

# Aqueous ring-opening metathesis polymerizations of heteropolycyclic carboxylic acids with transition-metal chlorides

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*exo,exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid was polymerized by aqueous ring-opening metathesis polymerization using the trichlorides of ruthenium and osmium as precursors to the initiating and chain propagating species to yield poly(2,5-[3,4-bis(carboxylic acid)furanylene]vinylene)s. Ruthenium-derived initiators gave polymers with 60% of *cis*-vinylenes whereas polymerization initiated by osmium compounds was irreproducible, giving products with either 65 or 95% *cis*-vinylenes. The inclusion of acrylic acid or maleic acid in the reaction mixture caused a marked reduction in the time to precipitation of polymer and the ultimate yield. *cis*-But-2-ene-1,4-diol was found to affect the time to precipitation of polymer in a similar manner without a reduction in yield and allowed control of the polymer molecular weight over the range  $M_n = 10^5$  to  $7 \times 10^2$  with respect to poly(ethylene oxide) standards.

(Keywords: ring-opening metathesis polymerization; carboxylic acids; catalysis; gel permeation chromatography)

## INTRODUCTION

The range of functionalized monomers available for use in ring-opening metathesis polymerization (ROMP) reactions has traditionally been limited by deactivation of the initiators and/or chain-carrying species<sup>1</sup>. Similarly, relatively little success has been disclosed concerning the ROMP of heterocyclic monomers<sup>2-7</sup> and with ROMP in purely aqueous solvent<sup>4,5,8</sup>.

Early publications reported the use of iridium salts and complexes as initiators for the polymerization of *exo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid in aqueous or ethanolic media<sup>9,10</sup>. Further investigation revealed that the trichlorides of ruthenium and osmium were also effective as initiators for the ROMP of both *exo*- and *endo*-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid in ethanol<sup>11,12</sup>.

In this paper we report the aqueous ROMP of *exo,exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (I) using the trichlorides of ruthenium and osmium as precursors to the initiating and chain-carrying species. Aqueous ROMP using the chlorides of iridium, rhodium and palladium has so far proved unsuccessful. The molecular weights of the polymers were altered by using *cis*-but-2-ene-1,4-diol as a chain transfer agent (CTA)<sup>5</sup>, which also reduced the time to precipitation of polymer during the reaction. Attempts to use acrylic acid and maleic acid in a similar manner were less successful, although some reductions in molecular weights were observed. Their action was complicated by a large reduction in both the time to precipitation of polymer and the product yield.

## EXPERIMENTAL

### Materials

Laboratory-grade reagents, solvents and metal halides

(Aldrich Chemical Co. Ltd) were used as supplied. Water for the polymerizations was doubly distilled.

### Monomer synthesis

*exo,exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (I) was obtained by hydrolysis of the Diels-Alder adduct of furan and maleic anhydride in warm water<sup>13</sup>. Recrystallization of the product from warm water yielded pure monomer in ~60% yield with respect to furan (m.p. 132–133°C, lit.<sup>14</sup> 134°C).

### Polymer syntheses

In general the polymerizations were performed by adding aqueous solutions of the metal halide to stirred aqueous solutions of the pure monomer (I) or to mixtures of the monomer and an acyclic olefin, *cis*-but-2-ene-1,4-diol, acrylic acid or maleic acid. All the polymerizations were performed at  $55 \pm 0.1^\circ\text{C}$  under a normal laboratory atmosphere and run for two days. During the course of each reaction, colour changes were observed in the reaction solution, and these were used as an approximate indication of the progress of the reaction, although the actual colour observed cannot be correlated with the formation of an initiating species. When  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  was used as the precursor to the initiator, the initial brown colour of the solution turned crimson red and then dark green. The polymer generally precipitated from solution shortly after the solution turned green. When  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  was used in a similar manner, the initial colour of the solution turned brown with the precipitation of polymer. No colour changes were observed for the attempted ROMP with any of the other transition-metal chlorides.

The product polymers, poly(2,5-[3,4-bis(carboxylic acid)furanylene]vinylene)s (II), were recovered by filtra-

tion and thoroughly washed with dilute hydrochloric acid. The disodium salt of the polymer (**IIb**) was recovered by addition of the diacid polymer (**II**) to aqueous sodium hydroxide followed by filtration and precipitation into methanol. Polymer **IIb** was purified by three successive reprecipitations into methanol from water, then recovered by filtration and finally dried and stored under vacuum. The polymers **IIb** were pale green/brown solids, the colour being due to the presence of 0.1–0.3% by weight transition-metal contamination.

Typical experimental conditions for the polymerizations of monomer **I** using various transition-metal halides as the precursors to the metathesis initiators are found in Table 1. Comparison of the polymerization in the presence of chain transfer agents (CTA) can be found in Tables 2, 3, 4 and 5.

#### Polymer characterization

All n.m.r. spectra of monomers and polymers were recorded using a Varian VXR-400-S n.m.r. spectrometer. Polymer molecular weights were assessed by aqueous g.p.c. in saline buffer (pH 6) of composition 0.141 M sodium chloride, 0.008 M sodium phosphate (monobasic) and 0.003 M sodium phosphate (dibasic). The equipment comprised a Kanuer HPLC 64 pump, Rheodyne 7125 injector with 100  $\mu$ l loop, Knauer refractive index detector and PLaquagel P3 30 cm column (Polymer

**Table 1** Polymerizations of monomer **I** initiated by various transition-metal chlorides in water<sup>a</sup>

	RuCl <sub>3</sub> ·3H <sub>2</sub> O	OsCl <sub>3</sub> ·3H <sub>2</sub> O	IrCl <sub>3</sub> ·3H <sub>2</sub> O
Monomer (g)	1.0	1.0	1.0
Catalyst (g)	0.07	0.07	0.07
Water (ml)	6.5	6.5	6.5
Temp. (°C)	55	55	55
Yield (%)	95	80	<sup>b</sup> –
<i>M<sub>n</sub></i>	>10 <sup>5</sup>	>10 <sup>5c</sup>	–
<i>cis</i> -Vinylens (%)	65 <sup>d</sup>	65 or 95 <sup>d,e</sup>	–

<sup>a</sup>Under similar conditions RhCl<sub>3</sub>·3H<sub>2</sub>O and PdCl<sub>2</sub> failed to initiate ROMP. Duration of polymerization was two days unless otherwise stated

<sup>b</sup>No polymer formed after one week

<sup>c</sup>High-molecular weight material was excluded from the g.p.c. column

<sup>d</sup>Determined by <sup>1</sup>H n.m.r. spectroscopy

<sup>e</sup>Polymerizations were irreproducible

**Table 2** Polymerizations of monomer **I** initiated by RuCl<sub>3</sub>·3H<sub>2</sub>O using *cis*-but-2-ene-1,4-diol as chain transfer agent (CTA)<sup>a</sup>

Ratio of reactants					
Monomer	CTA	[M] <sup>b</sup>	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i>	<i>cis</i> <sup>c</sup> (%)
16	0	0.72	>10 <sup>5d</sup>	–	65
16	27	0.84	5.9 × 10 <sup>3</sup>	2.39	64
16	54	0.84	2.6 × 10 <sup>3</sup>	2.41	65
16	72	0.84	2.4 × 10 <sup>3</sup>	1.98	62
16	81	0.84	2.3 × 10 <sup>3</sup>	2.04	60
16	108	0.84	1.9 × 10 <sup>3</sup>	2.41	59
16	210	0.91	0.7 × 10 <sup>3</sup>	2.07	30

<sup>a</sup>Duration of polymerizations was two days. Molar ratio monomer: RuCl<sub>3</sub>·3H<sub>2</sub>O = 16:1

<sup>b</sup>Concentration of monomer with respect to total volume of water and CTA; this is a homogeneous polymerization

<sup>c</sup>Determined by <sup>1</sup>H n.m.r. spectroscopy

<sup>d</sup>High-molecular-weight material was excluded from the g.p.c. column

**Table 3** Polymerizations of monomer **I** initiated by OsCl<sub>3</sub>·3H<sub>2</sub>O using *cis*-but-2-ene-1,4-diol as chain transfer agent (CTA)<sup>a</sup>

Ratio of reactants				
Monomer	CTA	[M] <sup>b</sup>	<i>M<sub>n</sub></i>	<i>cis</i> <sup>c</sup> (%)
23	0	0.72	>10 <sup>5d</sup>	65 <sup>e</sup>
23	0	0.72	>10 <sup>5d</sup>	65 <sup>e</sup>
23	0	0.72	– <sup>e</sup>	–
23	39	0.84	2.6 × 10 <sup>3</sup>	58
23	115	0.84	0.6 × 10 <sup>3</sup>	30

<sup>a</sup>Duration of polymerizations was two days. Molar ratio monomer: OsCl<sub>3</sub>·3H<sub>2</sub>O = 23:1

<sup>b</sup>Concentration of monomer with respect to total volume of water and CTA; this is a homogeneous polymerization

<sup>c</sup>Determined by <sup>1</sup>H n.m.r. spectroscopy

<sup>d</sup>High-molecular-weight material was excluded from the g.p.c. column

<sup>e</sup>Polymerizations were irreproducible

**Table 4** Polymerizations of monomer **I** initiated by RuCl<sub>3</sub>·3H<sub>2</sub>O using acrylic acid as chain transfer agent (CTA)<sup>a</sup>

Ratio of reactants				
Monomer	CTA	[M] <sup>b</sup>	<i>M<sub>n</sub></i>	<i>cis</i> <sup>c</sup> (%)
14	0	0.72	>10 <sup>5d</sup>	60
14	2	0.78	5 × 10 <sup>3d</sup>	62
14	4	0.78	8 × 10 <sup>3d</sup>	60
14	8	0.78	6 × 10 <sup>3d</sup>	58
14	38	0.78	– <sup>e</sup>	–
14	113	0.78	– <sup>e</sup>	–

<sup>a</sup>Duration of polymerizations was two days unless stated. Molar ratio monomer: RuCl<sub>3</sub>·3H<sub>2</sub>O = 14:1

<sup>b</sup>Concentration of monomer with respect to total volume of water; this is a homogeneous polymerization

<sup>c</sup>Determined by <sup>1</sup>H n.m.r. spectroscopy

<sup>d</sup>High-molecular-weight material was excluded from the g.p.c. column

<sup>e</sup>No polymer formed after one week

**Table 5** Polymerizations of monomer **I** initiated by RuCl<sub>3</sub>·3H<sub>2</sub>O using maleic acid as chain transfer agent (CTA)<sup>a</sup>

Ratio of reactants				
Monomer	CTA	[M] <sup>b</sup>	<i>M<sub>n</sub></i>	<i>cis</i> <sup>c</sup> (%)
19	0	0.72	>10 <sup>5d</sup>	60
19	1	0.78	>10 <sup>5d</sup>	58 <sup>e</sup>
19	1	0.78	>10 <sup>5d</sup>	62 <sup>f</sup>
19	7	0.78	>10 <sup>5d</sup>	60 <sup>g</sup>
19	7	0.78	>10 <sup>5d</sup>	61 <sup>f</sup>
19	15	0.78	– <sup>h</sup>	–

<sup>a</sup>Duration of polymerizations was two days unless stated. Molar ratio monomer: RuCl<sub>3</sub>·3H<sub>2</sub>O = 19:1

<sup>b</sup>Concentration of monomer with respect to total volume of water; this is a homogeneous polymerization

<sup>c</sup>Determined by <sup>1</sup>H n.m.r. spectroscopy

<sup>d</sup>High-molecular-weight material was excluded from the g.p.c. column

<sup>e</sup>Polymer precipitated from solution after 4 h: solution colour was red

<sup>f</sup>Polymer precipitated from solution after two days: solution colour was green

<sup>g</sup>Polymer precipitated from solution after 1 h: solution colour was red

<sup>h</sup>No polymer formed after one week

Laboratories Ltd). Molecular-weight calculations were made with a Chromatocoder 12 integrator (Quadrent Scientific) calibrated with poly(ethylene oxide) standards (Polymer Laboratories Ltd). All molecular-weight data are expressed in poly(ethylene oxide) equivalent molecular weights.

## RESULTS AND DISCUSSION

## Catalyst choice

The polymerization of monomer **I** by aqueous ROMP was only accomplished using  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  as the precursors to the initiator, although in the latter case the polymerization was irreproducible (Tables 1 and 3). Previous studies with osmium initiators also report ring opening at the ether oxygen as a competitive reaction, although no evidence for this was observed in the high polymers prepared here<sup>11,15</sup>. Michelotti suggested that iridium chlorides had considerably greater metathesis activity in ethanol than either ruthenium or osmium chlorides<sup>16</sup>. It is therefore surprising that iridium trichloride failed to initiate the polymerization of monomer **I** in view of previous successful polymerizations of other monomers in water<sup>5,9,10,17</sup>, although lack of success with other related 7-oxanorbornadiene derivatives has recently been reported<sup>6</sup>. Similarly, rhodium and palladium chlorides have so far failed to initiate the ROMP of monomer **I** in water, although a high probability of success was not expected following the experience of previous workers<sup>18,19</sup>.

## Polymer microstructure

The polymerization process is outlined in Figure 1, which also records the numbering system used throughout this paper.

The microstructural analysis of the high polymers **IIb** was made with reference to their homocyclic analogues, the poly(norbornene)s. Microstructural analysis is based on the assumption that the  $^{13}\text{C}$  n.m.r. resonance of the methine carbons adjacent to a *cis*-vinylene (positions 2 and 5) occurs at a shift approximately 5 ppm upfield from the resonance of the corresponding carbon adjacent to a *trans*-vinylene<sup>1</sup>. The monomer (**I**) used in this work is symmetrical and therefore cannot give rise to HH, TT or HT addition modes. There are however several ways in which the repeat unit can be incorporated into the polymer chain. The double bonds may be *cis* or *trans*;

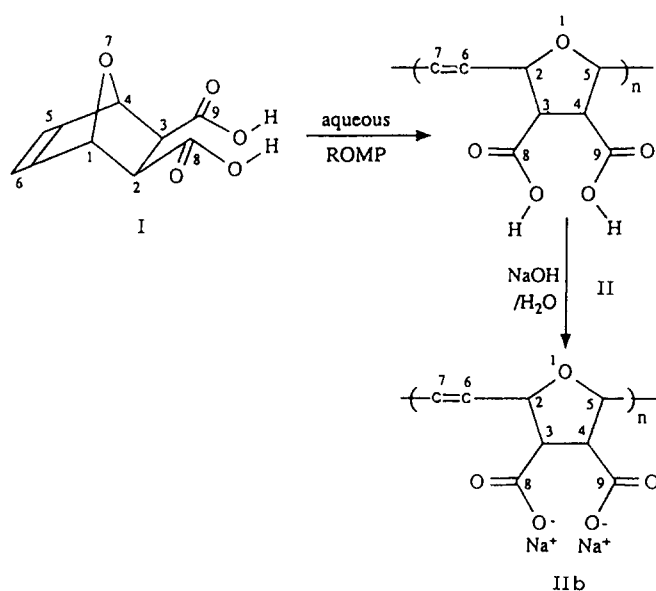


Figure 1 Reaction scheme and numbering system for the ROMP of monomer **I** to yield polymer **II** and disodium salt (**IIb**)

Table 6  $^{13}\text{C}$  n.m.r. spectral parameters<sup>a</sup> for polymer **IIb** (disodium salt) (100.577 MHz, D<sub>2</sub>O)

C at position	Chemical shifts (ppm)
8 and 9	182.44, 182.28
6 and 7	136.78, 136.44 ( <i>cis</i> ) 136.18 ( <i>trans</i> )
2 and 5	85.95, 85.65 ( <i>t</i> ) <sup>b</sup> 81.56, 81.13 ( <i>c</i> ) <sup>c</sup>
3 and 4	60.56, 60.34 ( <i>c</i> ) <sup>c</sup> 59.83 ( <i>t</i> ) <sup>b</sup>

<sup>a</sup>With respect to  $(\text{Me}_3\text{Si})\text{CD}_2\text{CD}_2\text{CO}_2\text{Na}$  at 1.70 ppm

<sup>b</sup>*t* refers to a position  $\alpha$  or  $\beta$  to a *trans*-vinylene

<sup>c</sup>*c* refers to a position  $\alpha$  or  $\beta$  to a *cis*-vinylene

and the allylic methines on either side of the double bond 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 dyad microstructures and a variety of triad, tetrad, etc., microstructures.

The  $^{13}\text{C}$  n.m.r. spectrum of the polymer prepared using ruthenium trichloride as initiator is displayed in Figure 2, with the assignments recorded in Table 6.

The carbonyl carbons resonate as a complex multiplet centred at 182.28 ppm. This splitting is the result of sequence effects in the main chain being carried over into the pendant groups, although they cannot be assigned<sup>11</sup>. The allylic carbons at positions 2 and 5 allow unambiguous assignment of the microstructure since allylic resonances adjacent to *cis*-vinyl groups occur approximately 5 ppm upfield of those adjacent to *trans*. Allylic carbons adjacent to *trans* double bonds are observed at 85.95 and 85.65 ppm, and those adjacent to *cis* double bonds at 81.60 and 81.13 ppm. The splitting may be due to sequence effects and/or tacticity effects<sup>1</sup>, and is consistent with the observed splitting of the vinylic region (C(6) and C(7)): *cis* signals at 136.78 and 136.44 ppm and *trans* at 136.18 ppm. Multiplicities are further observed in the three broad resonances associated with methine carbons at positions 3 and 4: the low-field resonance at 60.56 ppm results from carbons  $\beta$  to *cis*-vinylenes, and the high-field resonance at 59.83 ppm from carbons  $\beta$  to *trans*-vinylenes. The central resonance at 60.33 ppm cannot be unambiguously assigned.

Polymerizations of similar monomers in ethanol with both ruthenium and osmium compounds as initiators have produced high *trans* polymers<sup>6,11</sup>; changes in solvent are however well known to have marked effects on the ultimate polymer microstructure<sup>3</sup>.

The  $^1\text{H}$  n.m.r. spectra shown in Figure 3 are consistent with the assignments made from the  $^{13}\text{C}$  n.m.r. data.

The vinylic protons (6 and 7) resonate at 5.70 ppm (*trans*) and 5.44 ppm (*cis*), both as broad signals. The methine protons on positions 2 and 5 resonate at 4.99 ppm (adjacent to *cis*) and 4.57 ppm (adjacent to *trans*); their integration is consistent with the integration of the vinylic region. Finally, methine protons on positions 3 and 4 resonate together at 2.85 ppm (assignments in Table 7). Similar analyses of the spectra of several samples produced with other initiators show that the polymers produced in this work have predominantly *cis*-vinylic bonds, 65% for  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and 65 or 95% for  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$ .

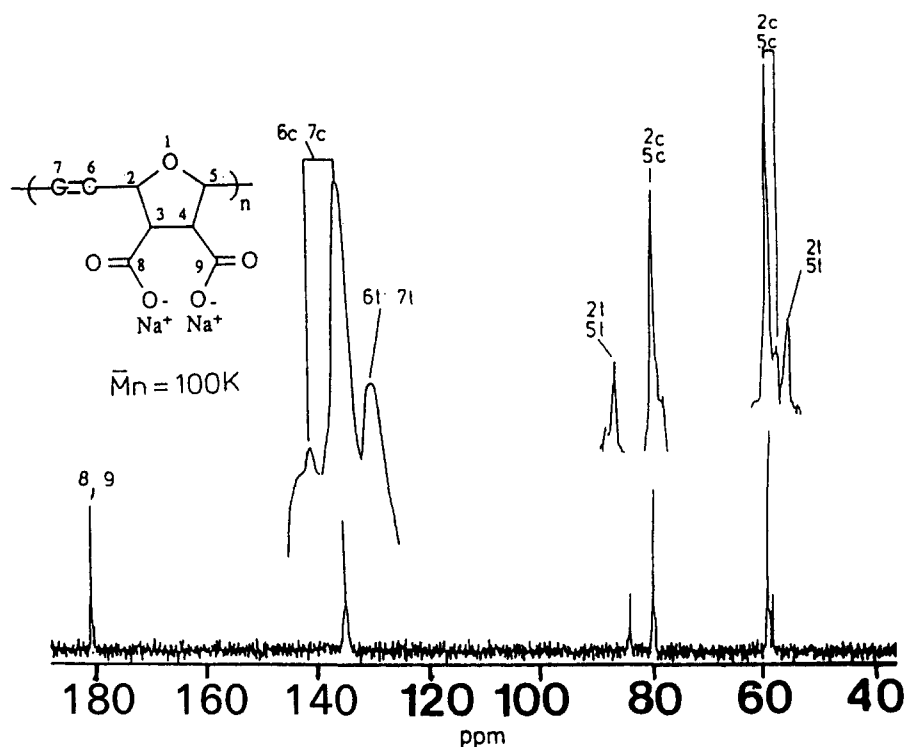


Figure 2  $^{13}\text{C}$  n.m.r. spectrum of polymer **IIb** prepared with  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  as precursor to the initiator

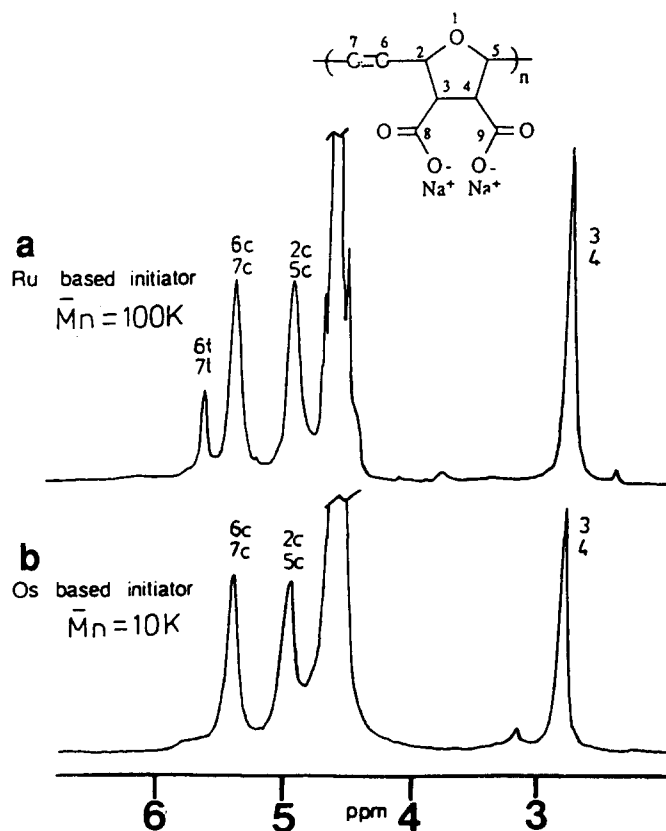


Figure 3  $^1\text{H}$  n.m.r. spectra of polymers **IIb** prepared with (a)  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  and (b)  $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$  as precursors to the initiator

#### Chain transfer agents

*cis*-But-2-ene-1,4-diol can be used as a chain transfer agent with both osmium and ruthenium initiators; however, the chain transfer efficiency is low (Tables 2 and 3)<sup>5</sup>. Oligomers of 2–20 units are prepared when

Table 7  $^1\text{H}$  n.m.r. spectral parameters<sup>a</sup> for polymer **IIb** (disodium salt) (399.952 MHz,  $\text{D}_2\text{O}$ )

H at position	Chemical shifts (ppm)
6 and 7	5.70 ( <i>trans</i> ) 5.44 ( <i>cis</i> )
2 and 5	4.99 ( <i>c</i> ) <sup>b</sup> 4.57 ( <i>t</i> ) <sup>c</sup>
3 and 4	2.85

<sup>a</sup>With respect to water at 4.67 ppm

<sup>b</sup>'c' refers to a position  $\alpha$  to a *cis*-vinylene

<sup>c</sup>'t' refers to a position  $\alpha$  to a *trans*-vinylene

the ratio of CTA: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  is greater than 80:1 (Figure 4). In contrast, acrylic acid and maleic acid appear to act as catalyst poisons when used in similar proportions, although reductions in molecular weight of the product polymers can be achieved by using acrylic acid in proportions CTA: $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  less than 8:1 (Tables 4 and 5). The action of maleic acid is complicated by its apparent acceleration of the polymerization. Thus in reactions including maleic acid, polymer begins to precipitate within minutes rather than hours, which is the case in the absence of this additive; this occurs without significant reduction in yield or molecular weight if the ratio of diacid to metal is less than 7:1. Acrylic acid decreases the time to precipitation of polymer to a less marked degree if used in a ratio of less than 8:1 acrylic acid:metal. When the ratio is 8:1, the polymer molecular weight is reduced from greater than  $10^5$  to 6000, while the yield of the reaction is reduced from 95% to 10%.

#### End-group effects

The observation and intensity of new end-group resonances in the  $^1\text{H}$  n.m.r. spectra of the polymers prepared using  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  as precursor to the initiat-

ing species and *cis*-but-2-ene-1,4-diol as chain transfer agent can also be correlated to the reduction of molecular weight observed using aqueous g.p.c. (Figures 5 and 6).

Proton resonances at 5.70, 5.44, 4.99, 4.57 and 2.85 ppm correspond to those of the high polymer, confirming that ROMP is taking place. The overall yield of polymer is largely unchanged over the whole molecular-weight range, indicating that the metal carbene formed by cross-metathesis with *cis*-but-2-ene-1,4-diol can initiate further metathesis. The end-groups are therefore vinyl alcohols (Figure 4), with signals observed at 5.83 ppm (vinylic) and 4.08 and 3.95 ppm (*cis*- and *trans*-methylene). This compares with the resonances of *cis*-but-2-ene-1,4-diol at 5.57 ppm (vinyl) and 4.02 ppm (methylene), which can be seen in some of the spectra as a residual impurity.

Protons in units at both ends of the polymer chain show chemical shifts distinct from those in the body of the chain. Thus the methine protons at positions 3 and 4 resonate at 2.85 ppm in a mid-chain unit (3h, 4h), but

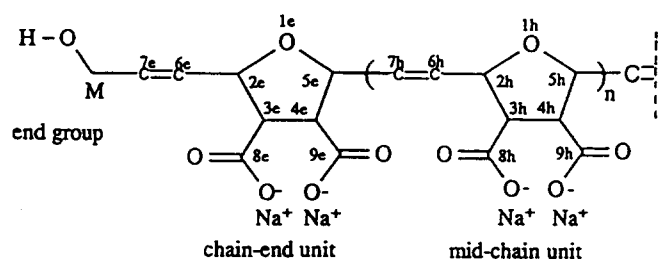


Figure 4 End-groups on polymer II

at 2.70 ppm in a chain terminal unit (3e). The vinylic resonances at 5.70 and 5.44 ppm are broadened, although no significant changes are observed in the resonances of methine protons at positions 2 and 5 (4.99 and 4.57 ppm); this is probably due to masking by the solvent. Other resonances, principally at 3.45 ppm and between 2.1 and 1 ppm, increase in relative intensity as the molecular weight is decreased, although they cannot be assigned as part of the ROMP polymer. They may be the product of competitive termination reactions or other polymerization mechanisms becoming prominent when high concentrations of chain transfer agent are used.

The increase of vinylic end-groups (Figure 5), principally at 5.83 ppm (7e, *trans*), correlates well with the reduction of polymer molecular weight calculated by g.p.c. (Figure 6 and Tables 2 and 3), suggesting that the first insertion product of the metathesis reaction is *trans*. Significantly, this effect was not observed with polymers where the backbone contains predominantly *trans*-vinylic bonds<sup>5</sup>. The relative intensity of the methine protons at positions 3 and 4 in mid-chain (3h, 4h, 2.85 ppm) and chain terminal units (3e, 2.70 ppm) enables a good approximation of the average oligomer length to be made. Thus in the spectrum in Figure 5c, where the integration of both resonances is equal, the average oligomer must be a dimer. This result is in good agreement with the g.p.c. data in Figure 6c.

## CONCLUSIONS

*exo,exo*-7-Oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (I) can be directly polymerized by aqueous ROMP using the chlorides of ruthenium and osmium as

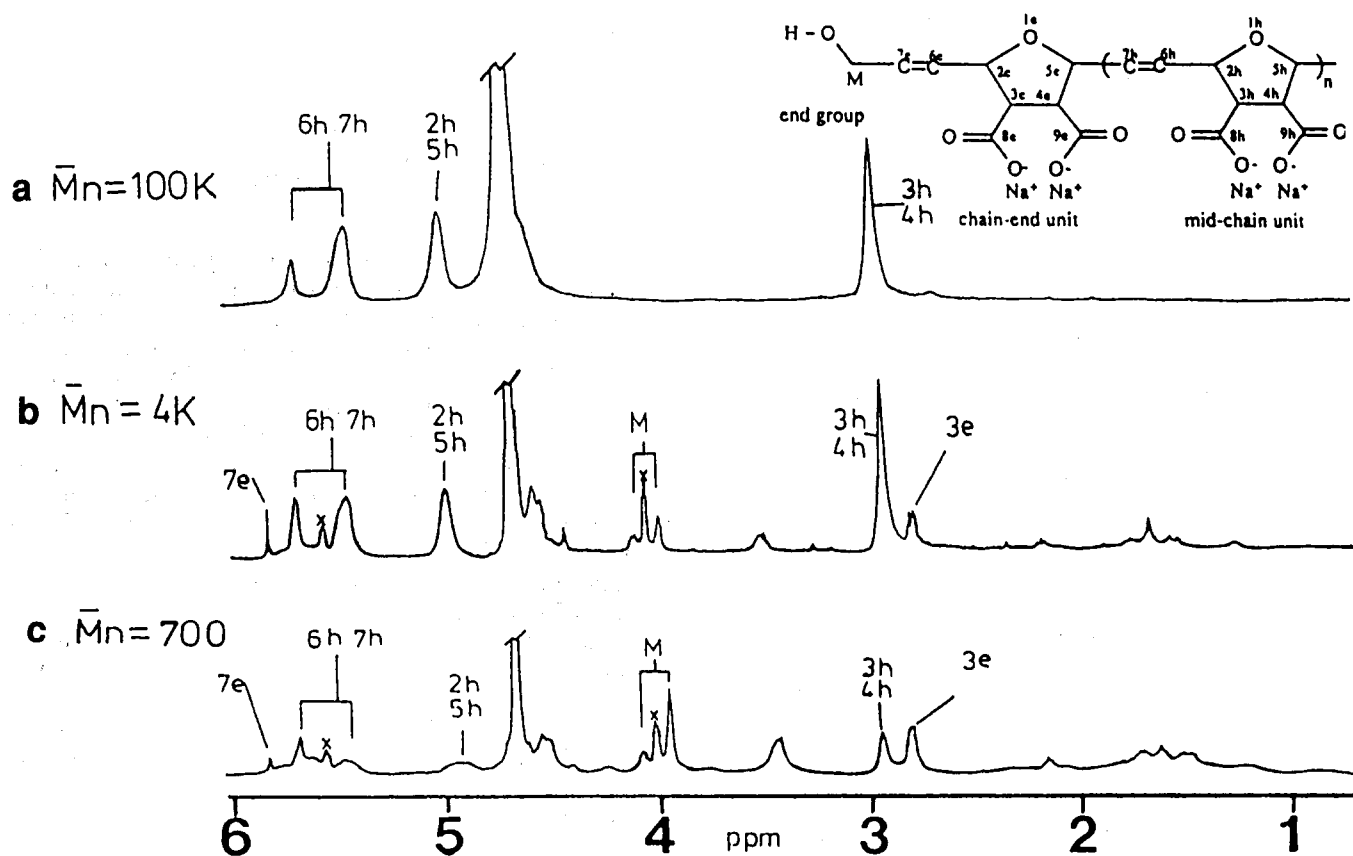


Figure 5  $^1\text{H}$  n.m.r. spectra of oligomers of polymer IIb: (a)  $M_n = 100 \times 10^3$ ; (b)  $M_n = 4 \times 10^3$ ; (c)  $M_n = 700$ ; for labelling, see text

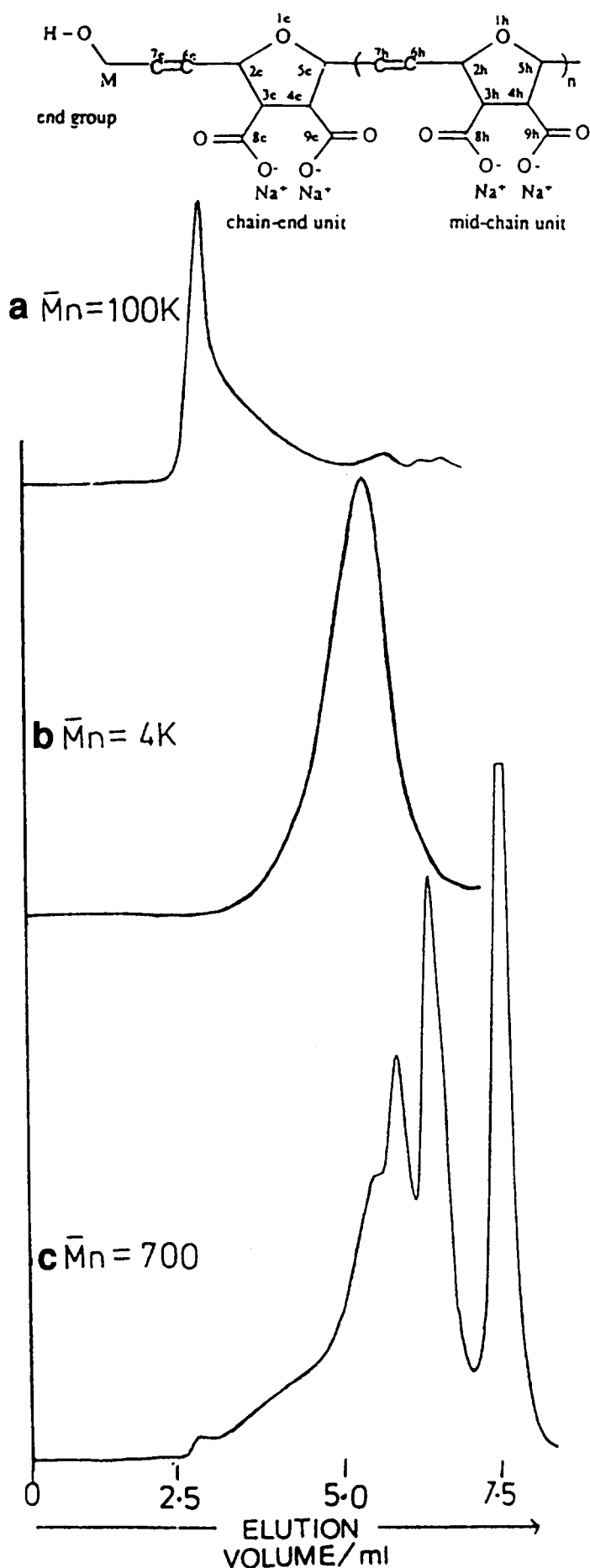


Figure 6 G.p.c. chromatograms of oligomers of polymer IIb: (a)  $M_n = 100 \times 10^3$ ; (b)  $M_n = 4 \times 10^3$ ; (c)  $M_n = 700$

precursors to the metathesis initiators. The polymerizations with osmium as initiator proved irreproducible, which supports observations with similar compounds and systems<sup>3,11</sup>. Surprisingly  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  was not found to be active under our reaction conditions<sup>6,17</sup>.

The molecular weight of the polymers can be altered using *cis*-but-2-ene-1,4-diol as a chain transfer agent, although oligomers can only be prepared by using the CTA as a co-solvent. The time to the precipitation of polymer in these reactions can be decreased by inclusion of acrylic acid in the reaction mixture, although formation of low-molecular-weight oligomers is accompanied by a dramatic reduction in yield.

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