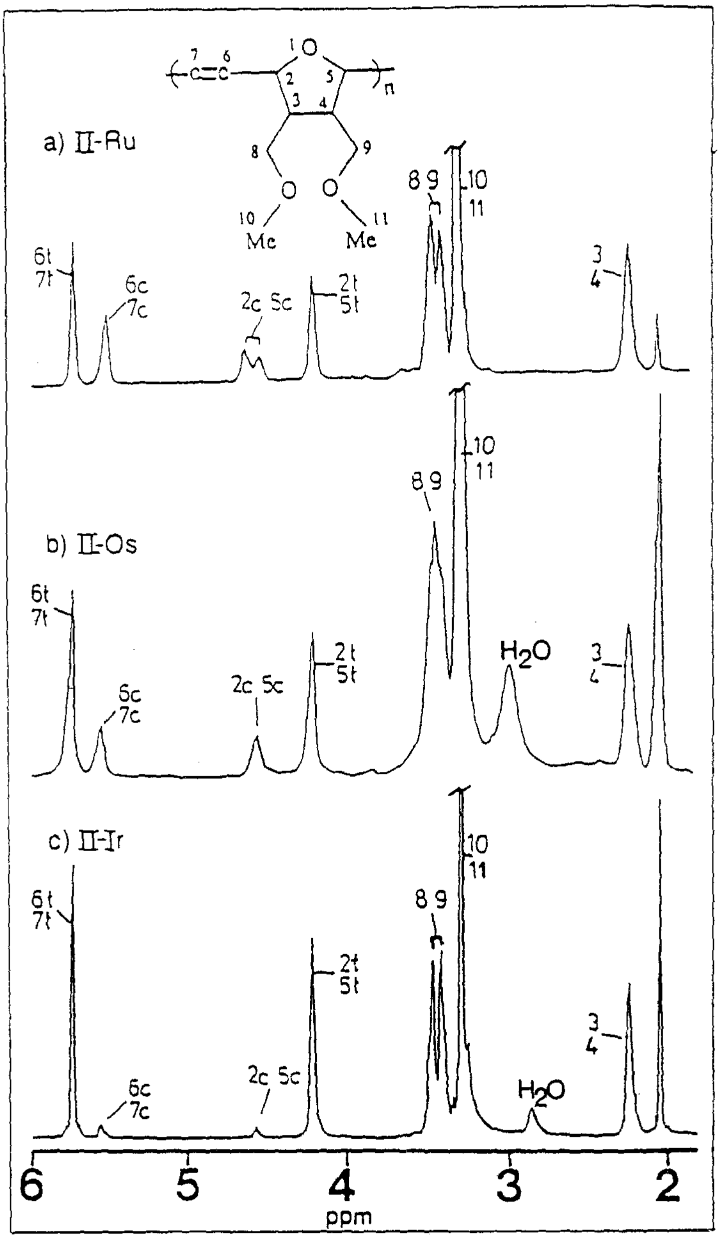
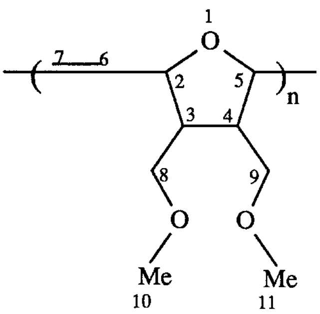


Figure 2: ^{1}H NMR spectra recorded at 399.952 MHz in $(CD_3)_2CO$ of polymers II prepared using a) $RuCl_3.3H_2O$, b) $OsCl_3.3H_2O$, and c) $IrCl_3.3H_2O$ as the precursors to the initiating and chain propagating species.

spectrum of **II-Os** (Figure 2b), and at 2.90 ppm in the spectrum of **II-Ir** (Figure 2c), and are assigned as water impurities.

TABLE 2: Principal ^{1}H NMR spectral parameters[1] of polymer **II** (399.952 MHz, $(CD_3)_2CO$).

polymer **PIII**	H at position	chemical shifts /ppm
	6 and 7	5.72 (trans) 5.52 (cis)
	2 and 5	4.63 (c)[2], 4.54 (c) 4.20 (t)[3]
	8 and 9	3.46, 3.41
	10 and 11	3.29
	3 and 4	2.29

1) with respect to acetone at 2.04 ppm.
2) "c" refers to a position α to a *cis* vinylene.
3) "t" refers to a position α to a *trans* vinylene.

^{13}C NMR of polymer II:

The proton decoupled ^{13}C NMR spectra are shown in Figure 3, and their assignments are recorded in Table 3.

Each polymer spectrum consists of a group of vinylic resonances (135-132 ppm, compared in Figure 4, C-6 and C-7), allylic resonances (82.5-77 ppm, compared in Figure 5, C-2 and C-5), methylene resonances (72-70 ppm, compared in Figure 6, C-8 and C-9), methine resonances (49-47 ppm, compared in Figure 7, C-3 and C-4), and methyl resonances (approx. 58.90 ppm). The spectra of **II-Ir** are the simplest, and those of **II-Ru** are the most complicated.

A major problem encountered in the assignment of the spectra of polymers of this type is in the determination of tacticity and/or sequence effects. There are four possible assembly modes for these polymers *vide supra;* therefore if more than four resonances are observed for a particular carbon they **must** arise from tacticity **and/or** sequence effects. However, it is not necessarily the case that the existance of such different structures will result in distinguishable shifts. The method employed by Ivin (4) to determine sequence and tacticity in ROMP products requires the analysis of spectra of polymers derived from unsymmetrical monomers and consequently cannot be used in this case.

The expanded ^{13}C NMR spectrum of polymer **II-Os** (Figure 4b) contains two resolved resonances resulting from *cis* vinylenes (134.25 and 134.13 ppm), and four resulting from *trans* vinylenes (133.39, 133.30, 133.13 and 133.02 ppm)(Table 3). The origin of this multiplicity cannot be unambiguously assigned on the basis of ^{13}C NMR data. If one considers a simple *trans* vinylene carbon, it can exist in a meso (m) or racemic (r) dyad environment (two possible resonances). If the nearest vinylenes influence its shift, three resonances are possible (ctc, ttc ≡ ctt, and ttt), and if the next nearest ring stereochemistry is important we have more possible environments: mmm, mmr, rmm, rmr,

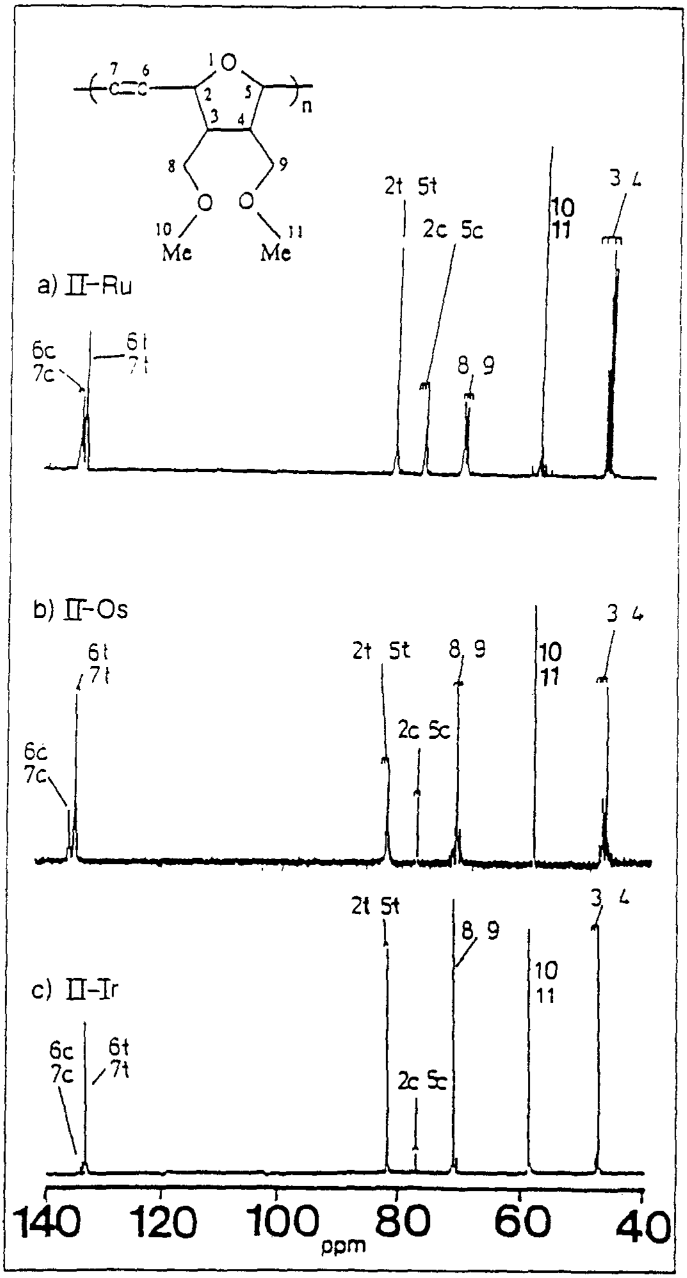
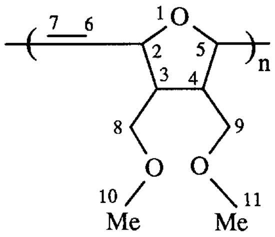


Figure 3: ^{13}C NMR spectra recorded at 100.577 MHz in $(CD_3)_2CO$ of polymers II prepared using a) $RuCl_3.3H_2O$, b) $OsCl_3.3H_2O$, and c) $IrCl_3.3H_2O$ as the precursors to the initiating and chain propagating species.

TABLE 3: Principal ^{13}C NMR spectral parameters[1] of polymer **II** (100.577 MHz, $(CD_3)_2CO$).



carbon position	double bond or nearest double bond	**II-Ru** / ppm	**II-Os** / ppm	**II-Ir** / ppm
6 and 7	*cis*	134.23	134.25	134.25
	cis	134.11	134.13	
	cis	133.84		
	trans		133.39	
	trans	133.33	133.30	133.30
	trans			133.20
	trans	133.12	133.13	133.12
	trans	132.97	133.02	
2 and 5	*trans*			82.40
	trans	82.25	82.24	82.26
	trans	82.08		
	trans	82.03	82.02	82.05
	trans	81.96		
	cis	77.68	77.72	
	cis	77.44		
	cis	77.36	77.38	77.39
	cis	77.22		
3 and 4	*cis*	48.80		
	cis	48.77	48.76	
	cis	48.34	48.30	48.37
	trans	48.05	48.02	48.10
	trans	47.62	47.61	47.69
8 and 9	*trans*	71.52		
	trans	71.41	71.37	71.43
	trans	71.29		
	trans	71.15	71.11	71.17
	cis	70.81	70.77	
	cis	70.73		
	cis	70.54	70.54	70.59
	cis	70.51		
10 and 11		58.90	58.90	58.90

1) with respect to acetone at 29.82 ppm.

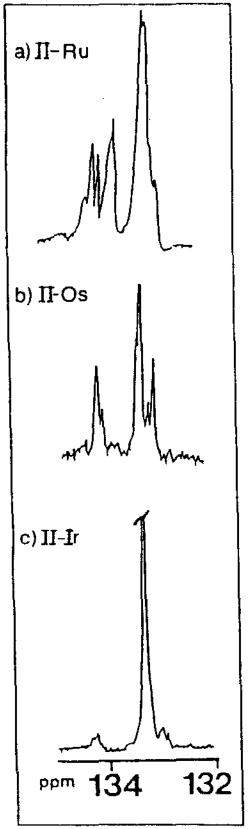


Figure 4
C6 and C7

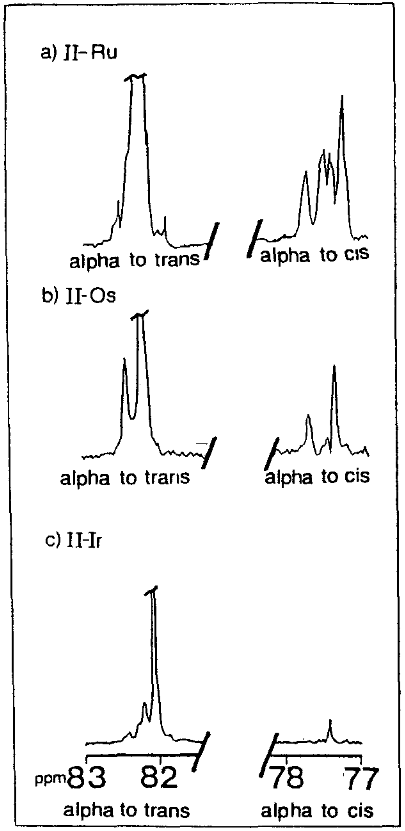


Figure 5
C2 and C5

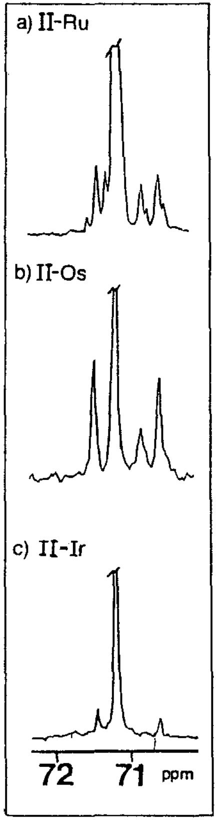


Figure 6
C8 and C9

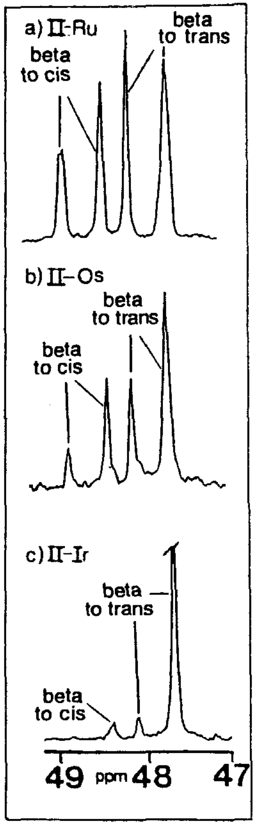


Figure 7
C3 and C4

Expanded ^{13}C NMR spectra recorded at 100.577 MHz in $(CD_3)_2CO$ of Polymers II-Ru, II-Os and II-In (see text) mrr, rrm, mrm, and rrr. Clearly the number of possible environments for a central *trans* vinylene multiplies considerably in pentad or higher sequences. Since there are four signals for a *trans* vinylene in this spectrum, it is certain that **II-Os** is **not** tactic, but it is not possible to assign these signals. The corresponding spectrum of **II-Ru** (Figure 4a) contains six resonances with approximately similar chemical shifts to those observed in the spectrum of **II-Os**, and an additional *cis* vinylene resonance at 133.84 ppm. Again the polymer is not tactic but no unambiguous deductions can be made concerning the detailed assignment of the microstructure. The spectrum of **II-Ir** (Figure 4c) contains one *cis* resonance at 134.25 ppm, one major *trans* resonance at 133.30 ppm, and two minor *trans* resonances at 133.20 and 133.12 ppm ($\sigma^c = 0.1$).

The allylic carbons (C-2 and C-5) allow an unambiguous assignment of vinylene content since it is invariably found in polymers of this kind that *cis*-allylic carbon signals occur approximately 5 ppm upfield from those arising from *trans*-allylic carbons (Figure 5) (4). The expansion of the proton decoupled ^{13}C NMR spectrum of polymer **II-Os** in this region (Figure 5b) contains four resonances, two resulting from carbons adjacent to *trans* double bonds (82.24 and 82.02 ppm), and two resulting from carbons adjacent to *cis* double bonds (77.72 and 77.38 ppm). In this case it is not possible to determine whether splitting of *cis*- and *trans*-allylic carbons is due to tacticity and/or sequences effects. The corresponding spectrum of **II-Ir** (Figure 5c) contains only the higher field *cis*-allylic resonance, and is consistent with the spectrum of the vinylic region of the same polymer, which contains only one *cis* resonance (Figure 4c). The spectrum of the *trans*-allylic region of **II-Ir** (Figure 5c) contains one major resonance at 82.05 ppm, and three relatively minor resonances; sequence/tacticity effects must be present. The spectrum of **II-Ru** (Figure 5a) contains eight resonances, four corresponding to *trans*-allylic carbons, and four to *cis*-allylic carbons. Again, sequence/tacticity effects must be present. Comparison with the corresponding region in the ^1H NMR spectrum (Figure 2a), which contained two *cis*-allylic resonances, reinforces the earlier argument that sequence effects are observed in the spectra of **II-Ru**.

The tacticity/sequence effects observed in the spectra of the vinylic and allylic carbons are also observed in the spectra of the methine carbons C-3 and C-4 (Figure 6). The spectrum of **II-Os** (Figure 6b) contains resonances for carbons β to *cis* double bonds at 48.76 and 48.30 ppm, and resonances β to *trans* double bonds at 48.02 and 47.61 ppm. The spectrum of **II-Ru** (Figure 6a) is somewhat more complicated in the methine region, presumably due to additional sequence effects, and the spectrum of **II-Ir** (Figure 6c) simpler.

The stereochemical constraints of the polymer backbone affect the chemical environment of the pendant groups, carbons C-8 and C-9 (Figure 7). Sequence effects are observed in the spectrum of **II-Ru** (Figure 7a), and may be present in polymers **II-Os** (Figure 7b) and **II-Ir** (Figure 7c), but this cannot be conclusively established.

CONCLUSIONS

The ^{13}C and ^1H NMR spectra of the polymers described here form a self-consistent set and reveal that the microstructures of all the polymers are complicated by sequence/tacticity effects. The effect of sequence on the chemical shifts is particularly strong in the case of **II-Ru**, as observed in the spectra of the *cis*-vinylic (Figure 4a) and *cis*-allylic (Figure 5a) regions. None of these polymers is stereoregular. Of the set described here polymer **II-Ir** has the most regular microstructure, being highly *trans* but of uncertain tacticity.

ACKNOWLEDGMENTS

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REFERENCES

1. Novak B.M. and Grubbs R.H. (1988), J. Am. Chem. Soc. 110: 962.
2. Novak B.M. and Grubbs R.H. (1988), J. Am. Chem. Soc. 110: 7542.
3. Feast W.J. and Harrison D.B., J. Mol. Cat., in press, 1990.
4. Ivin K.J. (1983), "Olefin Metathesis", Academic Press, London.

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