

Stereoregular fluoropolymers: 3. The ring opening polymerization of endo- and exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene

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(Received 16 September 1985; revised 11 February 1986)

An analysis of the high field ^{13}C n.m.r. spectra of the products leads to the conclusions that the ring opening polymerizations of exo-5-trifluoromethylbicyclo[2.2.1]hept-2-ene with OsCl_3 and of the endo-isomer with OsCl_3 and $\text{MoCl}_5/\text{Me}_4\text{Sn}$ catalysts all give atactic polymers with a high *trans* vinylene content; whereas the polymerization of the endo-isomer with ReCl_5 gives a polymer with 92% *cis* vinylenes which are probably assembled in a stereoregular manner.

(Keywords: fluoropolymer; ring opening; polymerization; trifluoromethylbicyclo[2.2.1]hept-2-ene)

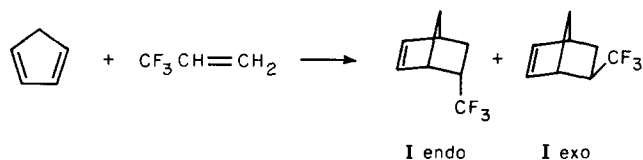
INTRODUCTION

The background and objectives of this study were set out in the first paper of the series¹. A significant part of the present understanding of stereoregulation in metathesis ring opening polymerization was obtained from detailed studies of the ^{13}C n.m.r. spectra of polymers of methyl substituted norbornenes². 5-Trifluoromethylnorbornenes are readily accessible and in this paper we report a study of the ^{13}C n.m.r. spectra of some of their polymers prepared using OsCl_3 , ReCl_5 and $\text{MoCl}_5/(\text{CH}_3)_4\text{Sn}$ catalysts.

EXPERIMENTAL

Monomers

The Diels–Alder reaction between cyclopentadiene and 3,3,3-trifluoropropene³ gave **I** as a mixture of exo and endo isomers as the major product, together with small amounts of diene dimer and polyadducts. The 1:1 adducts were easily recovered by distillation.



The ^{19}F n.m.r. spectrum of the mixture of isomers of **I** consists of two signals at 68.0 ppm (doublet $^3J_{\text{H-F}} = 15$ Hz) and at 66.1 ppm (doublet $^3J_{\text{H-F}} = 15$ Hz) [shifts are upfield from CFCl_3 as external reference] assigned to the exo and endo isomers respectively. This assignment follows that given by Gaede and Balthazor, which was based on a detailed analysis of the high resolution ^1H and ^{19}F spectra⁴. However, in previous analyses of the ^{19}F spectra of fluorinated monomers in this group we have used the generalizations of Stone^{5,6}, who asserted that fluorine atoms or trifluoromethyl groups in exo positions in norbornene derivatives occur at lower field than those in endo positions. We found Gaede and Balthazor's analysis

of this particular system more convincing and accordingly reversed our earlier assignments. We have performed the cycloaddition under various conditions (Table 1), and found that the proportion of the isomer corresponding to the ^{19}F resonance at 68.0 ppm increases relative to that giving the signal at 66.1 ppm both with increasing reaction duration and operating temperature. Generally in Diels–Alder reactions the endo adduct is produced under conditions of kinetic control whereas the exo adduct is favoured at equilibrium; this observation is therefore consistent with the assignment of the isomer displaying a ^{19}F resonance at 68.0 ppm to the exo form, and the signal at 66.1 ppm to the endo form. While the current picture is self-consistent, chemical proof remains desirable, since fluorine substitution often results in anomalous chemistry.

Separation of the exo and endo isomers by fractional distillation was attempted using a Fischer Spaltrohr system 0200/01 concentric tube column (90 plates and very low hold up); however, although there was an enrichment, total separation of isomers was not achieved. It was found that the isomers could be separated by preparative scale gas chromatography (10% DNP on Celite[®] 100°C).

Polymerizations

Techniques, solvents and reagents were as previously described¹. The results of polymerizations of **I** are summarized in Table 2. The product polymers were all soluble and were purified by successive reprecipitation from acetone into methanol, and dried under vacuum for

Table 1 Variation in the relative value of the ^{19}F n.m.r. integrations for monomer (**I**) as a function of reaction conditions

Temperature (°C)	Reaction time (days)	^{19}F n.m.r. integration		Yield (%)
		68.0 ppm	66.1 ppm	
20	3	10.6	100	3
160	3	37.0	100	72
200	7	55.5	100	75

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Table 2 Polymerization of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene

Expt.	Monomer	Catalyst	Cocatalyst	Molar ratio cat:cocat:monomer	Solvent ^a (cm ³)	Temperature (°C)	Time (h)	Yield (%)
A	Exo	OsCl ₃	None	1:200	CE, 0.3	40	12	38
B	Endo	OsCl ₃	None	1:200	CE, 0.2	40	5	30
C	Endo	MoCl ₅	Me ₄ Sn	1:2:200	C, 0.2	RT ^b	2 min	65
D	Endo	ReCl ₅	None	1:200	CE, 0.25	40	2	10

^aC—chlorobenzene, CE—1:1 mixture (vol. for vol.) of ethanol and chlorobenzene

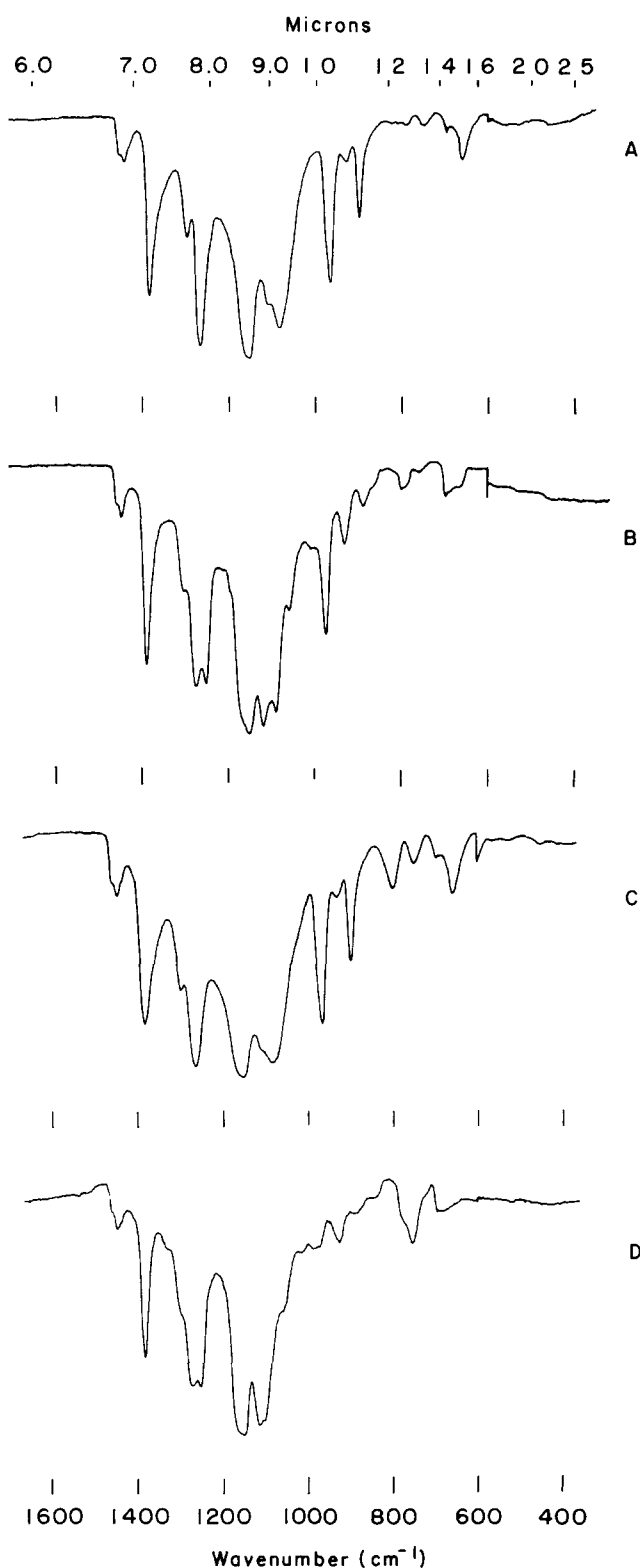
^bRT—room temperature, 15°C ± 5°C

Figure 1 Infra-red spectra of thin films of polymers A, B, C and D (Table 2)

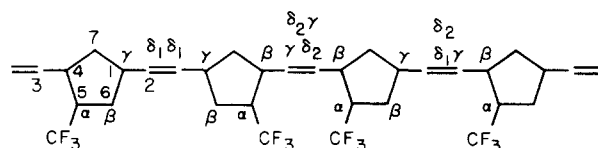
Table 3 Elemental analyses

	Polymer	Analysis		
		C	H	F
Found	A	59.7	5.1	
	B	59.1	5.2	
	C	58.9	5.9	35.1
	D	58.4	5.0	34.8
Calculated	A, B, C, D	59.3	5.6	35.2

24 h. They gave viscous solutions in acetone from which transparent films were cast for infra-red spectroscopic examination (see *Figure 1*). The elemental analysis results for the polymers examined are recorded in *Table 3*.

RESULTS AND DISCUSSION

Of the polymers obtained so far from 5-trifluoromethylbicyclo[2.2.1]hept-2-enes, that given by osmium-catalysed polymerization of the exo isomer gave the simplest spectrum, which is considered first. The spectrum and assignments are shown in *Figure 2*, and chemical shifts are recorded in *Table 4*. The resonance due to the carbon of the trifluoromethyl group is easily distinguished as a quartet at 129.0 ppm ($^1J_{C-F} = 277$ Hz). The remaining four signals at low field are assigned to the vinyl carbons C-2 and C-3, corresponding to TH, TT, HH and HT environments (T-Tail, H-Head with H being the CF₃ end of the repeat unit). These signals are approximately equal in intensity, which is consistent with an equal distribution of the HH, HT, TT and TH assembly modes. If α , β , γ and δ substituent shift effects for the CF₃ group are considered it can be shown that the chemical shift difference between the TH and TT signals ($\delta_1 + \delta_2 - \delta_1$, i.e. δ_2) is the same as the HH/HT splitting ($\gamma + \delta_2 - \gamma$, i.e. δ_2); δ_1 substituent effects are transmitted via single bonds and δ_2 via double bonds.



Assembly mode	TT	HH	TH	HT
Carbon number	C-2	C-3	C-2	C-3
Substituent shift effect	δ_1	$\gamma + \delta_2$	$\delta_1 + \delta_2$	γ

The magnitude and sign of the substituent shift effect is clearly of importance to a reliable interpretation of the spectral fine structure. In Ivin's pioneering work in this area using methyl substituents these shift effects are particularly well documented²; however, an analogous

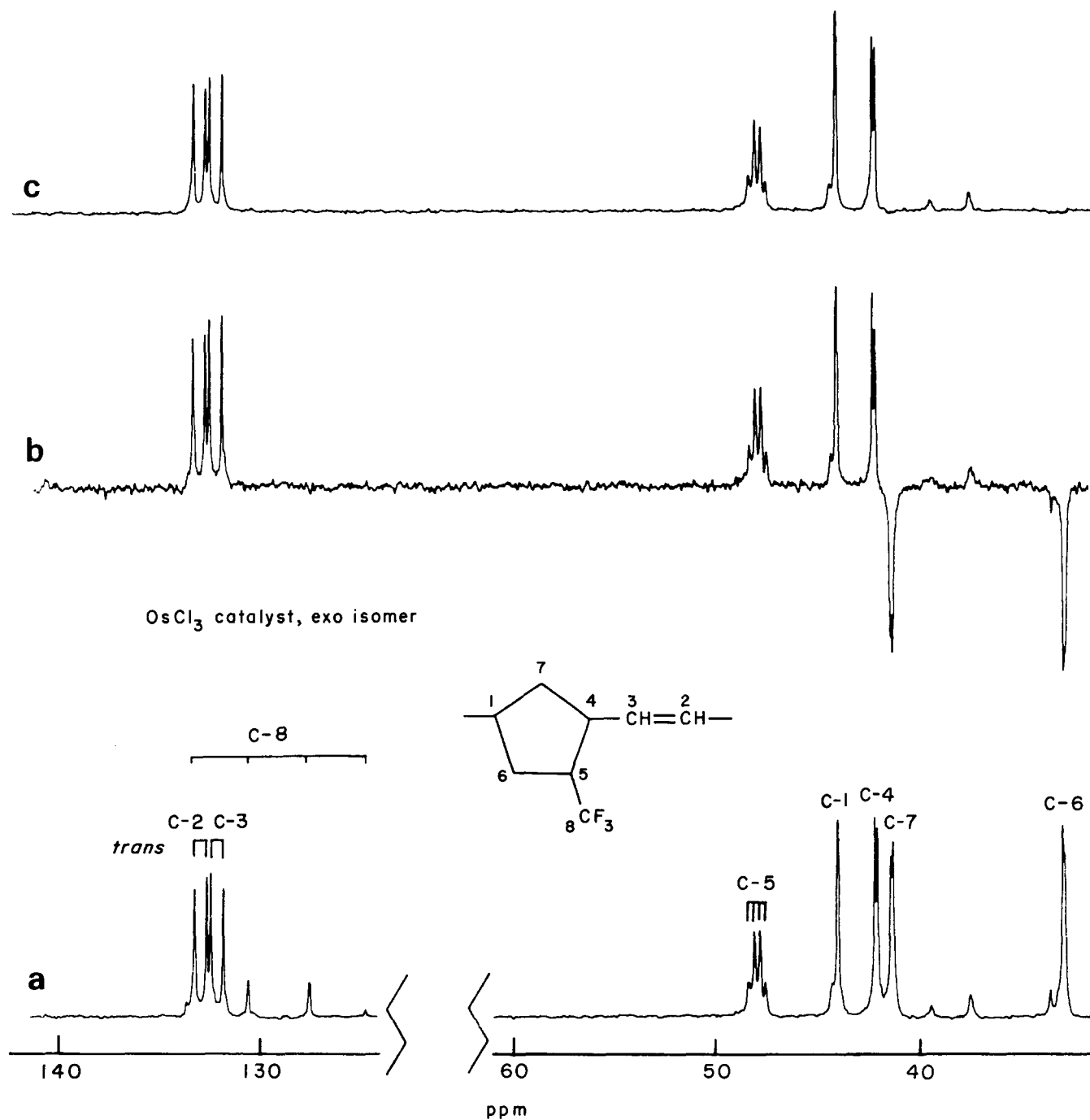
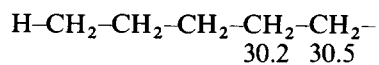
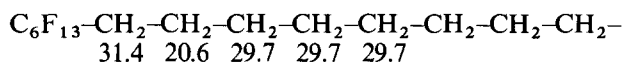
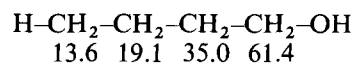
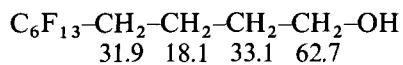


Figure 2 ¹³C n.m.r. spectrum of poly(exo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by OsCl₃ initiation, recorded as a solution in (CD₃)₂CO at 90.56 MHz with TMS internal reference. (a) The complete spectrum, (b) DEPT spectrum showing $\underline{\text{CH}}$ normally and $\underline{\text{CH}_2}$ inverted (c) DEPT spectrum showing only $\underline{\text{CH}}$ carbons

documentation for CF₃-substituents does not appear to be available. The effects of fluorine substitution are often large and rarely easily predicted. So far we have found only two relevant sets of data^{7,8}:



	α	β	γ	δ	ϵ
Δ	+17.0	-3	-3	-0.5	-0.8



	α	β	γ	δ
Δ	+18.3	-1	-2	+1.3

These admittedly rather limited data lead to a prediction of a large downfield shift for resonances of carbons α to a CF₃, a small upfield shift for β and γ carbon resonances, and a small unpredictable δ effect. Considering

Table 4 ^{13}C n.m.r. shifts of polymers of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene

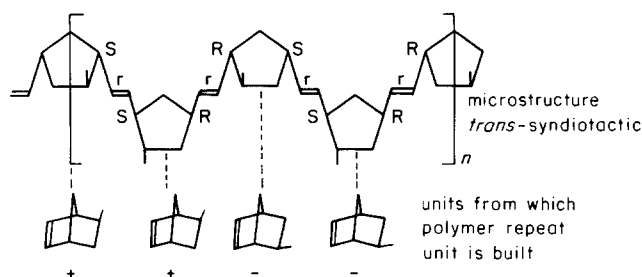
Shift (ppm)				
Endo, OsCl_3	Endo, MoCl_5	Endo, ReCl_5	Exo, OsCl_3	Assignment
134.01	133.62		133.29	C-2, <i>t</i> , TH
133.59	133.09	133.95		C-2, <i>c</i> , TH
133.13		133.63		C-2, <i>c</i> , TT
132.73	132.26	132.68	132.69	C-2, <i>t</i> , TT
130.43	130.00	130.43	132.48	C-3, <i>t</i> , HH
130.20	129.70			C-3, <i>t</i> , HH
129.62	129.06	129.91		C-3, <i>c</i> , HH
129.52	129.06	129.52		C-3, <i>c</i> , HT
129.19	128.66	129.17	131.86	C-3, <i>t</i> , HT
128.5 (q)	127.71 (q)	128.28 (q)	129.09 (q)	C-8
$^1J_{\text{C-F}} = 281 \text{ Hz}$	$^1J_{\text{C-F}} = 279 \text{ Hz}$	$^1J_{\text{C-F}} = 277 \text{ Hz}$	$^1J_{\text{C-F}} = 277 \text{ Hz}$	
~ 46 (m)	~ 46 (m)	46.6 (m)	47.9 (q) $^2J_{\text{C-F}} = 25.4 \text{ Hz}$	C-5
43.50	43.38	43.37	43.94	C-1, <i>t</i>
43.39	43.28			C-1, <i>t</i>
41.96	41.75	41.82		C-7, <i>c</i>
		41.47		C-7, <i>c</i>
		41.06		C-7, <i>c</i>
41.70	41.53		42.14	C-4, <i>t</i>
			42.01	C-4, <i>t</i>
40.21			41.46	C-7, <i>t</i>
40.06			41.27	C-7, <i>t</i>
		38.00		
37.81	37.03	37.63		C-1/4c
		37.36		
		37.05		
34.06	33.77	34.09	32.89	C-6, <i>c</i>
33.76	33.43	33.42	32.80	C-6, <i>c</i>

specifically the vinylic carbons C-2 and C-3 we come to the conclusion that the shifts will be in the order C-2, TH; C-2, TT; C-3, HH; C-4, HT which fortunately is the same order as derived by Ivin for the methyl substituted cases and makes qualitative comparison of spectra possible. This coincidence of shift patterns is remarkable when the usual differences in electronic effect associated with CF_3 - and CH_3 - groups are taken into account. The TH/TT shift difference in this case is 0.6 ppm and the HH/HT resonances is consistent with an assignment of the polymer as all *trans* or all *cis*, since the presence of *cis/trans* isomers would double the number of resonances. However, infra-red spectroscopy (Figure 1A) allows an unambiguous assignment as all-*trans*. The C-H out of plane deformations for *cis* and *trans* double bonds occur at *ca.* 730 and *ca.* 970 cm^{-1} respectively; these can be useful provided that there are no interfering bonds in this region. In the i.r. spectrum of this polymer there is a strong signal at 970 cm^{-1} and a vanishingly weak signal at 730 cm^{-1} , confirming the all-*trans* assignment.

The methylene and methine signals were distinguished with the aid of a DEPT spectrum. In order to assign these carbons it is necessary to consider their position relative to the trifluoromethyl group (see above). The signal for C-5, adjacent to the trifluoromethyl group, is easily identified by its multiplicity, a consequence of its coupling to the CF_3 group (quartet $^2J_{\text{C-F}} = 25.4 \text{ Hz}$). Signals due to C-1 and C-4 are assigned as shown on the basis of an expected upfield β -shift for C-4. Similarly the methylene carbons, C-6 and C-7, are assigned as shown by analogy with the spectra of polynorbornene⁹ and the expected small upfield β shift of C-6.

Each of these carbon resonances (except C-1), appears as two signals. This splitting is attributed to head-tail effects. The splitting of the C-1 resonance is probably too

small to resolve; the line is certainly somewhat broadened. The intensity of each signal in each pair is approximately equal, confirming that the number of HH, HT, TH and TT junctions is equal. The conclusion of this analysis is therefore that we have a polymer with an all-*trans* structure and an equal distribution of TH, TT, HH and HT assembly modes. The remaining question relates to the distribution of *m* and *r* dyads, and this cannot be unambiguously defined on the basis of the evidence presented above. It is possible to write a stereoregular microstructure satisfying the data available, for example:



In this stereoregular structure, i.e. all-*trans*-syndiotactic we have equal concentrations of enantiomers of exo-I incorporated and equal numbers of TH, TT, HH and HT assembly modes; but this requires an enantiomer selection by the catalyst in the sequence $++--$, which seems a little far fetched, although not impossible. We believe it more likely that this polymer is all-*trans* and atactic and that *m* and *r* dyad signals are unresolved.

The spectra of the polymers obtained from the endo isomer are rather more complicated. However, it is clear from comparison of the spectra and chemical shifts (see Table 4), that OsCl_3 (Figure 3) and MoCl_5 (Figure 4) give polymers with very similar microstructures, which are very different from the microstructure obtained from

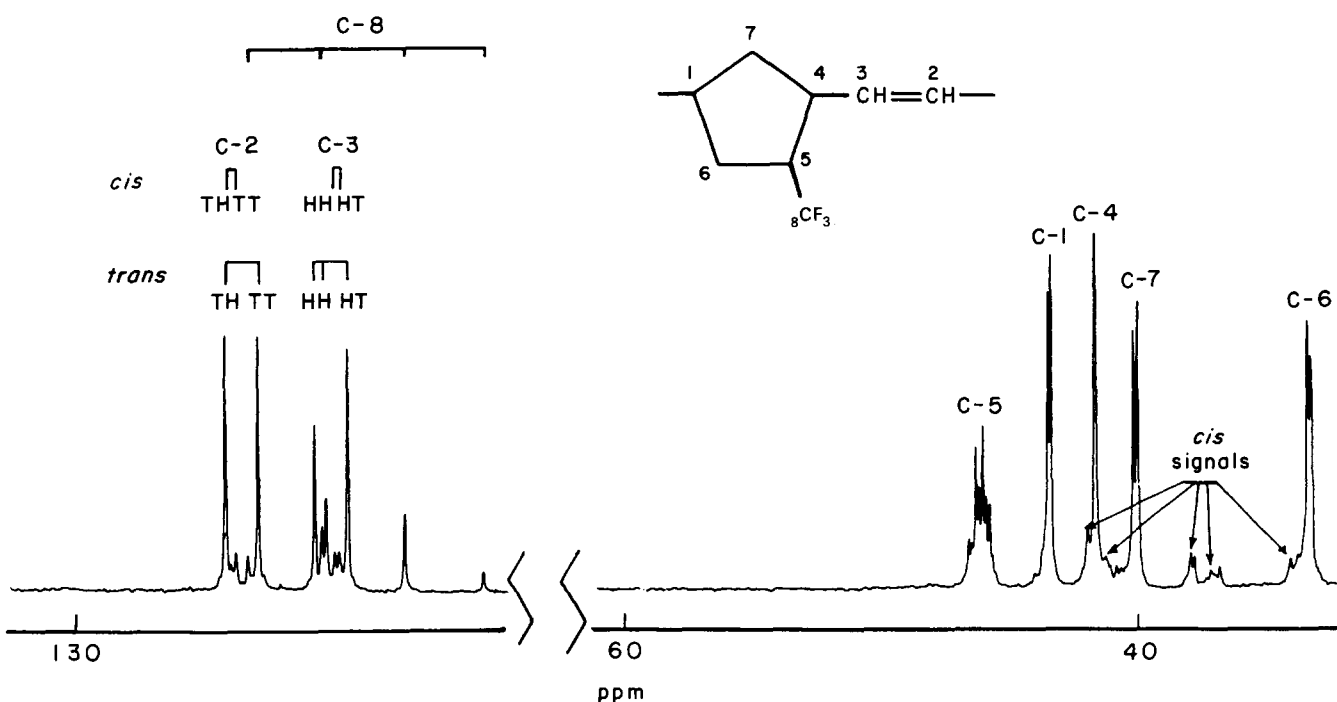
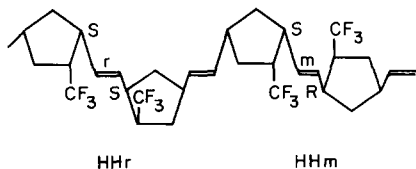
OsCl₃ catalyst, endo isomer


Figure 3 ¹³C n.m.r. spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by OsCl₃ initiation as a solution in (CD₃)₂CO at 90.56 MHz with TMS as internal reference

ReCl₅ (Figure 5) catalysis. The polymer obtained from OsCl₃-catalysed polymerization is the best resolved of this set and is considered first. As for the polymer made from exo monomer, the resonance for the carbon of the CF₃ group is easily identified as a quartet (¹J_{C-F} = 281 Hz). The olefinic resonances consist of four signals assigned to the *trans* TH, TT, HH and HT; the basis of the assignment is analogous to that used in the case discussed earlier although, as expected, the magnitude of the substituent shift effects is different. The *trans* assignment receives strong support from the infra-red spectrum of this polymer (Figure 1B), where a strong band is seen at 975 cm⁻¹ (*trans* olefinic CH bending) and there is virtually no absorption at 730 cm⁻¹ corresponding to *cis* olefinic CH bending. The HH signal is also resolved into two peaks, assigned to *m* and *r* dyads. The splitting can be attributed to the HH assembly modes shown below which differ only in the orientation of the cyclopentane ring. For HT and TT dyads the *m/r* splitting of olefinic carbon resonances is too small to observe as a result of the insignificant difference in environment between the two



forms. However, in the HHr dyad, the CF₃ substituents are forced into close proximity whereas in the HHm dyad they are reasonably well separated spatially. This must create a large enough difference in environment between the olefinic carbons in the two forms to allow their chemical shifts to be resolved. No such splitting was

observed in the polymer derived from exo monomer and OsCl₃ catalysis, so that it is evident that the stereochemistry of the substituent is important. This is reasonable since for the polymer derived from the exo-isomer the CF₃ and vinylenic units are *trans* on the cyclopentane, minimising strain, whereas for polymers derived from the endo-isomer they are *cis*. The TH/TT chemical shift difference for C-2 is 1.31 ppm, and the HH/HT splitting for C-3 is 1.1 ppm. These signals have slightly different intensities indicating that while the polymer is essentially atactic there may be a small measure of stereoselection; the earlier discussion and consideration of structural formulae would lead to the expectation of a predominance of the less strained HHm dyads but the effect, if real, is very small. Since this endo-isomer of II with OsCl₃ gives a high *trans* atactic polymer, it seems likely that the analogous polymer from the exo-isomer (see above) is also atactic. A set of four relatively weak signals also appear at low field and are assigned to carbons associated with *cis* double bonds. If the polymer is high *trans*, then the *cis* and *trans* double bonds may have a random or blocky distribution. If the former is the case then the *cis* (*c*) peaks we observe are in fact *ct* peaks, which should have a slightly different chemical shift from the *cc* peaks. If there is a blocky distribution, then the weak peaks we observe should superimpose exactly on the *cis* signals for a high *cis* polymer. In this case the weak *cis* signals seem to be slightly offset from the pure *cis* signals, indicating that they are in fact *ct* peaks, and that there is a random distribution of the small proportion of *cis* double bonds. This assignment is only tentative, and must be treated with caution since the small shifts involved could be a result of solvent or concentration effects. The σ_c value calculated from the olefinic carbons is 0.13, but this figure

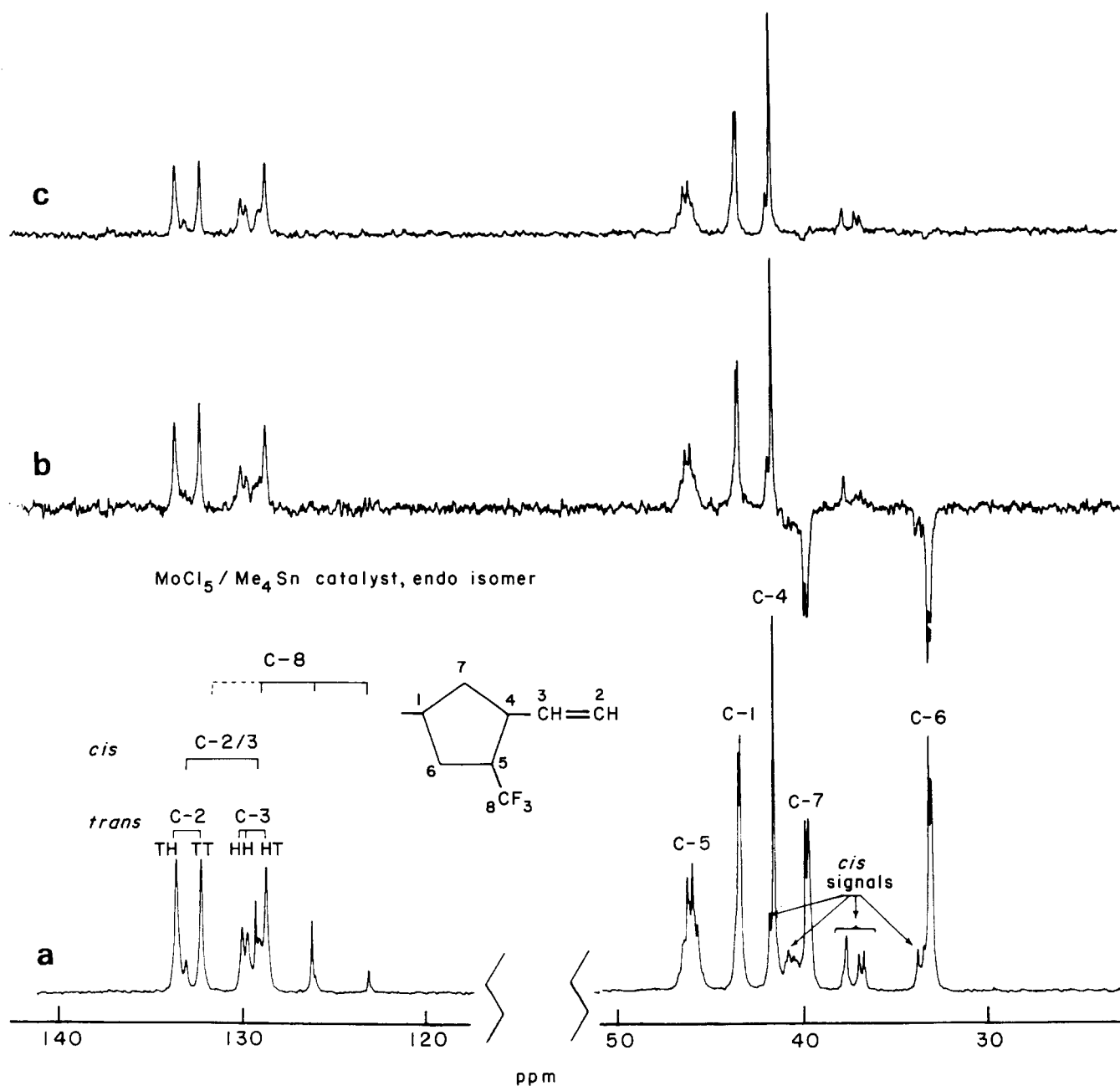


Figure 4 ^{13}C n.m.r. spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by MoCl₅/Me₄Sn initiation, recorded as a solution in CDCl₃ at 90.56 MHz with TMS as internal reference. (a) The complete spectrum, (b) DEPT spectrum showing $\underline{\text{C}}\text{H}$ normally and $\underline{\text{C}}\text{H}_2$ inverted and (c) DEPT spectrum showing only $\underline{\text{C}}\text{H}$ carbons

also has to be treated with caution as the resolution is not particularly good and consequently the integration not very reliable. Infra-red spectroscopy would suggest an even lower σ_c . The high field signals are assigned by analogy with earlier argument, as shown in Figure 3. The fine structure observed for the signals is a result of either head/tail effects and/or the atactic nature of the polymer. The low intensity signals correspond to the high intensity signals in the spectrum of a high *cis* polymer, and are therefore a result of carbons associated with *cis* double bonds. Hence we can conclude that OsCl₃ gives rise to a high *trans* atactic polymer.

The spectrum obtained from MoCl₅ catalysed polymerization of endo-I (Figure 4) is very similar to that of the polymer produced by OsCl₃ catalysis except that the weak peaks have increased in intensity and the resolution is not quite as good. A lack of exact

superimposability of the two spectra may be a consequence of the use of different solvents to record the spectra.

At low field the *trans* HH peak is again resolved into *m* and *r* forms. The *trans* TH/TT shift difference is 1.35 ppm, and the HH/HT difference is 1.2 ppm, consistent with values obtained from the high *trans* polymer obtained from OsCl₃. The relative intensity of the TH, TT, HH and HT peaks indicates that the polymer has an equal distribution of these assembly modes. The weak peaks at low field are assigned to carbons associated with *cis* double bonds. The peaks are not well resolved, and the *cis* TH peak is not observed or is hidden by a strong broadened *trans* peak. The σ_c value calculated from the computer printout for these signals is 0.12, which is lower than for the OsCl₃ polymer from endo-I and inspection of Figures 3 and 4 and the infra-red spectra, Figure 1B and C,

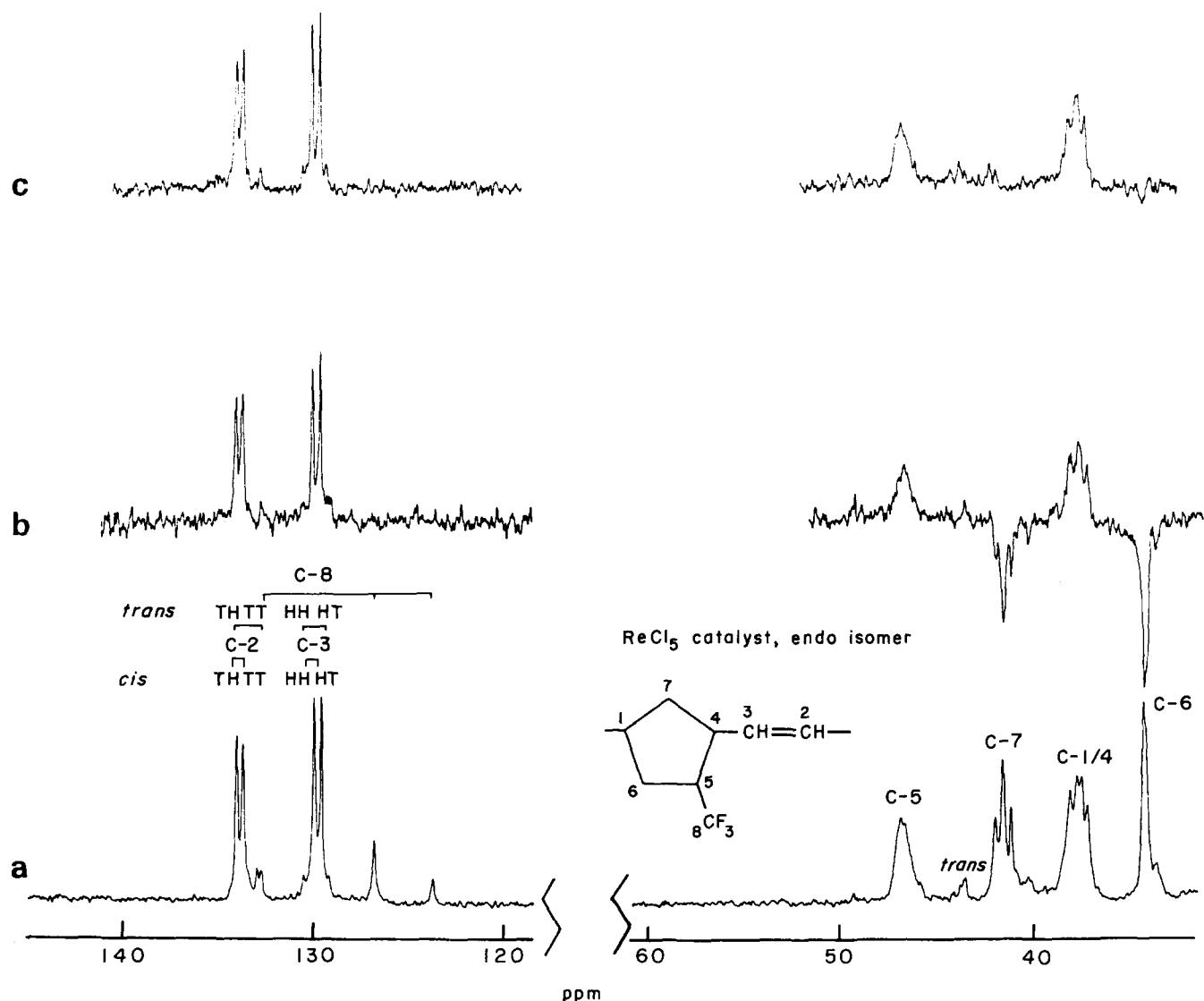


Figure 5 ^{13}C n.m.r. spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by ReCl_5 initiation, recorded as a solution in $(\text{CD}_3)_2\text{CO}$ at 90.56 MHz with TMS as internal reference. (a) The complete spectrum, (b) DEPT spectrum showing $\underline{\text{C}}\text{H}$ normally and $\underline{\text{C}}\text{H}_2$ inverted and (c) DEPT spectrum showing only $\underline{\text{C}}\text{H}$ carbons

leads to the conclusion that this must be an underestimate or the earlier value an overestimate. The high field signals are assigned as for the high *trans* polymer, made via OsCl_3 catalysis, and are consistent with an atactic polymer. Hence we can conclude that MoCl_5 gives rise to a high *trans* polymer.

The spectrum and assignments for the polymer obtained from ReCl_5 catalysis are shown in Figure 5, with chemical shifts recorded in Table 4. The high intensity signals at low field correspond to the weak signals in the high *trans* polymer, and hence it is clear that we have a high *cis* polymer. The peaks are assigned to the TH, TT, HH and HT environments. Normally the TH and HT signals must have the same intensity; this is also true for the HH and HT peaks. In this case, however, one of the central limbs of the CF_3 group overlaps with the *cis* HH and HT resonances, making these signals correspondingly more intense. Taking this into account the TH, TT, HH and HT signals have approximately the same intensity, indicating that the polymer has an equal distribution of these assembly modes. In the two high *trans* polymers derived from the endo monomer m/r environments were both present as evidenced by the splitting of the olefinic carbon in HH assembly modes; in

this example we see no such splitting and this leads to the conclusion that this polymer has an all meso- or all racemic dyad assembly, although which particular form cannot be distinguished on the basis of the available data. The weak signals at low field correspond to the *trans* olefinic signals. The σ_c value calculated from these signals is 0.92. At low field the spectrum is very different from that of a high *trans* polymer. The C-5 signal still appears at lowest field but is poorly resolved in this spectrum. The C-1 and C-4 signals are identified with the aid of a DEPT spectrum. These signals overlap, and the fine structure observed cannot be satisfactorily deconvoluted. The C-6 resonance appears as a broad singlet at highest field; the broadening is probably a result of HT/HH effects. The C-7 resonance apparently consists of 3 signals in the ratio 1:2:1. There are four possible situations for this carbon signal arising from head or tail orientation of adjacent substituents (TT/HT; TT/HH; HT/HT; HT/HH) and the observation of a triplet structure indicates coincidence of two environments¹⁰.

The weak intensity signals are clearly assigned to carbon associated with *trans* double bonds, but in this case the high field signals do not provide good evidence to confirm the assignment obtained from the low field signals

since the spectrum quality is not good enough. However, good evidence to confirm the assignment of a high *cis* polymer comes from the infra-red spectrum of this product, which shows a strong *cis* vinylene CH out of plane band at 750 cm^{-1} and only a very weak band for the *trans* vinylene units at 970 cm^{-1} .

CONCLUSIONS

The detailed analysis of the high field ^{13}C n.m.r. spectra of polymers of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene together with their infra-red spectra leads to the following conclusions:

(i) *exo*-5-trifluoromethylbicyclo[2.2.1]hept-2-ene gives with OsCl_3 ring-opened polymer with *trans* double bonds that is probably atactic;

(ii) *endo*-5-trifluoromethylbicyclo[2.2.1]hept-2-ene gives a high *trans* atactic polymer with both OsCl_3 and MoCl_5 ;

(iii) it is likely that *endo*-5-trifluoromethylbicyclo[2.2.1]hept-2-ene gives an essentially stereoregular *cis* ($\sigma_c = 0.92$) polymer with ReCl_5 , but it has not been possible to prove this unambiguously nor to identify whether the dyads are all meso or all racemic.

We believe that these results raise interesting questions concerning the factors controlling stereoregulation in

metathesis ring opening polymerization, and are encouraging in regard to the objective of preparing stereoregular fluoropolymers.

ACKNOWLEDGEMENTS

We thank the European Research Office of the US Army for a maintenance grant (P.M.B.) and Dr I. H. Sadler (Edinburgh University) for recording the ^{13}C n.m.r. spectra.

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