

# Stereoregular fluoropolymers: 1. The ring opening polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene

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(Received 16 September 1985; revised 11 February 1986)

The polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene through the agency of catalysts based on tungsten, molybdenum and ruthenium compounds gives poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)vinylene)s with varying proportions of *cis* vinylene units. Analysis of the infra-red and high field  $^{13}\text{C}$  n.m.r. spectra of the different polymers is consistent with the hypothesis that catalysts based on  $\text{WCl}_6$  give a polymer with a 50:50 random distribution of *cis* and *trans* vinylenes, those based on  $\text{RuCl}_3$  give predominantly *trans* vinylenes (ca. 70%), and those based on  $\text{MoCl}_5$  give higher *trans* vinylene selectivity (ca. 90%).

(Keywords: stereoregular fluoropolymers; ring opening polymerization; catalysts)

## INTRODUCTION

The recognition, study and exploitation of the stereoregular polymerization of alkenes is one of the more notable achievements of polymer science<sup>1</sup>. An ability to regulate the fine details of microstructure extends the range of materials available from a particular monomer, and frequently there are spectacular differences in properties between a stereoregular polymer and its atactic analogue.

Despite their relatively high cost, a number of fluoropolymers have shown sufficiently unusual properties to justify their development and exploitation.

In the light of the two preceding observations it is rather surprising that the literature contains relatively few references to stereoregular fluoropolymers<sup>2-6</sup> and, to the best of our knowledge, no examples of the genre are produced commercially<sup>2,7</sup>.

Stereoregular polymerization of vinyl monomers is usually achieved through the agency of Ziegler-Natta catalysts. A closely related process is metathesis ring opening polymerization which, in favourable cases, can be shown to give totally stereoregular materials<sup>8,9</sup>.

We became interested in the possibility of making stereoregular fluoropolymers a few years ago<sup>10</sup>, and this paper is the first in a series in which we will describe the results of our investigations into the synthesis, structure and properties of such materials. We chose as our starting point metathesis ring opening of polycyclic fluorinated alkenes and related monomers. In our first publications in this field we reported that partially

fluorinated bicyclo[2.2.1]heptenes and -heptadienes may be polymerized by ring opening at the unsubstituted double bond with a range of catalysts derived from  $\text{WCl}_6$ <sup>10</sup>. To extend these initial observations to the synthesis of stereoregular fluoropolymers required that appropriate monomers, catalysts and reaction conditions were found and that unambiguous analytical criteria for polymer microstructures established. Thus, for the generalized structure **1** undergoing ring opening at **A** to give polymer **2** (see *Figure 1*), complete definition of the microstructure of **2** requires: the distribution and sequence of *cis* and *trans* vinylenes; if ring **B** is unsymmetrically substituted, the distribution and sequence of head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT) assemblies; and the distribution and sequence of meso (m) and racemic (r) dyads (the allylic carbons on either side of the vinylene unit 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). In *Figure 1* the stereochemical relationship of  $R_f$  to the allyl-vinyl carbon-carbon bond also requires definition.

Analysis at this level has been completely established for a wide range of methyl substituted norbornenes and reported in a series of papers and a recent book<sup>11</sup>. It is now clear that the detailed outcome of this type of polymerization is a complicated function of the structure and concentration of both the monomer and the catalyst, the solvent, the temperature and even the sequence of mixing (see Chapters 11, 12 and 13 in ref. 11). For example, the polymerization of norbornene with tungsten-based catalysts leads to polymers with *cis* vinylene contents varying from 39% to 95%<sup>12</sup>. In order to simplify the possible outcomes we decided to look first at the polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (**3**), since this symmetrical monomer cannot give rise to HT, HH and

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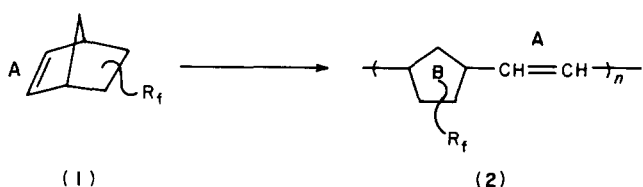


Figure 1 Ring opening polymerization of a fluorinated bicyclo[2.2.1]heptene derivative

TT effects and there are no complications from exo-/endo-isomerization.

## EXPERIMENTAL

### General

Standard vacuum line, inert atmosphere and dry box techniques were used in all operations involving solvents, catalysts, cocatalysts, monomer and polymers. The inert gas was nitrogen, the laboratory supply had <10 ppm O<sub>2</sub>, the gas was dried through liquid nitrogen cooled traps and circulated via glass or metal tubing, and flexible connections were of nylon tube.

### Solvents

Toluene was dried over sodium in the presence of benzophenone until a permanent blue colour was obtained, and distilled as required. Chlorobenzene was refluxed over P<sub>2</sub>O<sub>5</sub>, distilled, degassed and stored under dry nitrogen.

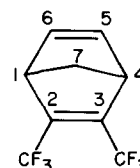
### Catalysts and cocatalysts

WCl<sub>6</sub> was prepared from WO<sub>3</sub> and hexachloropropene, and stored and manipulated as described previously<sup>10</sup>. TiCl<sub>4</sub>, RuCl<sub>3</sub>, OsCl<sub>3</sub>, (CH<sub>3</sub>)<sub>4</sub>Sn, MoCl<sub>5</sub>, ReCl<sub>5</sub> and (n-C<sub>4</sub>H<sub>9</sub>)Sn were used as supplied. (C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>Sn was purified as described previously<sup>10</sup>. Aluminium alkyls were supplied by K. Wade (this Department). C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>O)C=W(CO)<sub>5</sub> was prepared by the published route<sup>14</sup>.

### Monomer

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene is a known compound; in a typical synthesis hexafluorobut-2-yne (33.9 g, 209 mmoles), cyclopentadiene (13.8 g, 209 mmoles) and hydroquinone (0.05 g) were sealed under vacuum in a Pyrex ampoule (ca. 150 ml) and left at room temperature for 24 h. Previous reports advocated a period of heating; however, we observed that the reaction is exothermic and the initial two phase mixture generally became homogeneous overnight. On the rare occasions when we observed two phases remaining after 24 h the ampoule was heated to ca. 100°C for a further 24 h to ensure reaction. Monomer **3** was recovered by fractional distillation (Vigreux column, 10 cm, 1 atmosphere, b.p. 120°C–122°C) as a colourless liquid (38.5 g, 169 mmoles, 80%). This synthesis generally gave **3** in yields between 70% and 90%; the product was almost invariably contaminated with a trace of cyclopentadiene which was not removed by careful fractional distillation. Cyclopentadiene is a poison for some metathesis catalysts; however, we have found that when **3** is stored over maleic anhydride and filtered through a fine glass sinter prior to use, satisfactory 'polymerization grade' material was obtained in which no trace of cyclopentadiene could be detected by high field <sup>1</sup>H and

<sup>13</sup>C n.m.r. or by gas chromatography. The <sup>1</sup>H n.m.r. spectrum of **3** recorded at 300.13 MHz showed: an A Bqδ<sub>A</sub>, 2.08; δ<sub>B</sub>, 2.26; J<sub>AB</sub>, 6.95 Hz with A limbs unresolved (FWHM ~5 Hz) and B limbs as triplets J = 1.64 Hz (2H-7); a singlet δ, 3.90 (FWHM = 6 Hz) (H-1 and H-4); and three lines centred at δ, 6.92 ppm w.r.t. internal TMS (J = 1.95 Hz) (H-5 and H-6).



The proton decoupled <sup>13</sup>C n.m.r. spectrum recorded at 75.4 MHz showed signals at 53.3 (C-7), 74.0 (C-1, C-4), 122.9 q (J = 270 Hz) CF<sub>3</sub>, 142.9 (C-5, C-6) and 149.4 m (C-2, C-3) ppm w.r.t. internal TMS.

### Polymerizations

Polymerizations were carried out using a two necked round bottomed flask as the reaction vessel. A 'Teflon' (Dupont) coated stirrer bar was included and the contents were stirred magnetically in the initial stages of reaction and during dissolution of products. Generally both joints were fitted with three way 'Teflon' taps and connected to the vacuum and dry nitrogen line; sometimes only one neck was connected to the line, the other being closed with a rubber septum seal. All flasks, syringes, sinters, etc. were oven dried and stored in a vacuum desiccator prior to use. The monomer, solvents, catalyst solutions and cocatalysts were introduced into the reaction vessel using gas-tight syringes, either by inserting the syringe needle well into the flask via the bore of the tap and against a counter current of nitrogen, or through the septum seal. These experiments have been conducted over a period of eight years and several sequences of addition of the various components were investigated and various minor modifications of technique were used; for the examples reported in Table 1 these variables did not appear to have a major effect on the outcome of the polymerizations. There was an element of variability in the yields but product structures (see later) were not significantly changed. In most cases the activated catalyst was prepared in a separate flask and transferred to the reaction vessel using a syringe. In the cases when there was no polymerization the efficacy of the catalyst was checked by injecting a sample of the same catalyst into a solution of norbornene; all the catalysts mentioned in this work were effective in polymerizing norbornene by ring opening. The polymerizations were terminated by addition of methanol. The results of a selection of these experiments are recorded in Table 1. Most samples of polymer were soluble (CHCl<sub>3</sub> and/or (CH<sub>3</sub>)<sub>2</sub>CO) and were purified by reprecipitation into methanol or pentane. The samples were characterized by infra-red and <sup>13</sup>C n.m.r. spectroscopy. These materials were obtained as white granular precipitates; they could be solvent cast to give transparent films. They typically showed values of [η] between 0.3 and 1 dl g<sup>-1</sup>, for viscosities measured in MEK at 25°C.

## RESULTS AND DISCUSSION

### General

The objective of this work was to investigate the effect of catalyst and reaction conditions on the structure of the

**Table 1** Polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene, **3**

Expt. No.	Catalyst <sup>a</sup>	Cocatalyst	Molar ratio cat:co:cat:3	Solvent <sup>b</sup> (ml)	Temperature <sup>c</sup> (°C)	Time (h)	Yield <sup>d</sup> (%)
1	WCl <sub>6</sub>	none	1:370	T, 10	RT	3	11
2	WCl <sub>6</sub>	none	1:200	C, 1.1	50	48	4
3	WCl <sub>6</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Sn	1:2:400	T, 10	RT	0.5	70
4	WCl <sub>6</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Sn	1:2:150	T, 10	RT	1	80
5	WCl <sub>6</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Sn	1:2:150	C, 10	RT	1	76
6	WCl <sub>6</sub>	(n-C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> Sn	1:2:60	T, 10	RT	1	75
7	WCl <sub>6</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:60	T, 10	RT	1.5	20 <sup>e</sup>
8	WCl <sub>6</sub> /Na <sub>2</sub> O <sub>2</sub>	(i-C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> Al	1:3:350	T, 10	RT	3	77
9	WCl <sub>6</sub> /Na <sub>2</sub> O <sub>2</sub>	none	1:1:400	T, 10	RT	1	10
10	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> O)C=W(CO) <sub>5</sub>	none	1:60	T, 10	RT	48	0
11	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> O)C=W(CO) <sub>5</sub>	TiCl <sub>4</sub>	1:2:60	T, 10	RT	18	30
12	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> O)C=W(CO) <sub>5</sub>	TiCl <sub>4</sub>	1:2:60	T, 10	50	2	25
13	MoCl <sub>5</sub>	none	1:200	neat	80	48	2
14	MoCl <sub>5</sub>	(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> Sn	1:2:60	T, 10	RT	18	75
15	MoCl <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> AlCl	1:2:60	T, 10	RT	18	74
16	MoCl <sub>5</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:70	C, 10	RT	3	70
17	MoCl <sub>5</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:200	C, 3	-20	48	20 <sup>f</sup>
18	MoCl <sub>5</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:200	C, 1	50	2 min	25 <sup>e,g</sup>
19	MoCl <sub>5</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:200	C, 1	-20	48	2 <sup>g,f</sup>
20	RuCl <sub>3</sub>	none	1:200	CE, 0.5	50	36	21
21	RuCl <sub>3</sub>	none	1:200	CE, 2	65	65	30
22	RuCl <sub>3</sub>	(CH <sub>3</sub> ) <sub>4</sub> Sn	1:2:200	CE, 1.5	40	2.5	74

<sup>a</sup> We were unable to polymerize **3** with OsCl<sub>3</sub>, ReCl<sub>5</sub> or ReCl<sub>5</sub>/(CH<sub>3</sub>)<sub>4</sub>Sn although the catalysts were active with norbornene

<sup>b</sup> T—toluene, C—chlorobenzene, CE—1:1 (vol for vol) mixture of chlorobenzene and ethanol

<sup>c</sup> RT—room temperature, 15°C ± 5°C. The polymerization was often noticeably exothermic; no monitor of temperature was placed in the vessel

<sup>d</sup> After reprecipitation and drying under vacuum for at least 24 h

<sup>e</sup> Polymerization quenched at low conversion to aid work up

<sup>f</sup> Insoluble

<sup>g</sup> Chain transfer agent, oct-4-ene, added to limit molecular weight

polymer; however there are some points emerging from the data in *Table 1* which merit comment before we consider the details of chain microstructure.

It is clear from Experiments 1, 2, 13 and 20 that the single component catalysts WCl<sub>6</sub>, MoCl<sub>5</sub> and RuCl<sub>3</sub> all polymerize monomer **3**; but the Fischer carbene (Experiment 10), which initiates the polymerization of norbornene<sup>15</sup>, was ineffective for the room temperature polymerization of **3** without an activator. Neither OsCl<sub>3</sub> nor ReCl<sub>5</sub> polymerized **3** in any of several attempts with or without an activator; this failure was not a consequence of the presence of fluorine substituents in the monomer because related trifluoromethyl substituted norbornenes can be polymerized by these catalysts (see Paper 3 in this series). It may be that some potential catalysts can be inhibited by **3**, which may possibly act as a bidentate ligand.

At one point we were concerned that there might be chemical reaction between our catalyst systems and the toluene used as solvent in many of the polymerizations; the components have Lewis acid character and toluene is susceptible to electrophilic attack. In all our recent work we have used only chlorobenzene in order to avoid complications of this kind. However, experiments 4 and 5, which differ only in the solvent used, gave polymers which were virtually identical in structure and amount; their infra-red and <sup>13</sup>C n.m.r. spectra were superimposable and there was no evidence for incorporation of benzyl residues in the polymers. The results of experiments 1 and 2 are consistent with the hypothesis that toluene may play a role in the generation of the active catalytic species when no activator is present.

Molybdenum based catalysts showed a greater capacity than either tungsten or ruthenium systems to regulate the vinylene stereochemistry in the polymeri-

zation of **3**; consequently we made a more detailed study of the polymerization of **3** initiated by MoCl<sub>5</sub>/(CH<sub>3</sub>)<sub>4</sub>Sn. This catalyst rapidly polymerizes **3** at or above room temperature to a high molecular weight material which dissolved only slowly; the introduction of oct-4-ene as a chain transfer agent (experiment 18) allowed us to obtain a more readily soluble sample for <sup>13</sup>C n.m.r. investigation. The objective of experiment 17 (*Table 1*) was to increase the catalyst selectivity by lowering the reaction temperature; the reagents were mixed at ca. -50°C, sealed under nitrogen, and maintained at -20°C; although reaction occurred under these conditions the product was insoluble. When oct-4-ene was included in this reaction (experiment 19) in an attempt to lower the product's molecular weight the only effect was a decreased yield; possibly, at the lower temperature, the oct-4-ene occupies active catalyst sites with degenerative metathesis rather than acting as a chain transfer agent. The products of these low temperature polymerizations have proved insoluble in any of a wide range of solvents, yet it seems unlikely that crosslinking will be prevalent in these reactions conducted at -20°C in the dark but not occur in the same system at 50°C under normal laboratory lighting. It is possible that this insolubility is a consequence of the polymer microstructure produced under the low temperature conditions; unfortunately it also inhibits the investigation of microstructure by <sup>13</sup>C n.m.r.

#### Microstructure

The structure of polymers of this type can be studied by infra-red and n.m.r. spectroscopy; high field solution phase <sup>13</sup>C n.m.r. has generally proved a particularly valuable analytical probe. The general considerations involved were indicated in the Introduction, in the specific

case of polymerization of **3** there are only four possible assembly modes, as indicated in Figure 2.

In an earlier publication we discussed the  $^{13}\text{C}$  n.m.r. spectrum of a sample of poly(3,5-(1,2-bis(trifluoromethyl)cyclopentylene)vinylene) produced as in experiment 3, and concluded that the polymer had the overall structure expected from ring opening polymerization at the unsubstituted double bond and had a 54:46 distribution of *cis* and *trans* vinylenes respectively ( $\sigma_c = 0.54$ ). Since the proportion of *cis* vinylenes ( $\sigma_c$ ) was

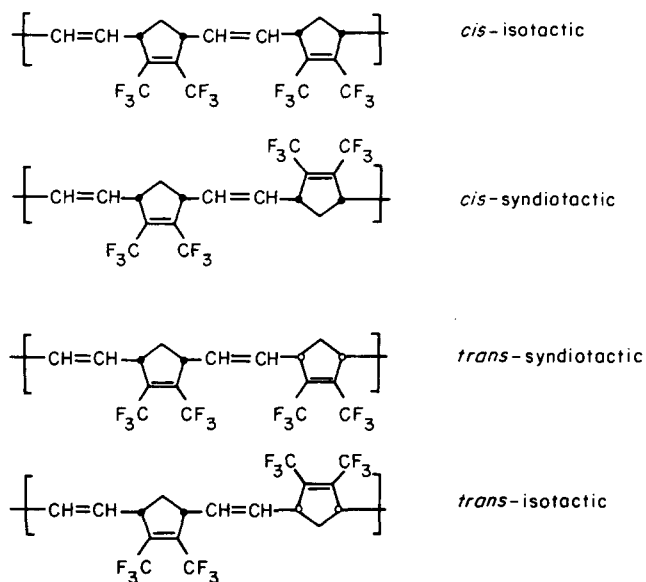


Figure 2 Possible assembly modes for poly(3,5-(1,2-bis(trifluoromethyl)cyclopentylene)vinylene); ●, C-H bond approaching; ○, C-H bond receding from the viewer

close to 0.5 there was some uncertainty concerning the reliability of the assigned line orders for the signals arising from vinyl, allylic and methylene carbons. To a large extent the assignments rested on analogies with earlier analyses of the spectra of poly(norbornene)s and poly(methyl-norbornene)s which had been worked out by Ivin and co-workers. In this extension of the work we have obtained polymers of **3** with a range of values of  $\sigma_c$  and as a consequence of these extra data we are able to make assignments on a more secure basis. The spectrum of a polymer of **3** produced using the catalyst  $\text{RuCl}_3/(\text{CH}_3)_4\text{Sn}$  is shown in Figure 3, which also illustrates the use of distortionless enhancement by polarization transfer (DEPT) in confirming the assignment of peaks<sup>16</sup>.

The lowest trace is the normal broad band decoupled spectrum, and is similar to that published previously (Polymer XII, Figure 1, ref. 10b), albeit with much improved signal-to-noise ratio and resolution; the middle trace shows only those carbons carrying a single hydrogen; and the upper trace shows carbons carrying a single hydrogen in the normal way, with those bearing two hydrogens inverted. Quaternary carbons do not appear in these DEPT spectra and methyl carbons (had they been present) would have appeared normally in the upper trace. The bands in this spectrum appear to be fairly symmetrical but also fairly broad. There is one interesting sign of fine structure in that the smaller of the two vinylic carbon signals appears to be split into a doublet. If the vinylic, allylic and methylene signals are assigned as shown in Figure 3, the computed values of  $\sigma_c$ , 0.36, 0.36 and 0.34, respectively, are internally consistent. In this assignment the line order for the allylic and methylene signals parallels that found in poly(norbornene) and poly(methyl norbornene)s although the line order for the

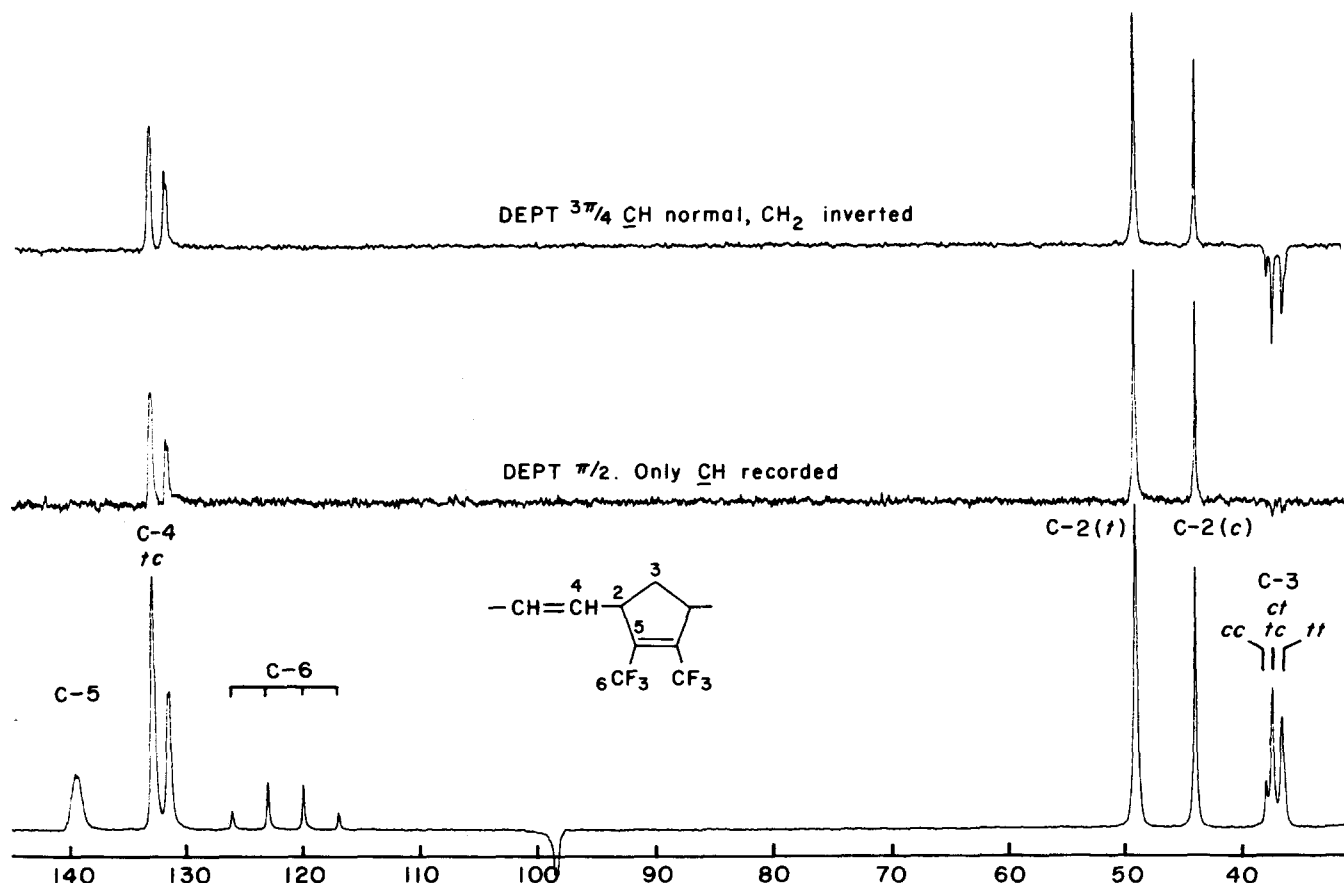


Figure 3  $^{13}\text{C}$  n.m.r. spectrum of polymer produced in experiment 22 (Table I) recorded as a solution in  $(\text{CD}_3)_2\text{CO}$  at 90.56 MHz

vinyl carbons, with C-4(c) about 1.5 ppm upfield of C-4(t), is the reverse of that found in poly(norbornene) and its derivatives. In the spectra of polymers formed by ring opening of monocyclic and bicyclic alkenes the signals from the allylic carbons adjacent to *cis* vinylenes are

always found *ca.* 5 ppm upfield from those due to carbons adjacent to *trans* vinylenes; the separation of *cis* and *trans* vinylene carbon resonances is smaller, *ca.* 0.4 to 1.5 ppm, and the observed line is variable; for example in polynorbornene *trans* vinylene carbons are found upfield

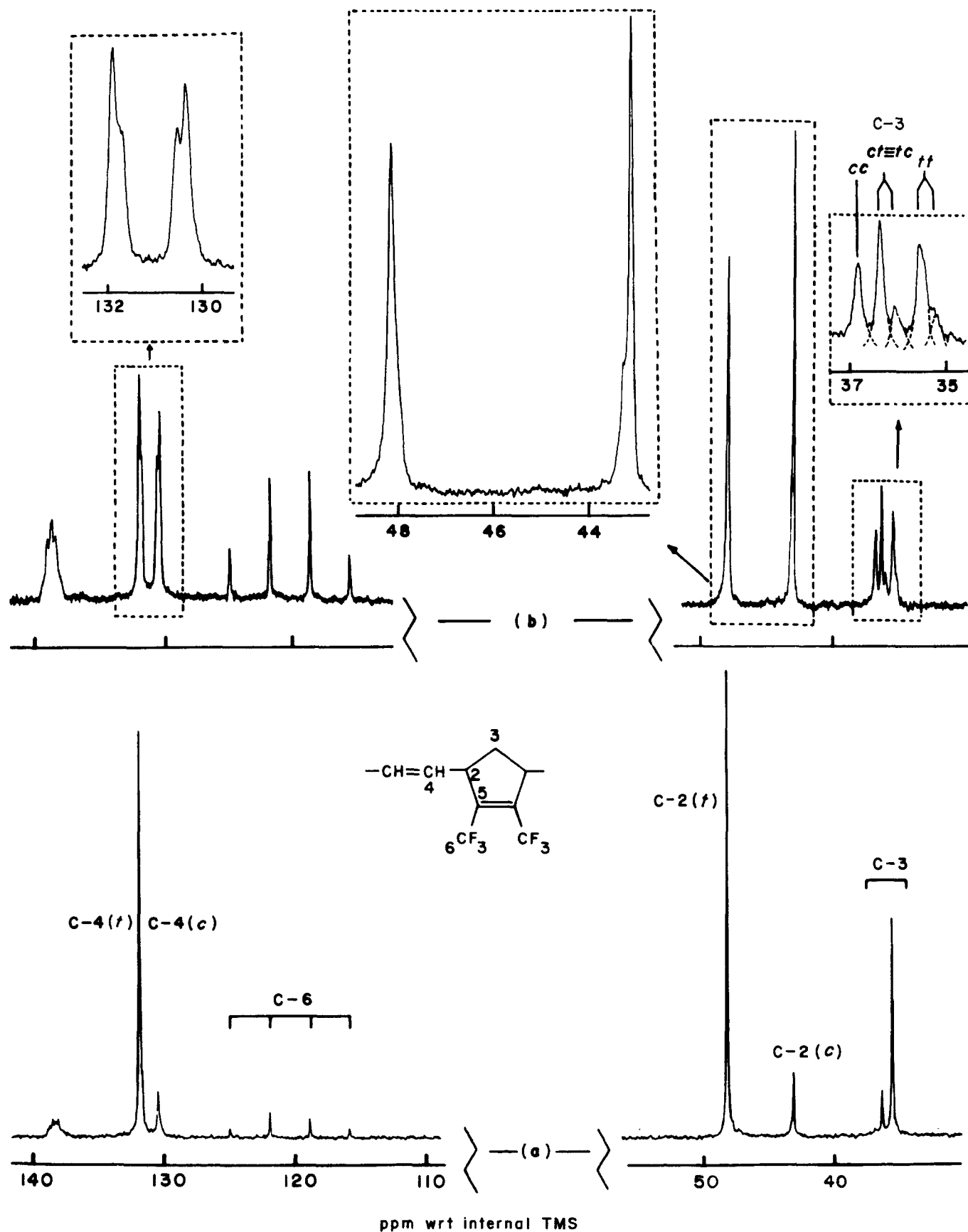


Figure 4  $^{13}\text{C}$  n.m.r. spectra of polymers produced in experiment 14 (Table I), (a), and experiment 4 (Table I), (b), recorded as solutions in  $(\text{CD}_3)_2\text{CO}$  at 90.56 MHz

with respect to their *cis* counterparts whereas in poly(1-pentenylene) the relative line order is reversed. Thus the assignments shown in *Figure 3* are internally consistent and in agreement with results reported previously. *Figure 4* records the spectra of polymers prepared from **3** using the catalyst systems  $\text{MoCl}_5/(\text{C}_6\text{H}_5)_4\text{Sn}$  (*Figure 4a*) and  $\text{WCl}_6/(\text{C}_6\text{H}_5)_4\text{Sn}$  (*Figure 4b*) at room temperature; the resolution in these spectra is somewhat better than that in *Figure 3*.

We have obtained high field  $^{13}\text{C}$  n.m.r. spectra on a variety of samples of poly(3,5-(1,2-bis-(trifluoromethyl)cyclopentenylene)vinylene) from three different spectroscopy laboratories with good agreement in observed chemical shifts and with spectral resolution somewhat better than that reported in our earlier work. The spectrum in *Figure 4b* displays the best resolution and the highest number of resolved signals with lines at: 138.3 (q,  $J = 25$  Hz, C-5); 131.8 and 131.1 (C-4t); 130.5 and 130.3 (C-4c); 120.4 (q,  $J = 270$  Hz C-6); 48.2 (C-2t); 43.1 and sh at 43.2 (C-2c); 36.9 (C-3cc); 36.4 and 36.1 (C-3ct  $\equiv$  C-3tc); 35.5 and 35.2 (C-3ti) for a spectrum recorded at 90.56 MHz in  $(\text{CD}_3)_2\text{CO}$  solution with TMS as internal reference. The multiplicities observed for vinyl, allyl and methylene signals must be a consequence of small differences in the environments of the particular nuclei. Thus, the four signals observed for the vinyl carbons could be due to *cis* and *trans* double bonds in meso and racemic dyads, or to *cis* and *trans* vinylic carbons with next nearest *cis* or *trans* neighbours; however, from these data it is not possible to decide whether these differences are a result of m/r-dyad effects or a consequence of vinylene sequence effects.

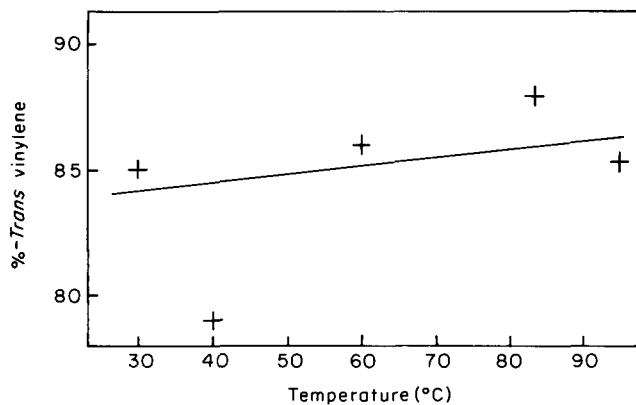
In *Table 2* illustrative values of  $\sigma_c$  computed from the vinylic, allylic and methylene carbon signals for eight samples are recorded.

It can be seen that catalysts based on tungsten gave polymers with values of  $\sigma_c \sim 0.5$  irrespective of the cocatalyst or solvent, those based on molybdenum gave polymers with  $\sigma_c \sim 0.1$ , and the ruthenium catalysts gave products with  $\sigma_c \sim 0.3$ . The tungsten derived catalysts also gave the most complex  $^{13}\text{C}$  n.m.r. spectra, the multiplicity of signals being consistent with a more or less random assembly of the various possible sub-units; such a result is reasonable for the reaction of an active non-discriminating catalyst with a readily polymerized monomer. Ruthenium catalysts generally give polymers with a high *trans* content; the results reported here are consistent with this trend. Molybdenum based catalysts have been reported to give polymers of norbornene varying from high-*cis* to high-*trans* vinylene content so that

the result reported here is unremarkable. It is clear from the above data that the most structurally regular polymer produced in this work is that derived from molybdenum based catalysts. It is also clear that the structural assignment rests heavily on analogy with earlier analyses of related systems. We have attempted to put the assignments on a firmer basis by studying the polymer structure as a function of polymerization temperature, and by careful analysis of the infra-red spectra of polymers with differing *cis/trans* vinylene contents.

Monomer **3** was polymerized with  $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$  in chlorobenzene at temperatures in the range  $20^\circ\text{C}$  to  $100^\circ\text{C}$ . As far as possible all experimental variables except the temperature were kept constant, the reaction vessel was submerged in a constant temperature bath and the polymerization temperature was measured in the chlorobenzene solution. However, because of the small scale of the experiments, the exothermicity of the reaction, and the difficulty of efficiently stirring a mixture whose viscosity changed rapidly during the reaction, it proved difficult to regulate the polymerization temperature with any real precision. *Figure 5* is a graph of % *trans* vinylene content as a function of polymerization temperature for the polymers produced in the experiments described above. The straight line drawn through the points represents a least squares fit to the data points. While it serves as a 'guide to the eye' there is no theoretical justification for assuming a linear relationship.

It is clear that the effect of temperature is not particularly marked in this system in the temperature range investigated. There is a slight trend towards an increase in *trans* content with increasing temperature,



**Figure 5** Graph of % *trans* vinylene content as a function of polymerization temperature for polymers of **3** derived from  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  initiation

**Table 2** Fraction of *cis* vinylenes ( $\sigma_c$ ) for samples of poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)vinylene)

Expt. No.	Catalyst	$\sigma_c$			Average
		From vinylene carbon signals	From allylic carbon signals	From methylene carbon signals	
4	$\text{WCl}_6/(\text{C}_6\text{H}_5)_4\text{Sn}$	0.47	0.48	0.44	0.46
7	$\text{WCl}_6/(\text{CH}_3)_4\text{Sn}$	0.47	0.47	0.45	0.46
12	$\text{C}_6\text{H}_5(\text{CH}_3\text{O})\text{C}=\text{W}(\text{CO})_5/\text{TiCl}_4$	0.54	0.51	0.49	0.51
14	$\text{MoCl}_5/(\text{C}_6\text{H}_5)_4\text{Sn}$	0.15	0.12	0.13	0.13
15	$\text{MoCl}_5/(\text{CH}_3)_2\text{AlCl}$	0.12	0.10	0.09	0.10
16	$\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$	0.15	0.15	0.10	0.13
20	$\text{RuCl}_3$	0.29	0.29	0.26	0.28
22	$\text{RuCl}_3/(\text{CH}_3)_4\text{Sn}$	0.36	0.36	0.34	0.35

which is consistent with reasonable expectation and marginally increases confidence in the earlier assignments. Lowering the reaction temperature increases the *cis* vinylene content of the polymer; at polymerization temperatures only a little below room temperature the polymer becomes insoluble (see Table 1 and earlier discussion). If the trend followed in Figure 5 is continued the onset of insolubility must occur at a fairly low *cis* content; a convincing rationalization of this observation is not immediately obvious.

We have carefully compared the infra-red spectra of thin films of polymers from experiments 7 and 16 (Tables 1 and 2). There are three regions of the spectra from which information concerning *cis/trans* vinylene content might be expected to be deduced; namely, the C–H stretching region above  $3000\text{ cm}^{-1}$  where the *trans* absorption occurs at a higher frequency than the *cis*, the  $>\text{C}=\text{C}<$  stretching region around  $1660\text{ cm}^{-1}$ , and the C–H out-of-plane bending region around  $965\text{ cm}^{-1}$  (*trans*) and  $700\text{ cm}^{-1}$  (*cis*)<sup>17</sup>. The spectra were recorded using a Nicolet 60SX Interferometer and are reproduced in Figures 6, 7 and 8.

Figure 6 shows the C–H stretching region. It is clear that in the molybdenum derived sample the band at  $3043\text{ cm}^{-1}$  (*trans*) is more intense than that at  $3022\text{ cm}^{-1}$  (*cis*), which is in good agreement with the assignment based on <sup>13</sup>C n.m.r. Figure 7 shows the  $>\text{C}=\text{C}<$  stretching region. This is dominated by the strong  $-(\text{CF}_3)\text{C}=\text{C}(\text{CF}_3)-$  band at  $1682\text{ cm}^{-1}$ ; the shoulder at  $1660\text{ cm}^{-1}$  on the major peak is probably the  $-\text{CH}=\text{CH}-$  stretching absorption and appears strongest in the molybdenum derived polymer. It would be hazardous to attach much weight to these data but, since this mode should be strongest for the *cis* vinylene, this evidence tends to contradict the earlier assignment. Figure 8 shows the region containing the vinylene C–H out-of-plane bending modes; as in the  $>\text{C}=\text{C}<$  stretching region the picture is complicated since there are clearly two overlapping bands in the *trans* ( $986$  and  $970\text{ cm}^{-1}$ ) and *cis* ( $730$  and  $718\text{ cm}^{-1}$ ) regions. It may be that in both cases both the bands are out-of-plane bending modes for vinylenes in meso and racemic dyads, in which case the Mo-derived polymer contains relatively more *trans* vinylenes than the W-derived product. If only one each of these pairs of bands arises from C–H out-of-plane

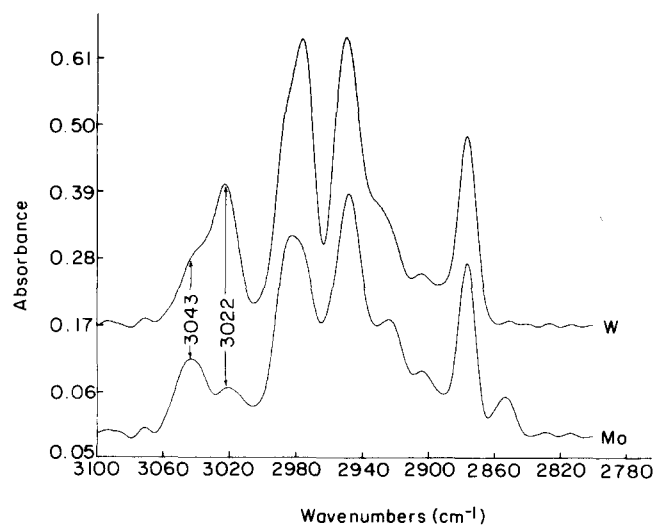


Figure 6 C–H stretching region in the infra-red spectra of polymers of 3 prepared using  $\text{WCl}_6/\text{Me}_4\text{Sn}$  (W) and  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  (Mo)

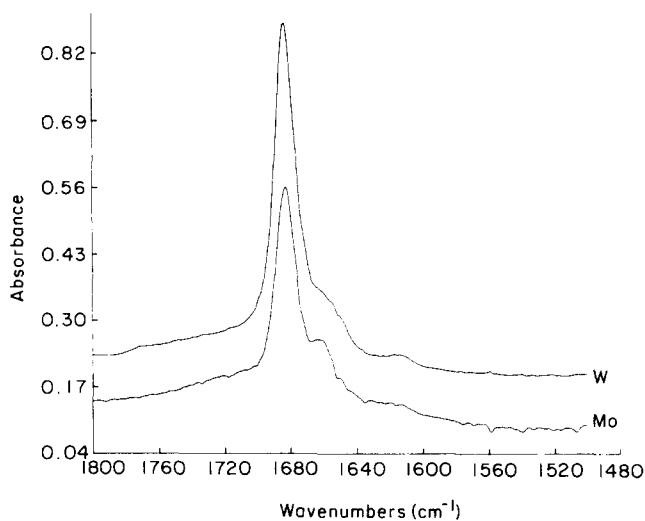


Figure 7  $>\text{C}=\text{C}<$  stretching region in the infra-red spectra of polymers of 3 prepared using  $\text{WCl}_6/\text{Me}_4\text{Sn}$  (W) and  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  (Mo)

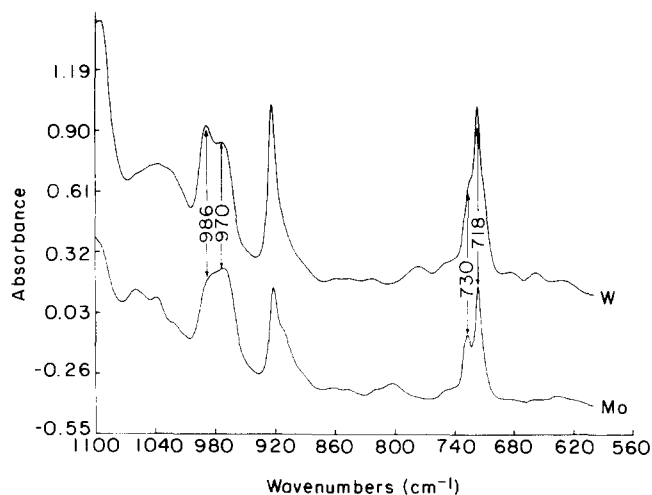


Figure 8 C–H out-of-plane bending region in the infra-red spectra of polymers of 3 prepared using  $\text{WCl}_6/\text{Me}_4\text{Sn}$  (W) and  $\text{MoCl}_5/\text{Me}_4\text{Sn}$  (Mo)

bending, assignment of the band at  $970\text{ cm}^{-1}$  to *trans* and that at  $730\text{ cm}^{-1}$  to *cis* units is also consistent with the Mo-derived polymer having a high *trans* vinylene content. Thus, the overall conclusion from an analysis of the infra-red spectra is consistent with the assignments made on the basis of <sup>13</sup>C n.m.r.

## CONCLUSIONS

2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene, 3, undergoes ring opening polymerization at the unsubstituted double bond to give polymers in which the proportion of *cis* vinylenes depends on the catalyst used; tungsten based catalysts gave  $\sigma_c \sim 0.5$ , ruthenium based catalysts gave  $\sigma_c \sim 0.3$ , and molybdenum based catalysts gave  $\sigma_c \sim 0.1$  at room temperature. It was not possible on the basis of data available to decide whether the simplicity of the <sup>13</sup>C n.m.r. spectra of polymers with a high *trans* vinylene content was a consequence of stereoregularity or simply the vinylene sequence effect.

## ACKNOWLEDGEMENTS

We thank the National University of Malaysia and the Malaysian Government (A.B.A.), SERC (B.W.), and the

European Research Office of the US Army (P.M.B.) for maintenance grants. We are indebted to three laboratories for n.m.r. data; some  $^{13}\text{C}$  n.m.r. spectra were provided by Professor K. J. Ivin (The Queen's University of Belfast) and some by Dr F. Heatley (Manchester University), but the majority were provided by Dr I. H. Sadler (Edinburgh University) through SERC's High Field NMR Service. We also thank Mr P. J. Lux for recording the infra-red spectra.

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