AD-A174 018 SYNTHESIS OF NEW STEREOREGULAR FLUOROPOLYMERS(U) DURHAM UNIV (ENGLAND) DEPT OF CHEMISTRY W J FEAST AUG 86 DAJA45-83-C-0036 1/1

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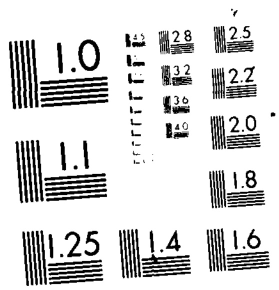

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SYNTHESIS OF NEW STEREOREGULAR FLUOROPOLYMERS

Final Technical Report

by

W.J. Feast

August 1986

Principle Investigator: Dr. W.J. Feast
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The research reported in this document has been made possible through the support and sponsorship of the U.S. Government through its European Research Office. T~~his report is intended only for the internal management use of the Contractor and the U.S. Government.~~

SUMMARY

This report is subdivided into four papers. The first presents an overview and survey of the work carried out. In the initial stages of the work a broadly based survey of metathesis polymerization of fluorinated monomers was conducted; ~~subsequently~~ more detailed studies of particular monomer types were conducted. In ~~the first paper~~ all the monomers investigated are reviewed along with other systems examined in related projects.

~~The second paper~~ is concerned ~~with~~ a detailed study of the polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene, again relevant results from related projects are included.

The third paper ~~is concerned with~~ a detailed study of the polymerization of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene, and is exclusively the work of this project.

The fourth paper ~~is concerned with~~ 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene as monomer.

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Preface

The work described in this report was funded in response to a research proposal submitted to the European Research Office of the U.S. Army in March 1982. The abstract of the proposal is reproduced below.

> "The aim of the proposed work is to prepare and characterize a series of new stereoregular fluoropolymers. The synthetic method to be used is ring-opening polymerization of fluorinated polycyclic monomers using metathesis catalysts. Some work has been carried out in the Durham laboratories which establishes both the feasibility of the proposed syntheses and the possibility that the new materials will have technologically interesting properties."

In the event the student funded by the contract, Miss Patrique Michelle Blackmore, started work in Durham on the 1st September 1983 after completing her undergraduate studies in Newcastle University. The progress of the work was monitored through submission of five semi-annual reports and this final technical report supersedes and updates all previous documents. Miss Blackmore has completed the studies required for a Ph.D. degree and has, at the time of writing, almost completed the preparation of her thesis which will probably be submitted and examined in September/October 1986.

The work has been successful and provided much useful and interesting data. All the work has now been written up and submitted to Journals for publication, consequently this final report has been revised and edited to incorporate the comments and criticisms of external referees, and the author believes that this process has substantially improved the clarity of the record and the validity of the interpretations presented.

The work divides itself rationally into four papers. The first, an overview, summarizes the total effort of this group in this field. The second concentrates on the polymerization of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene and, while the major part of this work was done on this contract, contributions from other workers, namely Drs. J.H. Edwards, A.B. Alimuniar and B. Wilson, are included so as to make the story as complete as possible. The third paper was exclusively the work of Miss Blackmore and presents a convincing case for the successful preparation of stereoregular fluoropolymers via polymerization of 5-trifluoromethylnorbornene. The fourth and final paper describes work on 2-trifluoromethylbicyclo[2.2.1]-hepta-2,5-diene, in this section a small contribution was made by Mr. P.C. Taylor as part of his undergraduate training but again the major part of the work is to the credit of Miss Blackmore.

The project has successfully established the feasibility of the original proposal. It is now clear that stereoregular fluoropolymers can be prepared via metathesis ring opening polymerization. We hope to be able, at some time, to expand this new field by preparing and polymerizing new fluorinated monomers and characterizing the products. Also we hope to begin a programme of study of the physical properties of these systems and to try to develop an understanding of structure-property relationships in these systems.

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August 1986

PAPER 1

SYNTHESIS OF NEW STEREOREGULAR FLUOROPOLYMERS

AN OVERVIEW

Summary

In this paper we review the possibilities which exist for the synthesis of stereoregular fluoropolymers via ring opening of substituted bicyclo[2.2.1]heptenes and -heptadienes, and summarize the results of our efforts to realize these possibilities.

Introduction

Stereoregular fluoropolymers are virtually unknown. By contrast, improved materials properties and process advantages have lead to the widespread adoption of the Ziegler-Natta type of catalyst in the synthesis of stereoregular hydrocarbon polymers. Since fluoropolymers display a wide range of useful properties it seems probable that at least some members of the category of stereoregular fluoropolymers will display interesting properties. Considerations of this kind lead to the conclusion that the preparation of well characterized stereoregular fluoropolymers represents a worthwhile challenge for synthetic chemistry: this paper reviews one approach to answering this challenge and the progress made so far.

Discussion

Metathesis ring opening polymerization has been known for almost as long as the stereoregular polymerization of alkenes and has found some commercial exploitation. In recent years considerable effort has been expended on attempts to understand the mechanism of this rather unusual reaction, and to examine the range of its applicability. It is now clear that under favourable circumstances totally stereoregular materials can be produced, and that a wide range of substituents can be tolerated by some catalysts.[3] In particular, it was known that fluorinated bicyclo[2.2.1]heptenes and -heptadienes could be polymerized by ring opening at the -CH=CH- double bond using the tungsten hexachloride/tetraphenyl tin catalyst system.[4]

The essential steps in establishing the syntheses which are the objective of our program are:-

i) synthesis of appropriate monomers,

ii) demonstration of ring opening polymerization (preferably with a wide range of catalysts),

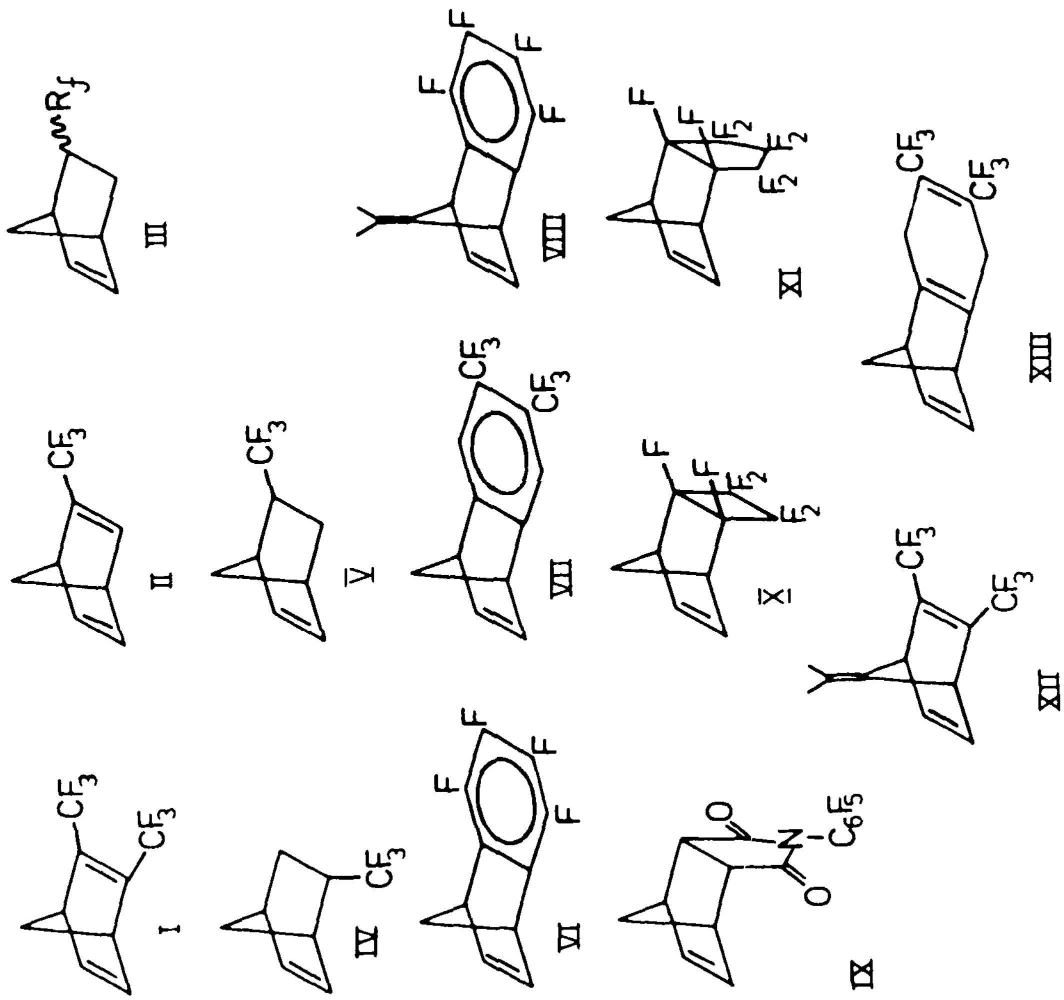
iii) unambiguous proof of the details of polymer microstructure.

In this review we shall deal with points (i) and (ii), and discuss the progress made on point (iii). The longer term objective is, of course, to study the properties of well characterized stereoregular fluoropolymers.

a)Monomers

Since bicyclo[2.2.1]heptene and bicyclo[2.2.1]hepta-2,5-diene and their derivatives were known to undergo ring opening polymerization with a wide range of catalysts and the resulting polymers have been the subjects of many detailed studies of microstructure, fluorinated derivatives of these two structures seemed appropriate monomers with which to begin our programme. Prior to the start of this study, the Diels-Alder reactions of fluorinated dienophiles with cyclopentadienes and fulvenes had been thoroughly investigated,[5] consequently detailed descriptions of the preparation and characterization of a large number of potential monomers were already available. We and co-workers have now examined more than thirty of these fluorinated polycyclic alkenes and a selection of the structural types which have been investigated is shown in Figure 1.

Figure 1. An illustrative selection of the variety of fluorinated derivatives of bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]hepta-2,5-diene which will undergo metathesis polymerization.



The reaction of perfluorobut-2-yne or 3,3,3-trifluoropropyne with cyclopentadiene yields the simple trifluoromethyl substituted bicyclo[2.2.1]hepta-2,5-dienes (I and II) and the adducts of fluorinated alkenes are represented by the monosubstituted bicycloheptene (III) which completes the first row of structures in Figure 1. Crossing the first row from left to right is accompanied by increasing monomer complexity. Thus, 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (I) is a single compound; 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene (II) is chiral and is produced as a racemic mixture; and the 5-substituted bicyclo[2.2.1]heptenes (III) can display the additional complication of exo-/endo- isomerism, almost invariably the product of synthesis is a mixture of both forms and since they are both racemic the monomer is usually obtained as a mixture of four compounds. Such mixtures of isomers are usually difficult to separate; however, the endo- and exo- isomers of 5-trifluoromethylbicyclo[2.2.1]heptene (IV and V respectively), shown in the second row of Figure 1, have been successfully separated by preparative gas chromatography. The aryl derivatives shown in the third row were obtained either as the Diels-Alder adducts of tetrafluorobenzyne (VI and VIII)[6] or by dehydrogenation of the adduct (XIII) of 2,3-dimethylenebicyclo[2.2.1]hept-5-ene with perfluorobut-2-yne (VII).[7] The remainder of the structures shown in the figure were obtained via the appropriate Diels-Alder syntheses.

b) Polymerizations

All the monomers depicted in Figure 1 undergo ring opening polymerization in the presence of an appropriate metathesis catalyst.[4,8-12] All the products were soluble; the majority of the materials we have made were readily soluble in common solvents such as acetone, chloroform and tetrahydrofuran, but some samples displayed unusual behaviour; for example, poly(1,4-(2-perfluoroalkylcyclopentylene)vinylene)s with normal perfluoropentyl and heptyl substituents (the polymers of II where R = C_5F_{11}- or C_7F_{15}-) were only soluble in methyl heptafluorobuterate, whereas samples of the polymer of I, poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)vinylene), prepared using a tungsten based catalyst were soluble in methanol as well as the usual range of common solvents while samples prepared using molybdenum based catalysts were insoluble in methanol and only sparingly soluble in other solvents. We have carried out gel permeation chromatographic analyses on most of the polymers and the retention volumes observed were equivalent to those of polystyrene samples with molecular weights in the 10,000 to 100,000 range with molecular weight distributions generally in the range 2.5 to 4.5. These observations show that this approach gives access to a range of new linear, or lightly branched, fluoropolymers: the properties of these new materials are under investigation, what concerns us at present is establishing their structures.

c)Polymer structure

The outcome of metathesis ring opening polymerization is different from conventional addition polymerizations in two significant ways. Thus, all the unsaturation of the monomer is retained in the polymer repeat unit in contrast to conventional addition polymerizations. The other difference lies in the nature of the possible assembly modes and the consequences for stereoregulation in ring opening metathesis; this is perhaps best illustrated by comparing the metathesis polymerization of benzonorbornadiene (tricyclo[4.2.1.$0^{2,7}$]undeca-2,4,6,9-tetraene) with the more familiar example of styrene, Figure 2.

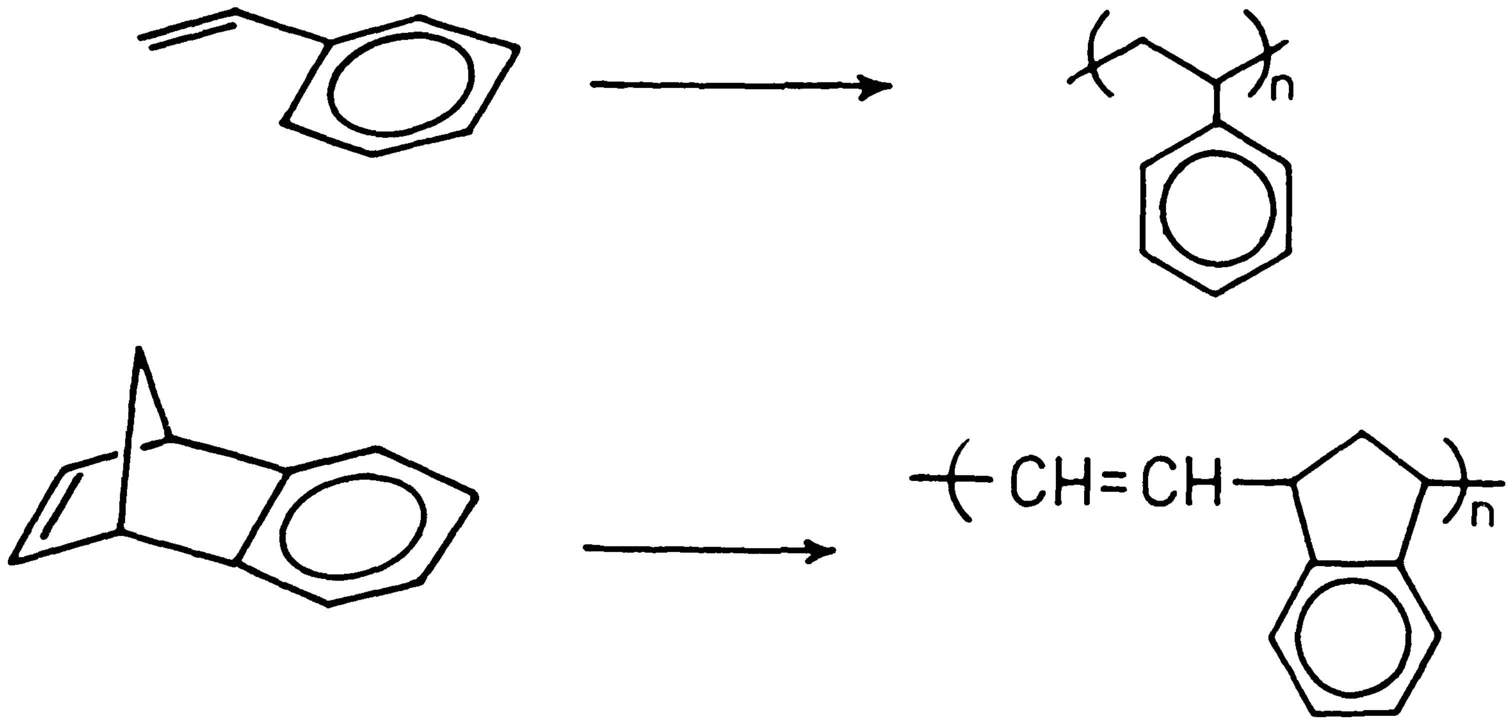


Figure 2. Comparison of styrene and benzonorbornadiene polymerizations.

As is well known, polystyrene has chiral centres at the methine carbons and consequently there can be meso or racemic dyads giving rise to syndiotactic and isotactic polymers. By contrast polybenzonorbornadiene has two chiral centres per repeat unit and a vinylene unit which can adopt E or Z stereochemistry; as a result this polymer can, in principle, give rise to four distinct stereoregular homopolymers. In this particular example there is a further distinction between the kinds of polymers accessible from the two monomers in that the orientation of the aromatic rings in the polybenzonorbornadienes is rigidly fixed with respect to the polymer backbone whereas in polystyrene there is free rotation about the single bond which links the phenyl group to the backbone. When the monomer is unsymmetrically substituted the situation is further complicated by the possibility of head-head (HH), tail-tail (TT), and head-tail (HT) isomerism, the consequences of this can be seen by considering the propagation step depicted in Figure 3.

The chain carrying metal carbene and the incoming monomer may have an H (R at C_α) or a T (R at C_β) configuration, and the incoming monomer may be incorporated so as to give a HH, TT, HT, or TH stereochemistry around the newly formed vinylene, which may have E or Z stereochemistry. The cyclopentane rings may be introduced in a meso or racemic sense. In the product polymer HT and TH are indistinguishable and there are therefore twelve stereochemically different ways in which a pure endo- or exo-monomer of the type depicted in Figure 3 may be incorporated as a result of this propagation step; and, since such monomers will usually be found as endo/exo mixtures the number of possible assembly modes is in practice considerably higher than that. Clearly the analysis of such potentially complicated

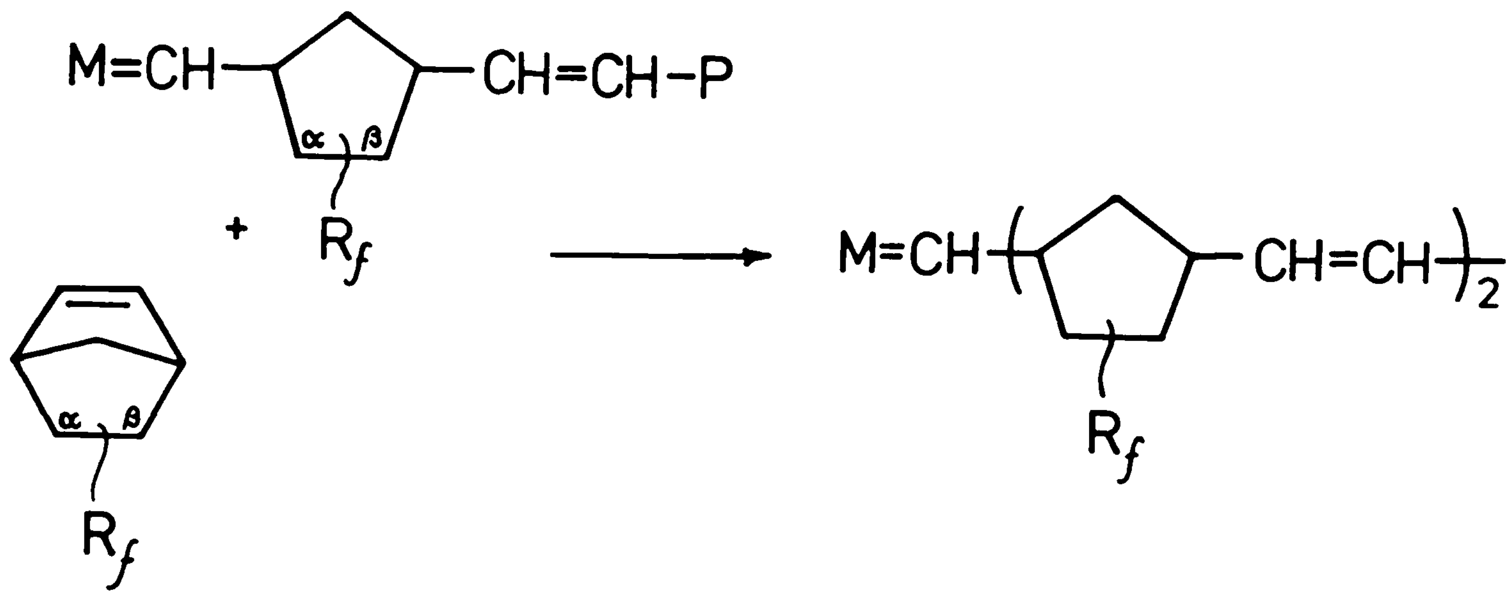


Figure 2. Propagation step in metathesis ring opening polymerization of a substituted bicyclo[2.2.1]hep-2-ene.

systems will be difficult and it is desirable to simplify the problem as far as possible, either by selecting simple monomers without isomers, or separating endo- and exo-isomers, or seeking catalysts which selectively polymerize one isomer of a mixture when separation proves impossible. This approach is, in effect, following the example set in earlier workers' studies of related systems.

Establishing the structures of the fluorinated polymers produced in this programme is heavily dependent on detailed analyses of the infrared and nmr spectra of related sets of polymers and these will be reported elsewhere, along with the details of experimental procedures and further characterization data. In summary, it can be said that in the ir spectra the most useful data is generally derived from the out-of-plane C-H bending modes at $970 cm^{-1}$ (E vinylene) and $730 cm^{-1}$ (Z vinylene) but that these absorptions are not always adequately separated from other bands. Although useful data has sometimes been derived from ^{1}H and ^{19}F nmr spectra, by far the most useful information comes from analysis of ^{13}C spectra. In particular, E/Z contents can almost invariably be assigned, generally the allylic methine carbons provide the most unambiguous data since the signal from an allylic carbon adjacent to a Z-vinylene invariably occurs ca.4 to 5 ppm upfield from that due to one adjacent to an E-vinylene. Frequently internal consistency can be established via an analysis of the vinylene and methylene resonances. In favourable cases information concerning tacticity can also be deduced from the ^{13}C spectra, although in this aspect of the analysis the assignment of atactic polymers is often certain whereas there is usually some ambiguity about the assignment of detailed microstructure in more regular polymers.

In the initial stages of this programme we have attempted to screen a wide range of both monomers and catalysts. The monomer types have been described above. The catalysts used were WCl_6 alone or activated with Ph_4Sn, $(C_4H_9)_4Sn$, $(CH_3)_4Sn$, or $(CH_3)_2AlCl$; $(CO)_5W{=}C(OCH_3)C_6H_5$ with and without $TiCl_4$ activation; $MoCl_5$ alone or activated with Ph_4Sn, and $(CH_3)_4Sn$; $OsCl_3$; $IrCl_3/CF_3$-COOH; $RuCl_3$; $ReCl_5$.

We have not, as yet, found a catalyst/monomer system in which exclusively one component of the monomer mixture is polymerized although there is some selectivity in some cases. Thus, polymerization of roughly 50:50 mixtures of the exo-/endo-isomers of 2-trifluoromethyl-2,3,3-trifluorobicyclo[2.2.1]hept-5-ene or 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene, the Diels-Alder adducts of cyclopentadiene with perfluorpropene and perfluorocyclopentene respectively, with catalysts derived from tungsten hexachloride results in preferential consumption of the endo-isomers.[4,10] This observation contrasts with the earlier report that the exo-isomer of the adduct of maleic anhydride with cyclopentadiene is more readily polymerized than the endo-isomer.[13] In the light of the usually accepted mechanistic picture for the polymerization of bicyclo[2.2.1]hept-2-enes and -2,5-dienes, which assumes that the monomer presents its exo face to the active catalyst site,[14] it is difficult to see why substituents at the remote C5 and C6 sites should have a pronounced effect on the course of the propagation reaction, unless they influence either the geometry of the exo-face and/or the donor properties of the double bond, both effects are possible but would be expected to be small. On the other hand substituents may be expected to have a profound effect on the conformations accessible to the polymer chain it has been found [illegible]. Whatever the cause of the limited selectivity observed, [illegible] polymerization of one isomer from a mixture of [illegible] has so far eluded us.

Polymerization of the simple symmetrical monomers I, VI, VII, and VIII has been investigated with a range of catalysts, most work having been done with the $WCl_6/(CH_3)_4Sn$ and $MoCl_5/(CH_3)_4Sn$ systems. If, as is generally accepted, approach to the propagating chain end metal carbene or metallocyclobutane is from the exo-face of the monomer we might reasonably expect that there would be little difference between I, VI, and VII, but that monomer VIII, with the isopropylidene [illegible] might be more sterically demanding. This expectation is justified in the observed proportions of Z-vinylene units in the different polymers; thus, for I, VI, and VII the tungsten based catalyst invariably gave 50 to 60% of Z-vinylenes, whereas with monomer VIII there was a Z content of only [illegible]%. A similar differentiation between the monomers of this set was observed in the case of molybdenum based catalysts, where I, VI, and VII gave Z-vinylene contents of 15 to [illegible]% whereas the Z-content of the polymer from VIII was less than [illegible]%. For all the polymers with low Z-vinylene contents the ^{13}C-nmr spectra were much simpler than those recorded for samples having an approximately 50% Z-vinylene content; unfortunately this observation is consistent with either a dependence on vinylene sequence effects, or tacticity effects, or both, and is not capable of unambiguous interpretation.

When the polymerizations of I and II initiated by six different catalyst systems are compared the results, with respect to Z-vinylene content, are generally very similar. This observation supports the hypothesis that in these norbornadiene derivatives substituents remote from the double bond undergoing reaction have little effect on the course of the reaction; however, there was one anomolous result in that monomer I could not be polymerized by $ReCl_5$ in any of several attempts, although this catalyst gave a polymer with a high Z-vinylene content with II. This may be a consequence of steric effects in the propagation step or differing susceptibilities of monomers I and II towards polymerization by a fairly inefficient initiator.

Only in the case of the monomers IV and V was clear unambiguous evidence concerning tacticity effects obtained.[9] This turned out to be analogous to the earlier work of [illegible] and co-workers on the polymerization of 5-methylbicyclo[2.2.1]heptenes; thus, when the substituent shift effect of the group at the 5-position is taken into account one is lead to the conclusion that in an all Z- or an all E-vinylene polymer with equal distribution of HH, TT, TH and HT environments there will be four signals for the vinylene carbons in the ^{13}C-nmr spectrum; exclusively HH TT or HT arrangements would result in only two signals; splitting of any of these signals is indicative of different vinylene environments resulting from meso/racemic dyad effects, and this effect is most likely to be detectable in HH dyads where steric compression will be most marked. In the event no splitting was detected for polymers derived from the exo-monomer V. This is not surprising since in the resulting polymer the trifluoromethyl and vinylene groups have an anti [illegible] and consequently any effects on the vinylene carbons are not expected to be large even in HH dyads. On the other hand the spectra of polymers of monomer IV prepared using $OsCl_3$ and $MoCl_5$/$(CH_3)_4Sn$ display splittings of 0.0[illegible] and 0.[illegible]0ppm respectively for the HH vinylene signals in high E-vinylene content polymers, whereas in the high Z-vinylene content polymer of IV obtained using $ReCl_5$ as initiator no splitting of the HH vinylene carbon resonance was observed even though the steric compressions in the high Z polymer would be expected to be greater than in the high E material. This last observation is, of course, consistent with the hypothesis that the polymerization of IV with $ReCl_5$ results in a high degree of stereoregulation, although it does not prove that this is the case.

Conclusions

Bicyclo[2.2.1]hept-2-enes and -hepta-2,5-dienes substituted at the C5 and C6 positions undergo ring opening polymerization with a range of metathesis catalysts, reaction occurs at the unsubstituted double bond to generate a range of new linear or lightly branched fluoropolymers. In general the proportion of E- and Z-vinylene units in the resulting polymers is governed chiefly by the nature of the transition metal in the initiating catalyst system although substituents on the one carbon bridge can also affect the outcome of the reaction, and with unreactive catalysts such as $ReCl_5$ substituents at the remote C5 and C6 positions may have an effect. Although it remains to be rigorously proved, the evidence available suggests that stereoregular polymers will prove to be accessible via this approach.

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PAPER 2

THE RING OPENING POLYMERIZATION OF 2,3-BIS(TRIFLUOROMETHYL)BICYCLO[2.2.1]HEPTA-2,5-DIENE

Summary

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 infrared and high field ^{13}C-nmr spectra of the different polymers is consistent with the hypothesis that catalysts based on WCl_6 give a polymer with a 50:50 random distribution of cis and trans vinylenes, those based on $RuCl_3$ give predominantly trans vinylenes (ca.70%), and those based on $MoCl_5$ give a higher trans vinylene selectivity (ca.90%).

INTRODUCTION

The recognition, study and exploitation of the stereoregular polymerization of alkenes is one of the more notable achievements of polymer science.[1] 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.

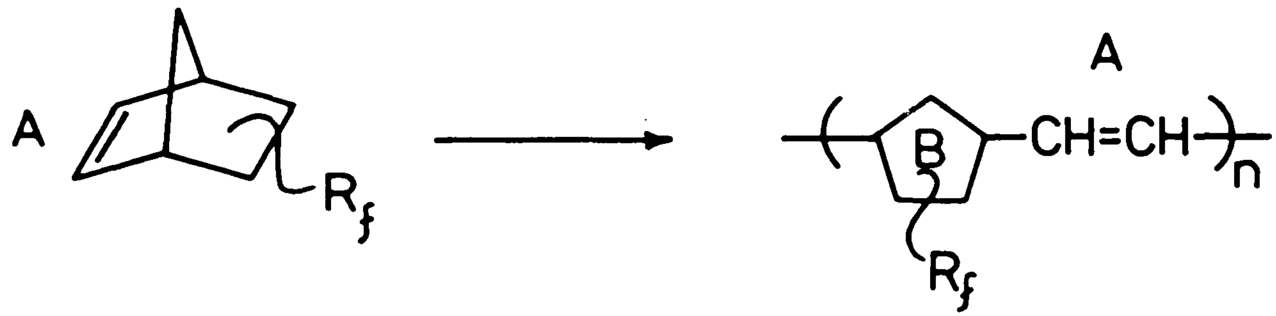
Despite their relatively high cost, a number of fluoropolymers have shown sufficiently unusual properties to justify their development and exploitation.

In the light of the two preceding observations it is rather surprising that the literature contains relatively few references to stereoregular fluoropolymers[2-6] and, to the best of our knowledge, no examples of the genre are produced commercially.[1,7]

of the structural types which have been investigated is shown in Figure 1.

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.[8,9]

We became interested in the possibility of making stereoregular fluoropolymers a few years ago,[10] 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 choose 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 WCl_6.[10] To extend these initial observations to the synthesis of stereoregular fluoropolymers required that appropriate monomers, catalysts, and reactions conditions were found, and that unambiguous analytical criteria for polymer microstructures be 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). The stereochemical relationship of R_f to the allyl-vinyl carbon-carbon bond also requires definition in the case shown in Figure 1.



(1) (2)

Figure 1

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.[11] 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 ref.11). For example, the polymerization of norbornene with tungsten based catalysts leads to polymers with cis vinylene contents varying from 95% to 39%.[12] 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 TT effects and there are no complications from exo-/endo- isomerization.

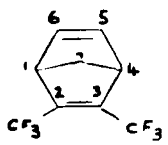
EXPERIMENTAL

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 <10ppm O_2, the gas was dried through liquid nitrogen cooled traps and circulated via glass or metal tubing, 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_2O_5, distilled, degassed and stored under dry nitrogen.

Catalysts and cocatalysts. WCl_6 was prepared from WO_3 and hexachloropropene, stored and manipulated as described previously.[10] $TiCl_4$, $RuCl_3$, $OsCl_3$, $(CH_3)_4Sn$, $MoCl_5$, $ReCl_5$ and $(n\text{-}C_4H_9)$ Sn were used as supplied. $(C_6H_5)_4Sn$ was purified as described previously.[10] Aluminium alkyls were supplied by K.Wade(this Department). $C_6H_5(CH_3O)C{=}W(CO)_5$ was prepared by the published route.[14]

<u>Monomer</u>.2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene is a known compound; in a typical synthesis hexafluorobut-2-yne (33.9g,209mmoles), cyclopentadiene (13.8g,209mmoles) and hydroquinone (0.05g) were sealed under vacuum in a Pyrex ampoule (ca. 150ml) and left at room temperature for 24hrs. 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 24hrs. the ampoule was heated to ca. 100°C for a further 24hrs. to ensure reaction. Monomer **3** was recovered by fractional distillation (Vigreux column, 10cm, 1 Atmosphere, b.r. 120-122°C)as a colourless liquid (38.5g,169mmoles,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 ^{1}H and ^{13}C nmr or by gas chromatography. The ^{1}H nmr spectrum of **3** recorded at 300.13MHz showed: an ABq δ_A, 2.08; δ_B , 2.26; J_{AB} ,6.95Hz with A limbs unresolved (FWHM ~5Hz) and B limbs as triplets J=1.64Hz(2H-7); a singlet δ , 3.90 (FWHM=6Hz) (H-1 and H-4); and three lines centred at δ , 6.92 ppm wrt internal TMS (J=1.95Hz) (H-5 and H-6).



The proton decoupled ^{13}C nmr spectrum recorded at 75.47MHz showed signals at 53.3 (C-7), 74.0 (C-1,C-4), 122.9 q (J=270Hz) CF_3, 142 9 (C-5,C-6) and 149.4 m (C-2,C-3) ppm wrt internal TMS.

Polymerizations. Polymerizations were carried out using a two necked round bottom flask as the reaction vessel. A teflon 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 dessicator 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 transfered 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 ($CHCl_3$ and/or $(CH_3)_2CO$) and were purified by reprecipitation into methanol or pentane. The samples were characterized by infrared and ^{13}C nmr 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 $dl.g^{-1}$,for viscosities measured in MEK at 25°C.

Table 1. Polymerizations of 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hept-2,5-diene, 3

Expt. No.	Catalyst[a]	Cocatalyst	Molar Ratio Cat:Cocat:3	Solvent[b] (ml)	Temperature[c] (^oC)	Time (hrs.)	Yield[d] %
1	WCl_6	none	1:370	T, 10	RT	3	11
2	"	"	1:200	C, 1.1	50	48	4
3	"	$(C_6H_5)_4Sn$	1:2:400	T, 10	RT	0.5	70
4	"	"	1:2:150	"	"	1	80
5	"	"	"	C, 10	"	1	76
6	"	$(nC_4H_9)_4Sn$	1:2:60	T, 10	"	1	75
7	"	$(CH_3)_4Sn$	"	"	"	1.5	20[e]
8	WCl_6/Na_2O_2	$(iC_4H_9)_3Al$	1:3:350	"	"	3	77
9	"	none	1:1:400	"	"	1	10
10	$C_6H_5(CH_3O)C{=}W(CO)_5$	"	1:60	"	"	48	0
11	"	$TiCl_4$	1:2:60	"	"	18	30
12	"	"	"	"	50	2	25
13	$MoCl_5$	none	1:200	neat	80	48	2
14	"	$(C_6H_5)_4Sn$	1:2:60	T, 10	RT	18	75
15	"	$(CH_3)_2AlCl$	"	"	"	"	74
16	"	$(CH_3)_4Sn$	1:2:70	C, 10	"	3	70
17	"	"	1:2:200	C, 3	-20	48	20[f]
18	"	"	"	C, 1	50	2 mins	25[e,g]
19	"	"	"	C, 1	-20	48	2[g,f]
20	$RuCl_3$	none	1:200	CE, 0.5	50	36	21
21	"	"	"	CE, 2	65	65	30
22	"	$(CH_3)_4Sn$	1:2:200	CE, 1.5	40	2.5	74

a) We were unable to polymerize 3 with $OsCl_3$, $ReCl_5$ or $ReCl_5/(CH_3)_4Sn$ although the catalysts were active with norbornene.

b) T-toluene, C-chlorobenzene, CE-1:1 (vol for vol) mixture of chlorobenzene and ethanol.

c) RT-room temperature, roughly 15 ± 5^oC. The polymerization was often noticeably exothermic, no monitor of temperature was placed in the vessel.

d) After reprecipitation and drying under vacuum for at least 24 hrs.

e) Polymerization quenched at low conversion to aid work up.

f) Insoluble.

g) Chain transfer agent, oct-4-ene, added to limit molecular weight.

RESULTS AND DISCUSSION

General. The objective of this work was to investigate the effect of catalyst and reaction conditions on the structure of the polymer; however there are some points emerging from the data in Table 1 which merit comment before we consider the details of chain microstructure.

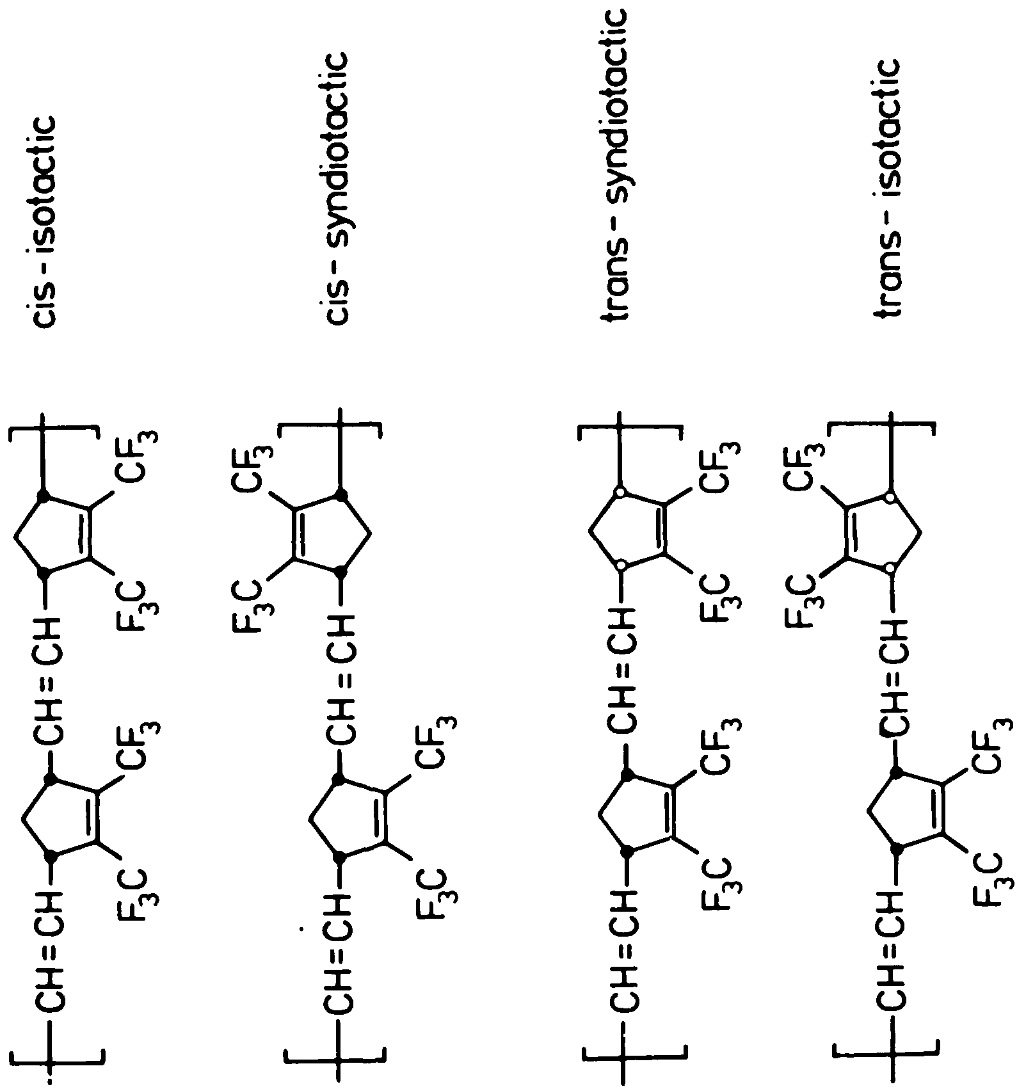
It is clear from Experiments 1, 2, 13, and 20 that the single component catalysts WCl_6, $MoCl_5$, and $RuCl_3$ all polymerize monomer 3; but the Fischer carbene (Experiment 10), which initiates the polymerization of norbornene,[15] was ineffective for the room temperature polymerization of 3 without an activator. Neither $OsCl_3$ or $ReCl_5$ 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 Part III, 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 considerations 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 infrared and ^{13}C nmr 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 polymerization of 3; consequently we made a more detailed study of the polymerization of 3 initiated by $MoCl_5/(CH_3)_4Sn$. This catalyst rapidly polymerizes 3 at or above room temperature to a high molecular weight material which dissolves 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 ^{13}C nmr 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 occured 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 cross linking 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 ^{13}C nmr.

<u>Microstructure</u>. The structure of polymers of this type can be studied by infrared and nmr spectroscopy, high field solution phase ^{13}C nmr 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.

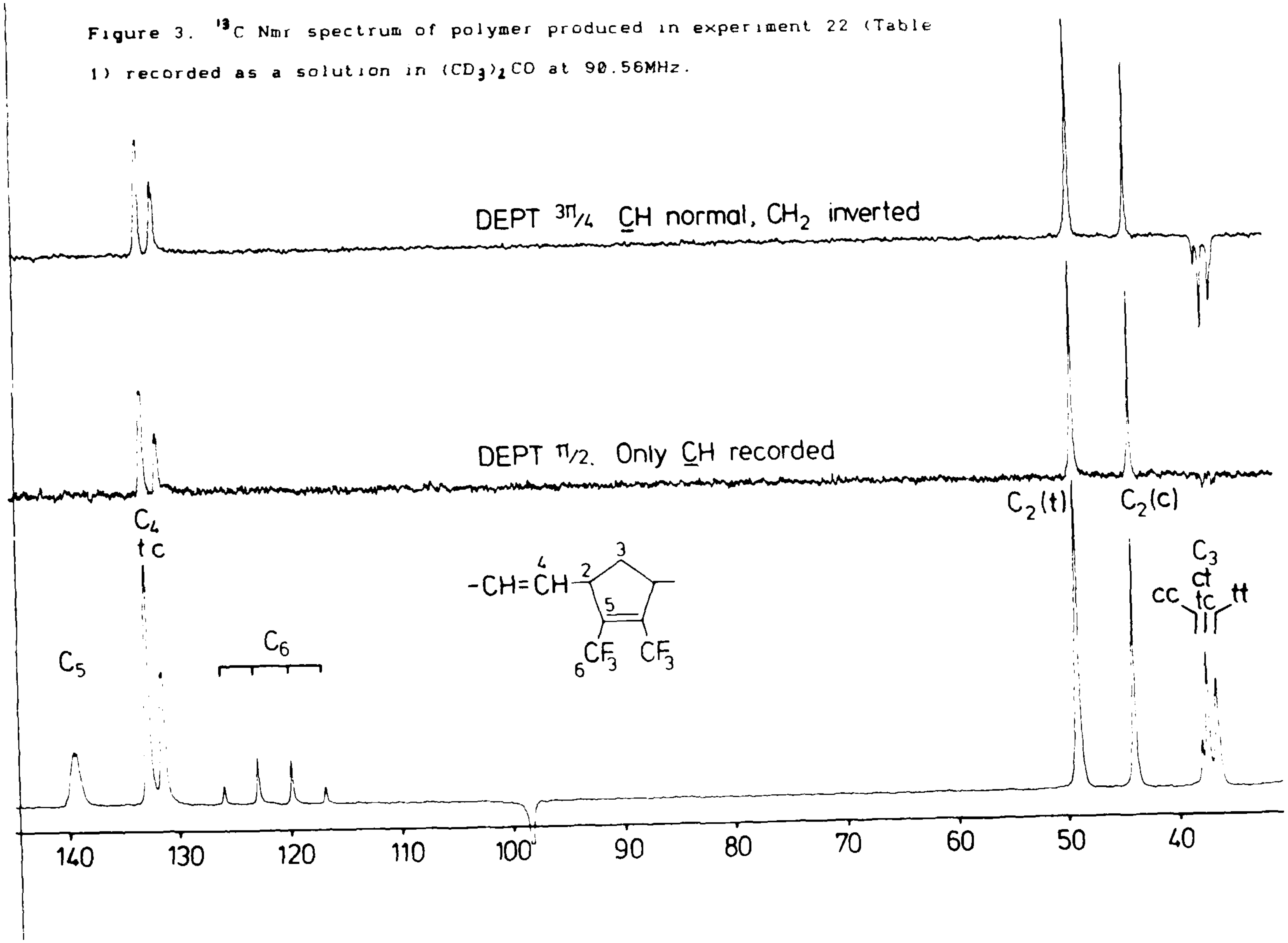
Figure 2. Possible assembly modes for poly(3,5-(1,2-bis(trifluoromethyl)-cyclopentylene)vinylene); ● C-H bond approaching, ○ C-H bond receding from the viewer.



In an earlier publication we discussed the ^{13}C nmr spectrum of a sample of poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)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 (σ_c = 0.54). Since the proportion of cis vinylenes (σ_c) was so close to 0.5 there was some uncertainty concerning the reliability of the assigned line orders for the signals arising from vinyl, allyl, and methylene carbons. To a large extent the assignments rested on analogies with earlier analyses of the spectra of polynorbornenes and polymethylnorbornenes 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 σ_c and as a consequence of this extra data are able to make assignments on a more secure basis. The spectrum of a polymer of 3 produced using the catalyst $RuCl_3/(CH_3)_4Sn$ is shown in Figure 3, which also illustrates the use of distortionless enhancement by polarization transfer (DEPT) in confirming the assignment of peaks.[16]

The lowest trace is the normal broad band decoupled spectrum, and is similar to that published previously (Polymer XII, Fig.1 Ref.10b) albeit with much improved signal to noise 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 σ_c , 0.36, 0.36, and 0.34 respectively, are internally consistent. In this assignment the line

Figure 3. ^{13}C Nmr spectrum of polymer produced in experiment 22 (Table 1) recorded as a solution in $(CD_3)_2CO$ at 90.56MHz.



order for the allylic and methylene signals parallels that found in polynorbornene and polymethyl norbornenes although the line order for the vinylic carbons, with C-4(c) about 1.5ppm upfield of C-4(t), is the reverse of that found in polynorbornene 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.5ppm 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 1.5ppm, and the observed line order is variable, for example in polynorbornene trans vinylene carbons are found upfield 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 $MoCl_5/(C_6H_5)_4Sn$ [4a] and $WCl_6/(C_6H_5)_4Sn$ [4b] at room temperature, the resolution in these spectra is somewhat better than that in Figure 3. We have obtained high field ^{13}C nmr 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. Spectrum 4b displays the best resolution and the highest number of resolved signals with lines at; 138.3 (q,J=25Hz,C-5); 131.8 & 131.1 (C-4t); 130.5 & 130.3 (C-4c); 120.4 (q,J=270Hz C-6); 48.2 (C-2t); 43.1 & sh at 43.2 (C-2c); 36.9 (C-3cc); 36.4 & 36.1 (C-3ct ≡ C-3tc); 35.5 & 35.2 (C-3tt) for a spectrum recorded at 90.56MHz in $(CD_3)_2CO$ 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

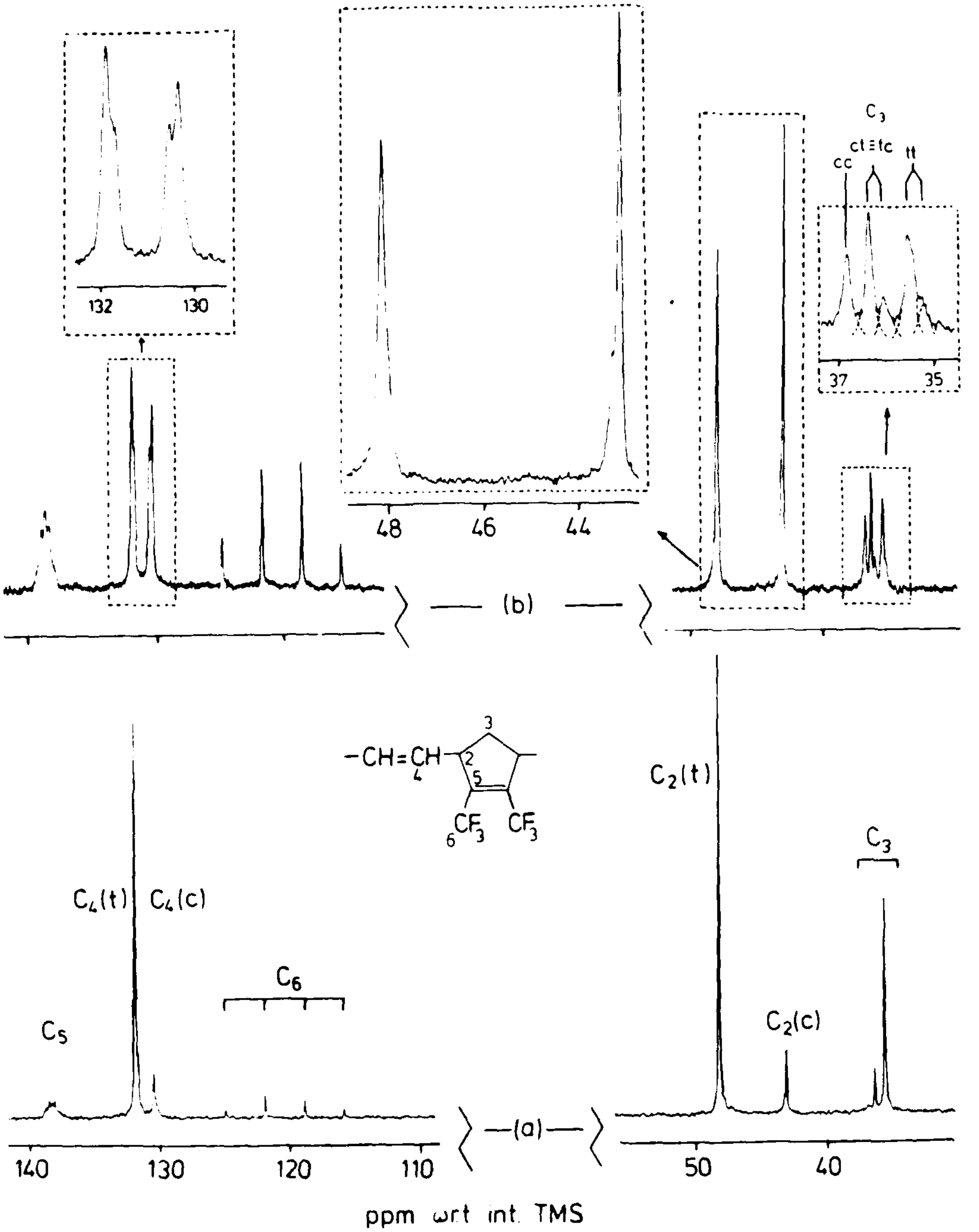


Figure 4. [13]C Nmr spectra of polymers produced in experiment 14 (Table 1), 4a, and experiment 4 (Table 1), 4b, recorded as solutions in $(CD_3)_2CO$ at 90.56MHz.

nearest cis or trans neighbours; however, from this 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 σ_c computed from the vinylic, allylic, and methylene carbon signals for eight samples are recorded

Table 2. Fraction of cis vinylenes (σ_c) for samples of poly(3,5-(1,2-bis(trifluoromethyl)cyclopentenylene)vinylene)

Expt. No.	Catalyst	σ_c			
		From vinylene carbon signals	From allylic carbon signals	From methylene carbon signals	Average
4	$WCl_6/(C_6H_5)_4Sn$	0.47	0.48	0.44	0.46
7	$WCl_6/(CH_3)_4Sn$	0.47	0.47	0.45	0.46
12	$C_6H_5(CH_3O)C{=}W(CO)_5/TiCl_4$	0.54	0.51	0.49	0.51
14	$MoCl_5/(C_6H_5)_4Sn$	0.15	0.12	0.13	0.13
15	$MoCl_5/(CH_3)_2AlCl$	0.12	0.10	0.09	0.10
16	$MoCl_5/(CH_3)_4Sn$	0.15	0.15	0.10	0.13
20	$RuCl_3$	0.29	0.29	0.26	0.28
22	$RuCl_3/(CH_3)_4Sn$	0.36	0.36	0.34	0.35

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}C nmr spectra, the multiplicity of signals being consistent with a more or less random assembly of the various possible sub-units; such a result being 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 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 infrared spectra of polymers with differing cis/trans vinylene contents.

Monomer 3 was polymerized with $MoCl_5/(CH_3)_4Sn$ in chlorobenzene at temperatures in the range 20°C to 100°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, 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.

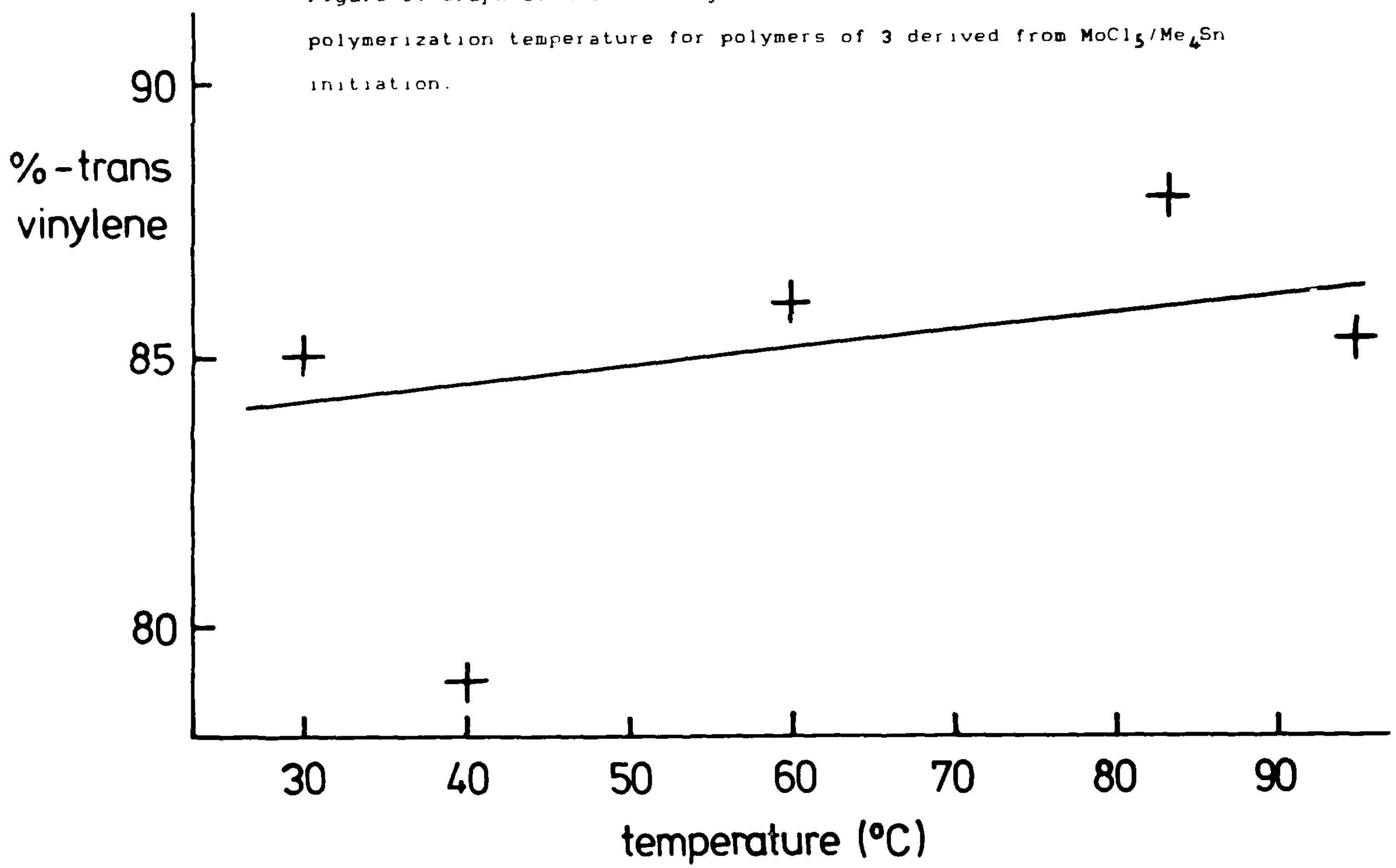


Figure 5. Graph of %-trans vinylene content as a function of polymerization temperature for polymers of 3 derived from $MoCl_5/Me_4Sn$ initiation.

We have carefully compared the infrared spectra of thin films of polymers from experiments 7 and 16 (Tables 1 & 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 3000cm^{-1} where the trans absorption occurs at a higher frequency than the cis, the >C=C< stretching region around 1660cm^{-1}, and the C-H out of plane bending region around 965cm^{-1} (trans) and 700cm^{-1} (cis).[17] The spectra were recorded using a Nicolet 60SX Interferometer and are reproduced in Figure 6, 7 and 8. Figure 6 shows the C-H stretching region, it is clear that in molybdenum derived sample the band at 3043cm^{-1} (trans) is more intense than that at 3022cm^{-1} (cis) which is in good agreement with the assignment based on ^{13}C nmr. Figure 7 shows the >C=C< stretching region this is dominated by the strong -$(CF_3)C=C(CF_3)$- band at 1682cm^{-1}, the shoulder at 1660cm^{-1} on the major peak is probably the -CH=CH- stretching absorption and appears strongest in the molybdenum derived polymer, it would be hazardous to attach much weight to this 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 >C=C< stretching region the picture is complicated since there are clearly two overlapping bands in the trans (986 & 970cm^{-1}) and cis (730 & 718cm^{-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 bending, assignment of the bands at 970cm^{-1} to trans and that at 730cm^{-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 infrared spectra is consistent with the assignments made on the basis of ^{13}Cnmr.

Figure 6. C-H Stretching region in the infrared spectra of polymers of **3** prepared using WCl_6/Me_4Sn (W) and $MoCl_5/Me_4Sn$ (Mo).

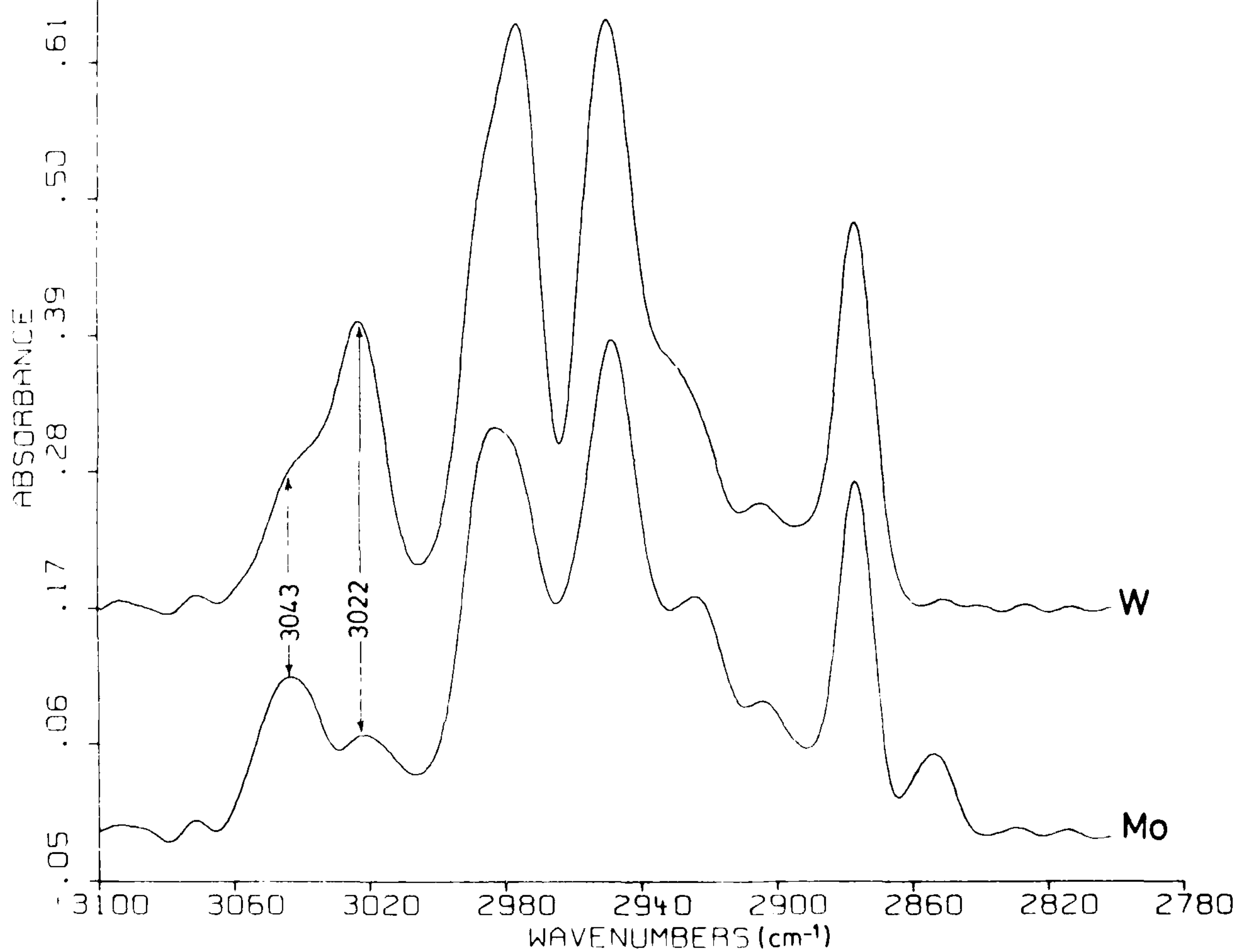
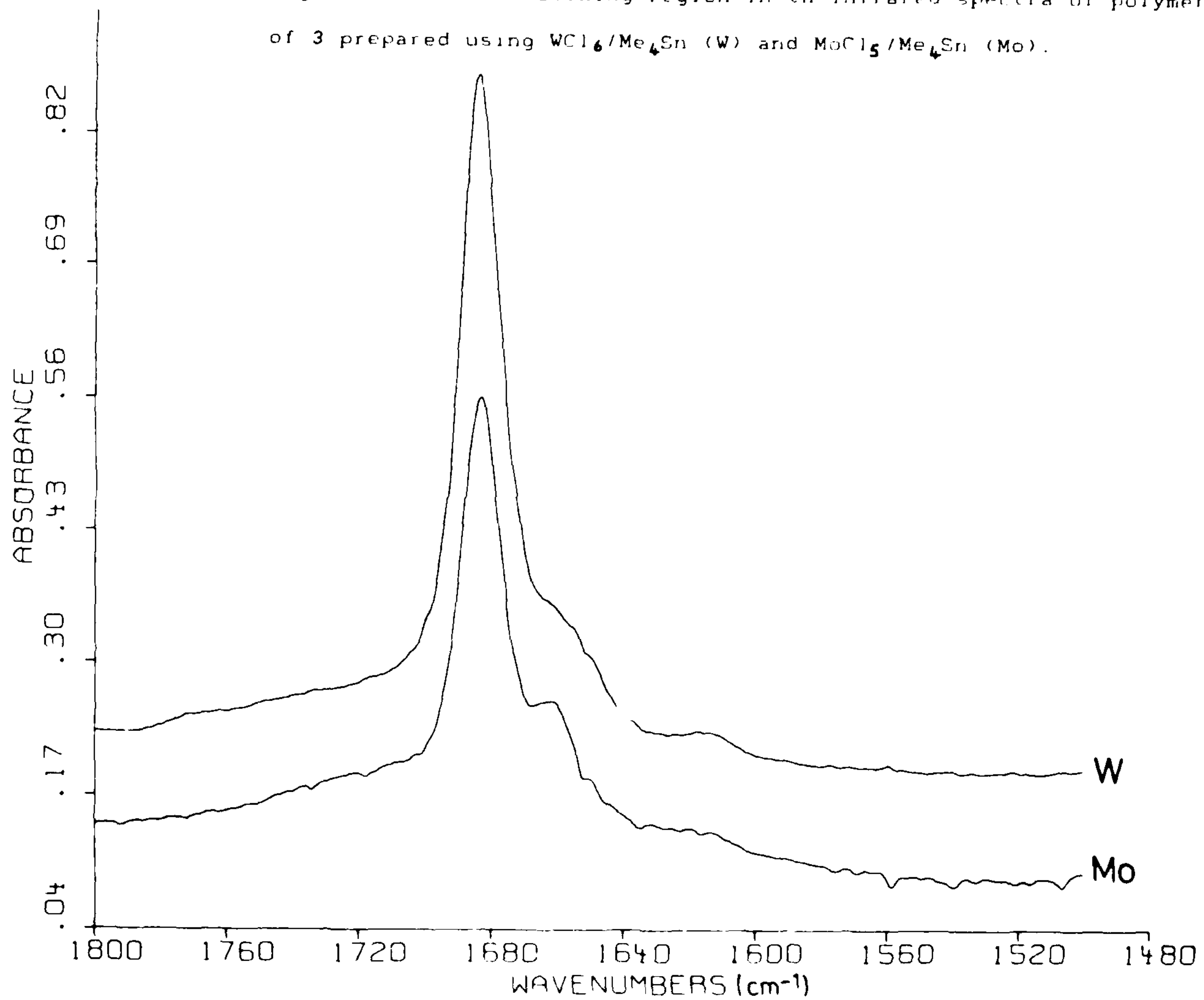


Figure 7. >C=C< Stretching region in the infrared spectra of polymers of 3 prepared using WCl_6/Me_4Sn (W) and $MoCl_5/Me_4Sn$ (Mo).



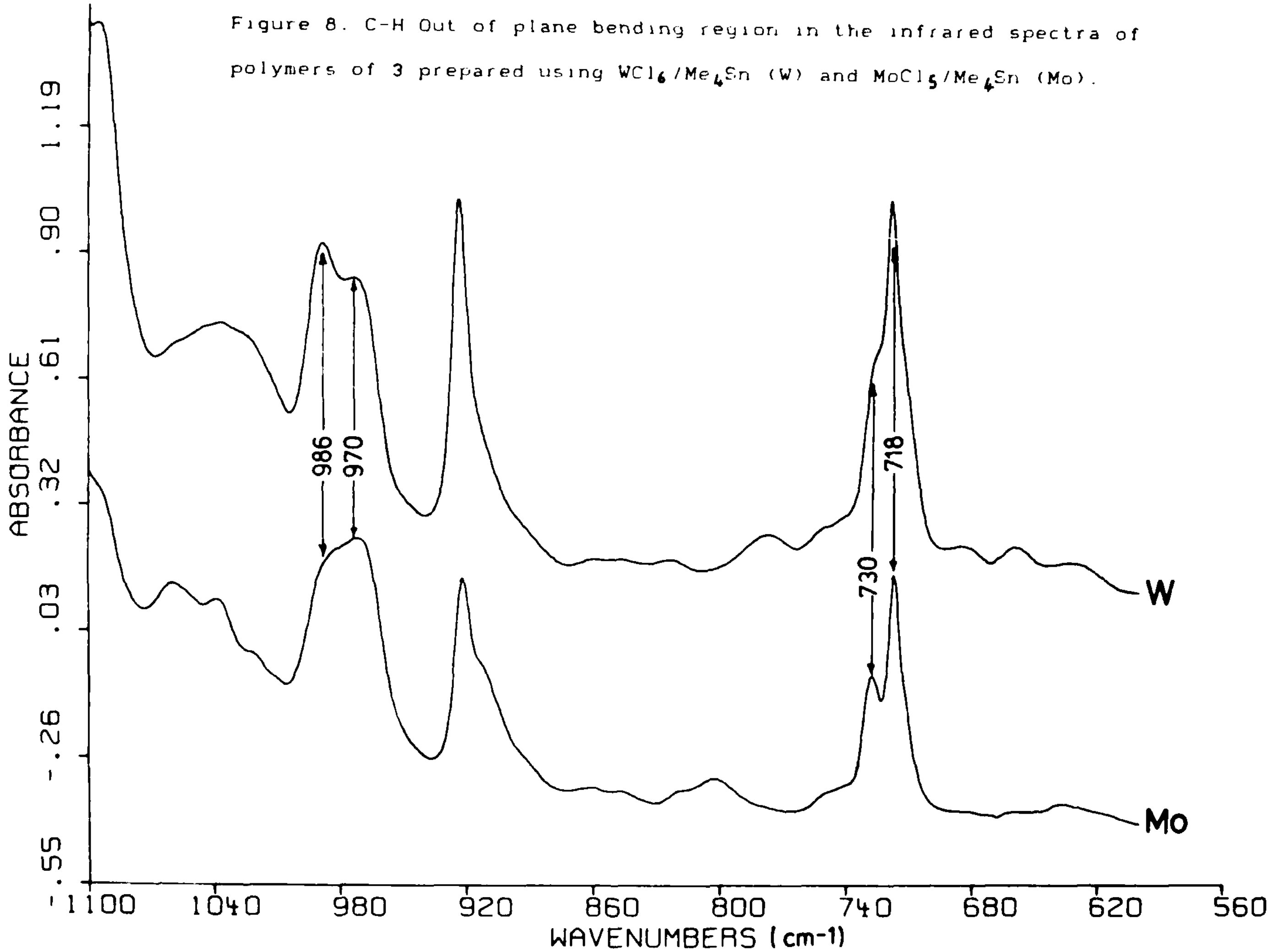


Figure 8. C-H Out of plane bending region in the infrared spectra of polymers of 3 prepared using WCl_6/Me_4Sn (W) and $MoCl_5/Me_4Sn$ (Mo).

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 ^{13}C nmr spectra of polymers with a high trans vinylene content was a consequence of stereoregularity or simply the vinylene sequence effect.

References and Notes

1. For one perspective see "The Chain Straighteners", F.M.Mcmillan, The MacMillan Press, London, 1979.

2. It may be argued that polytetrafluoroethylene is linear and may therefore be regarded as stereoregular in the same sense as high density polyethylene.

3. Stereospecific polymerization of hexafluoropropene has been described (D.Sianesi and G.Caporiccio, Macromol.Chimie,**60**, 213 (1963)).

4. Polymerization of trifluoromethyl substituted alkenes with Ziegler catalysts gives polymers with higher m.pts than radically derived analogues (C.G.Overberger and E.B.Davidson, J.Pol.Sci.,**62**,23 (1962)), suggesting stereoregular products; the continuation of this work (C.G.Overberger and G.Khattab, J.Pol.Sci.,**A1**,**7**,217 (1969)) was concerned with reactivity rather than polymer microstructure, a re-examination of these materials with the aid of high field nmr might prove interesting.

5. Radical polymerization of polyfluoroalkylmethacrylates can lead to predominantly syndiotactic polymers (W.M.Lee, B.R.McGarvey and F.R.Eirich, J.Pol.Sci.,**C**, **22**, 1197 (1969) and refs therein); similarly poly(methyl α-fluoroacrylate) was provisionally assigned as the syndiotactic material (C.U.Pittman, M.Ueda, K.Iri and Y.Imai, Macromolecules,**13**, 1031 (1980)).

6. Detailed ^{1}H, ^{19}F and ^{13}C nmr spectroscopic examination of commercial samples of poly(vinyl fluoride), poly(vinylidene fluoride), poly(fluoromethylene) and poly(trifluoroethylene) (A.E.Tonelli, F.C.Schilling and R.E.Cais, Macromolecules, **14**, 560 (1981)) showed that they contained varying proportions of HT, HH and TT monomer placements and were not stereoregular. There has been a report of polymerization of vinyl fluoride with Ziegler-Natta catalysts (R.N.Haszeldine, T.G.Hyde and P.J.T.Tait, Polymer, **14**, 221 (1973)), no evidence of microstructure was presented.

7. For example, in a recent review of "Trends and Perspectives for the Technological and Commercial Development of Fluorine Chemicals" there was no mention of stereoregular fluoropolymers (F.Lombardo, J.Fluorine Chem., **18**, 1 (1981)).

8. The two processes often use similar combinations of catalysts, but the closeness of the relationship between the two processes is a matter of debate; see K.J.Ivin, J.J.Rooney, C.D.Stewart, M.L.H.Green and R.Mahtab, J.Chem.Soc., Chem.Comm., 604, (1978) and ref.11, pp92-97.

9. J.G.Hamilton, K.J.Ivin, J.J.Rooney and L.C.Waring, J.Chem.Soc., Chem.Comm., 159 (1983).

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11. K.J.Ivin "Olefin Metathesis", Academic Press, London, 1983.

12. Ref.11, p.253, Table 13.2.

13. W.W.Porterfield and S.Y.Tyree, Inorg. Synth.,**9**, 133 (1967).

14. E.O.Fischer and A.Maasbol, Angew. Chem. Internl. Edn.,**3**, 580 (1964).

15. T.J.Katz and N.Acton, Tetrahedron Letters, 4251 (1976).

16. D.M.Dodderell, D.T.Pegg and M.R.Bendall, J.Magnetic Res.,**48**, 323 (1982).

17. A.S.Wexler, Spectrochimica Acta, **21**, 1725 (1965).

PAPER 3

THE RING OPENING POLYMERIZATION OF ENDO- AND EXO-5-TRIFLUOROMETHYLBICYCLO-[2.2.1]HEPT-2-ENE

Summary

An analysis of their high field ^{13}C nmr spectra 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 $MoCl_5/Me_4Sn$ 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.

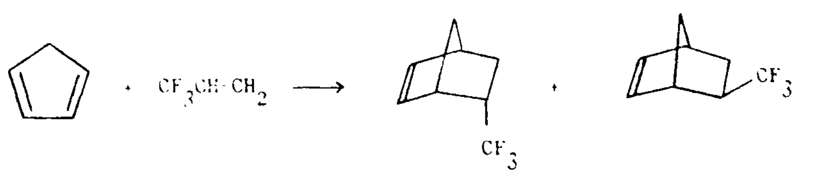
INTRODUCTION

The background and objectives of this study were set out in the first paper of the series.[1] A significant part of the present understanding of stereoregulation in metathesis ring opening polymerization was obtained from detailed studies of the ^{13}C nmr spectra of polymers of methyl substituted norbornenes.[2] 5-Trifluoromethylnorbornenes are readily accessible and in this paper we report a study of the ^{13}C nmr spectra of some of their polymers prepared using $OsCl_3$, $ReCl_5$ and $MoCl_5/(CH_3)_4Sn$ catalysts.

EXPERIMENTAL

Monomers

The Diels Alder reaction between cyclopentadiene and 3,3,3-trifluoropropene[3] 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



I endo I exo

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 $^{3}J_{H-F}$ = 15 Hz) and at 66.1 ppm (doublet $^{3}J_{H-F}$ 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 ^{1}H and ^{19}F spectra.[4] However, in previous analyses of the ^{19}F spectra of fluorinated monomers in this group we have used the generalisations 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 a chemical proof remains desirable, since fluorine substitution often results in anomalous chemistry.

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 68.0 ppm	66.1 ppm	Yield/ %
20	3	10.6	100	3
160	3	37.0	100	72
200	7	55.5	100	75

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 described.[1] The results of polymerizations of I are summarized in Table 2. The product polymers

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)	Temp. (°C)	Time (hrs.)	Yield %
A	Exo	$OsCl_3$	None	1:200	CE, 0.3	40	12	35
B	Endo	$OsCl_3$	None	1:200	CE, 0.2	40	5	30
C	Endo	$MoCl_5$	Me_4Sn	1:2:200	C, 0.2	RT	2 mins	65
D	Endo	$ReCl_5$	None	1:200	CE, 0.25	40	2	10

a) C - chlorobenzene, CE - 1:1 mixture (vol. for vol.) of ethanol and chlorobenzene.
b) RT - room temperature, roughly 15 ± 5°C.

were all soluble and were purified by successive reprecipitation from acetone into methanol, and dried under vacuum for 24 hrs. 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.

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	[illegible]
	D	58.4	5.0	[illegible]
Calculated	A, B, C, D	59.3	5.6	[illegible]

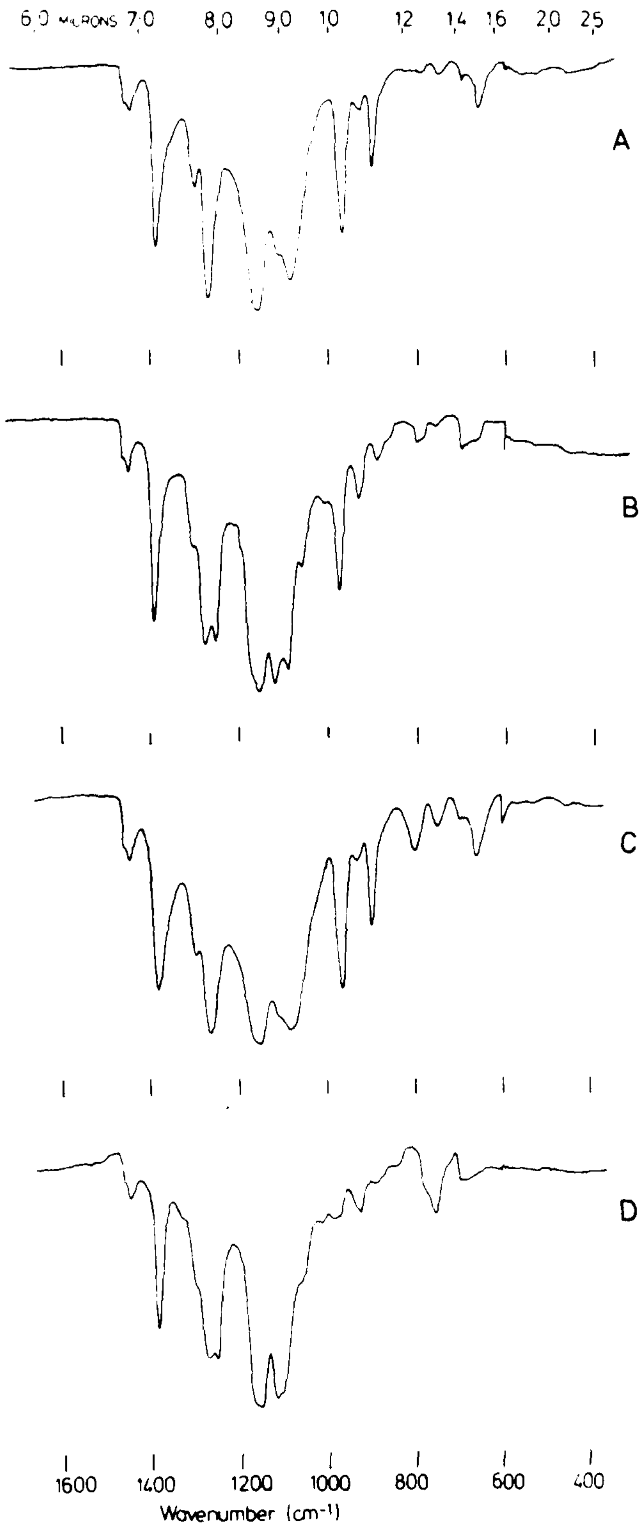


Figure 1. Infrared spectra of thin films of polymers A, B, C and D (Table 2).

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.

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

Shift ppm				Assignment
Endo, $OsCl_3$	Endo, $MoCl_5$	Endo, $ReCl_5$	Exo, $OsCl_3$	
134.01	133.62		133.20	C2, t, TH
133.59	133.00	133.95		C2, c, TH
133.13		133.63		C2, c, TT
132.73	132.20	132.68	132.60	C2, t, TT
130.43	130.00	130.43	132.48	C3, t, HH
130.20	129.70			C3, t, HH
129.62	129.06	129.91		C3, c, HH
129.52		129.52		C3, c, HT
129.19	128.66	129.17	131.86	C3, t, HT
128.5 (q)	127.71 (q)	128.28 (q)	129.09 (q)	C8
$^1J_{C-F}$ = 281 Hz	$^1J_{C-F}$ = 270 Hz	$^1J_{C-F}$ = 277 Hz	$^1J_{C-F}$ = 277 Hz	
~46 (m)	~46 (m)	46.6 (m)	47.9 (q) $^2J_{C-F}$ = 25.4 Hz	C5
43.50	43.38	43.37	43.94	C1, t
43.39	43.28			C1, t
41.96	41.75	41.82		C7, c
		41.47		C7, c
		41.06		C7, c
41.70	41.53		42.14	C4, t
			42.01	C4, t
40.21			41.46	C7, t
40.06			41.27	C7, t
		38.[illegible]		
37.81	37.03	37.63		
		37.36		C1/4c
		37.05		
34.06	33.77	34.09	32.89	C6, c
33.76	33.43	33.42	32.80	C6, c

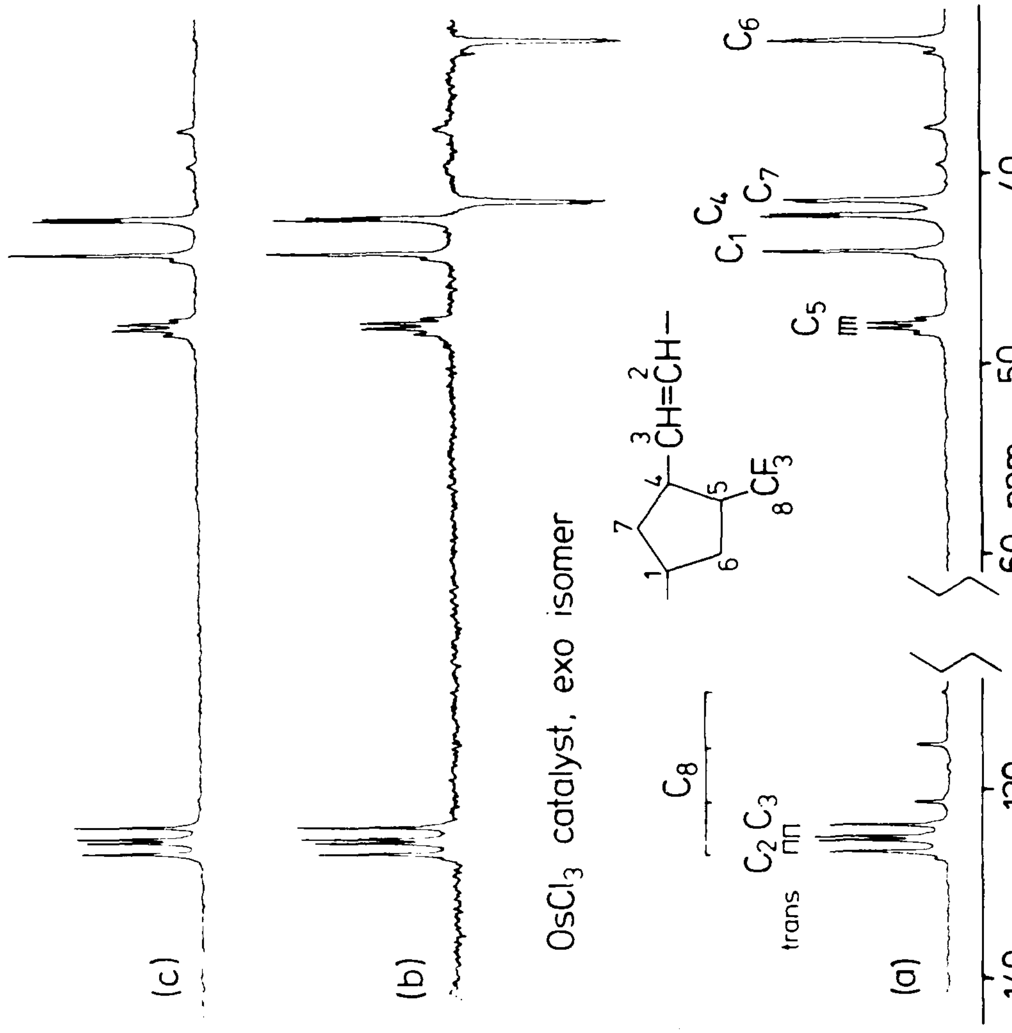
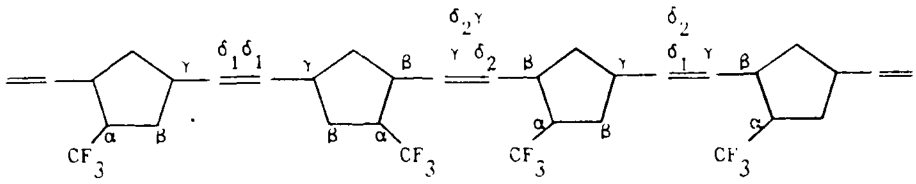


Figure 2. ^{13}C Nmr spectrum of poly(exo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by $OsCl_3$ initiation, recorded as a solution in $(CD_3)_2CO$ at 90.56 MHz with TMS as internal reference.
a) The complete spectrum, b) DEPT spectrum showing $\underline{C}H$ normally and $\underline{C}H_2$ inverted and c) DEPT spectrum showing only $\underline{C}H$ carbons.

The resonance due to the carbon of the trifluoromethyl group is easily distinguished as a quartet at 120.0 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 CF_3 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 CF_3 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 documented;[2] however, an analogous documentation for CF_3-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]

C_6F_{13}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-
31.4 20.6 29.7 29.7 29.7

H-CH_2-CH_2-CH_2-CH_2-CH_2-
14.4 23.4 32.7 30.2 30.5

	α	β	γ	δ	ε
Δ	+17.0	-3	-3	-0.5	-0.8

$$C_6F_{13}-CH_2-CH_2-CH_2-CH_2-OH$$
$$\quad 31.0 \quad 18.1 \quad 33.1 \quad 62.7$$

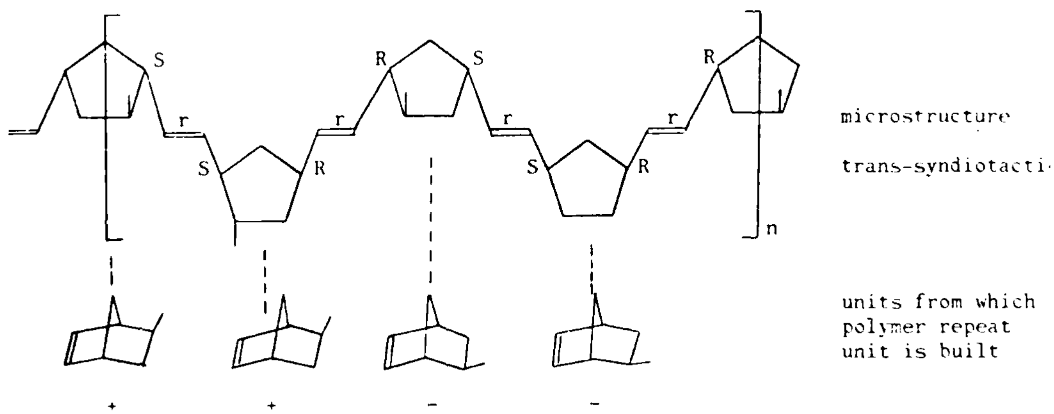
$$H-CH_2-CH_2-CH_2-CH_2-OH$$
$$13.6 \quad 19.1 \quad 35.0 \quad 61.4$$

	α	β	γ	δ
Δ	+18.3	-1	-2	+1.3

This admittedly rather limited data leads to a prediction of a large downfield shift for resonances of carbons α to a CF_3, a small upfield shift for β and γ carbon resonances, and a small unpredictable δ effect. Considering 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 splitting is 0.63. This analysis of the vinyl carbon resonances is consistent with an assignment of the polymer as all trans or all cis, since cis/trans isomerization would double the number of resonances. However, infrared spectroscopy (Figure 1, A) 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 providing 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.

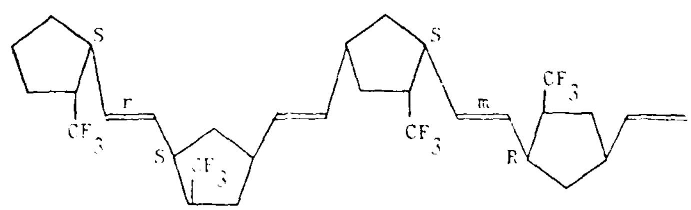
The methylene and methine signals were distinguished with the aid of a DEPT spectrum. In order to assign these carbons it is necessary to consider their position relative to the trifluoromethyl group (see above). The signal for C-5, adjacent to the trifluoromethyl group is easily identified by its multiplicity (quartet $^2J_{C-F}$ 25.4 Hz), a consequence of its coupling to the CF_3 group. 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 polynorbornene[9] 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 <u>all trans</u> 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; <u>but</u> this requires an enantiomer selection by the catalyst in the sequence ++-- which seems a little far fetched, although not impos ible. 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 $ReCl_5$ (Figure 5) catalysis. The polymer obtained from $OsCl_3$ catalysed polymerisation 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 CF_3 group is easily identified as a quartet ($^1J_{C-F}$ = 271 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 the magnitude of the substituent shift effect would be expected to be different as a result of the different stereochemistry, and it clearly is. This trans assignment receives strong support from the infrared spectrum of this polymer (Figure 1, B) 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. Normally, mr splitting of olefinic carbon resonances is too small to observe as a result of the insignificant difference in



HHr HHm

environment between the two forms. However, in the HHr dyad, the CF_3 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 vinyl carbons in the two forms to allow them to be resolved. No such splitting was observed in the polymer derived from exo monomer and $OsCl_3$ catalysis, so it is evident that the stereochemistry of the substituent is important. This is reasonable since for the polymer derived from the exo-isomer the CF_3 and vinylene 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.

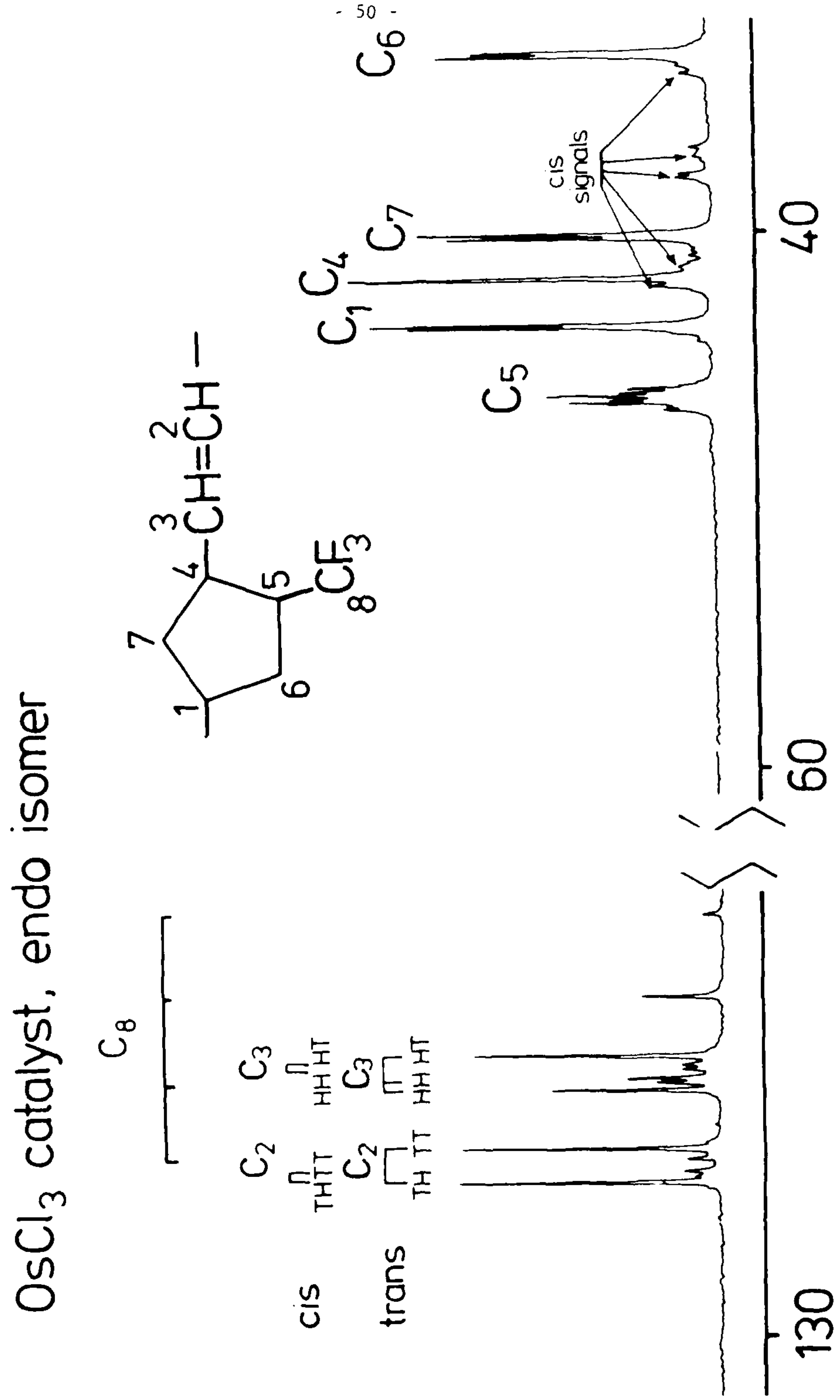


Figure 3. ^{13}C Nmr spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by $OsCl_3$ initiation as a solution in $(CD_3)_2CO$ at 90.56 MHz with TMS as internal reference.

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 $OsCl_3$ 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, which 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 blocky cis signals, indicating that they are in fact ct peaks, and that there is a random distribution of low concentration 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 also has to be treated with caution as the resolution is not particularly good and consequently the integration not very reliable. Infrared 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 $OsCl_3$ gives rise to a high trans atactic polymer.

The spectrum obtained from $MoCl_5$ catalysed polymerization of endo-I (Figure 4) is very similar to that of the polymer produced by $OsCl_3$ catalysis except the weak peaks have increased in intensity and the resolution is not quite as good. A lack of exact superimposibility of the two spectra may be a consequence of the requirement to use different solvents.

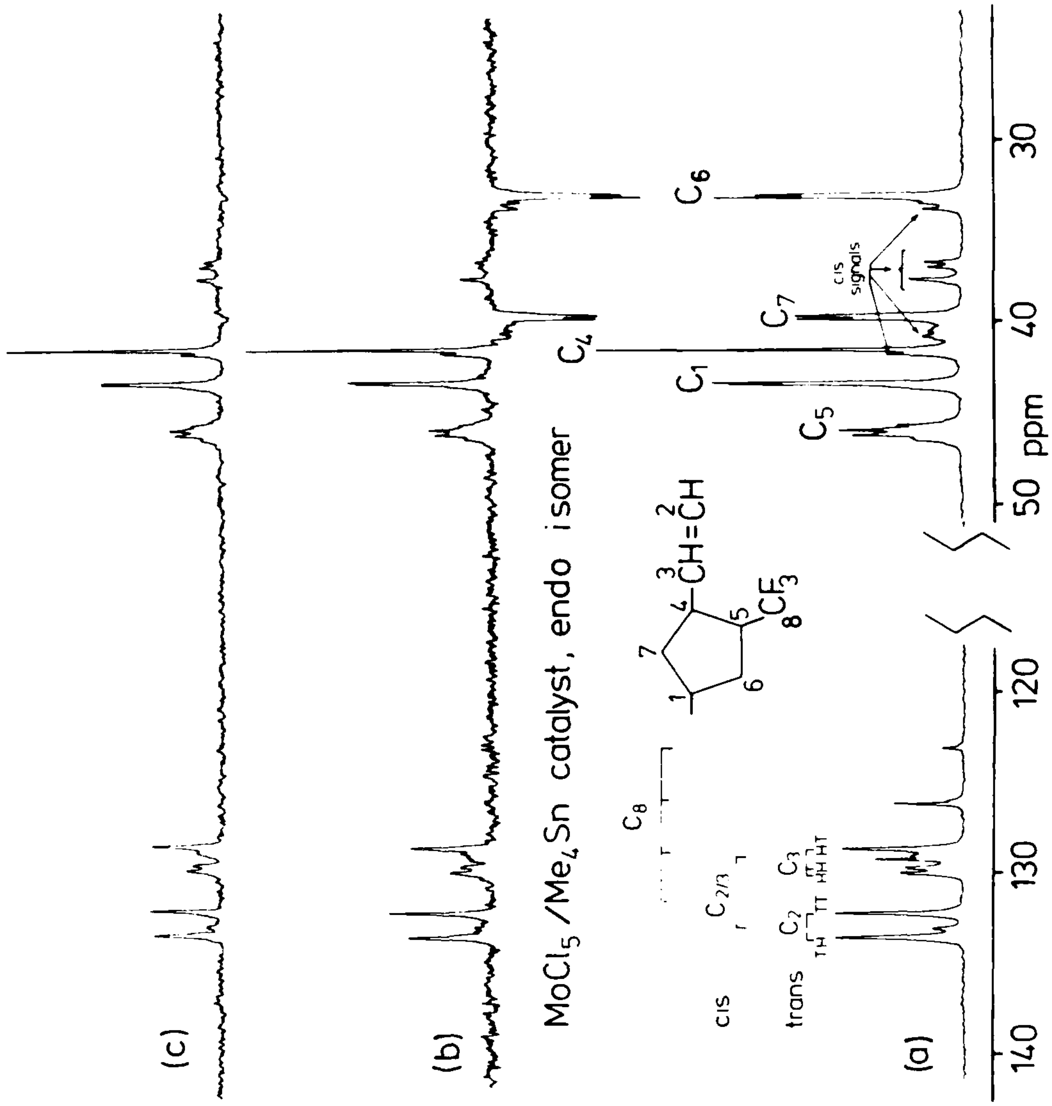


Figure 4. ^{13}C Nmr spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by $MoCl_5/Me_4Sn$ initiation, recorded as a solution in $CDCl_3$ at 90.56 MHz with TMS as internal reference. a) The complete spectrum, b) DEPT spectrum showing CH normally and CH_2 inverted and c) DEPT spectrum showing only CH carbons.

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 $OsCl_3$. 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 breadened trans peak. The σ_c value calculated from the computer printout for these signals is 0.12 which is lower than for the $OsCl_3$ polymer from endo I and inspection of Figures 3 and 4 and the infrared spectra, Figure 1, B and C, 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 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_2 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 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 vinylic 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.

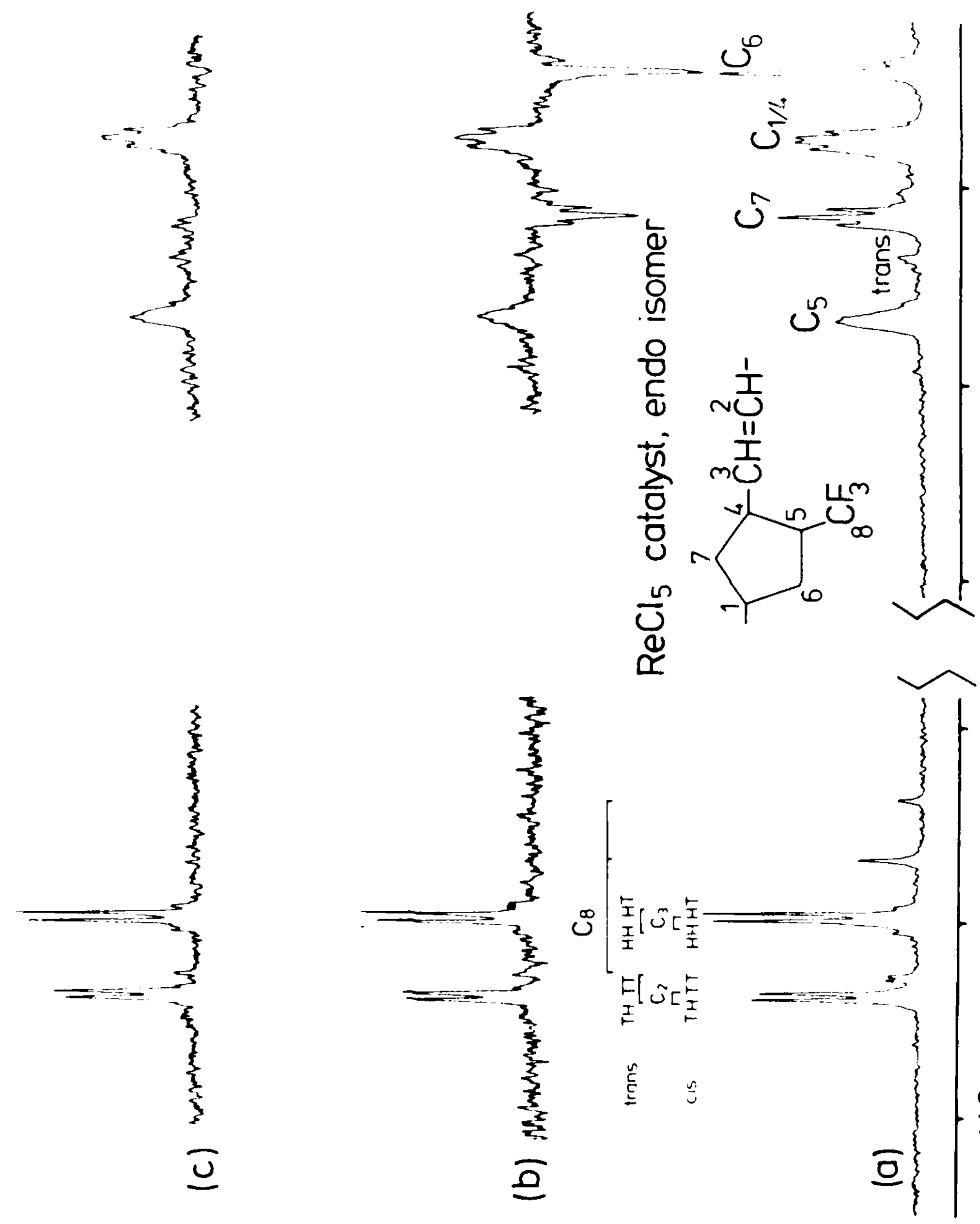


Figure 5. ^{13}C Nmr spectrum of poly(endo-4-trifluoromethyl-1,3-cyclopentylene-vinylene) prepared by $ReCl_5$ initiation, recorded as a solution in $(CD_3)_2CO$ at 90.56 MHz with TMS as internal reference. a) The complete spectrum, b) DEPT spectrum showing CH normally and CH_2 inverted and c) DEPT spectrum showing only CH carbons.

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 environments.[10]

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 infrared 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 nmr spectra of polymers of 5-trifluoromethylbicyclo[2.2.1]hept-2-ene together with their infrared 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 which 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 (σ_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.

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PAPER 4

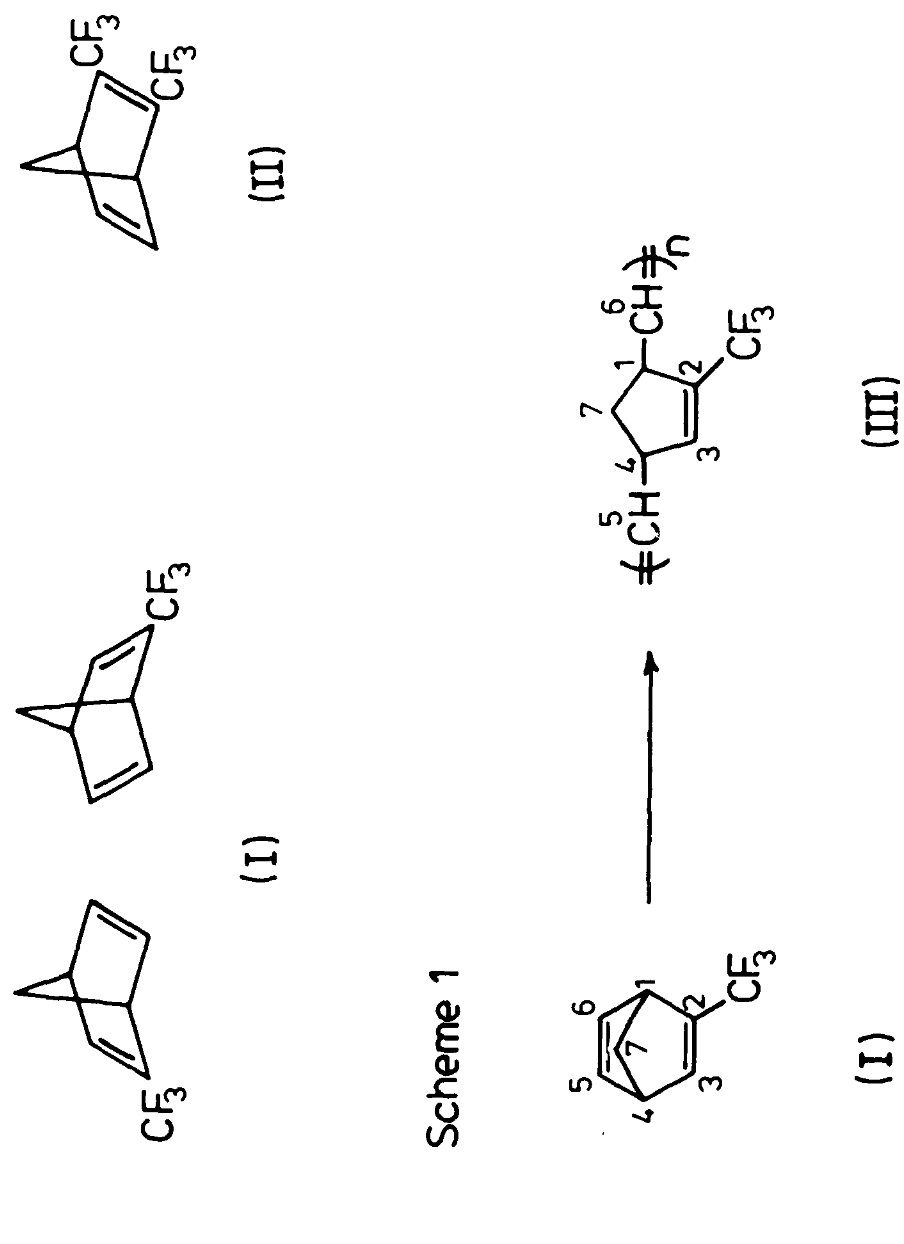
THE RING OPENING POLYMERIZATION OF 2-TRIFLUOROMETHYLBICYCLO[2.2.1]HEPTA-2,5-DIENE

ABSTRACT

2-Trifluoromethylbicyclo[2.2.1]hepta-2,5-diene undergoes metathesis ring opening polymerization under the influence of the initiators $WCl_6/(CH_3)_4Sn$, $MoCl_5/(CH_3)_4Sn$, $OsCl_3$, $RuCl_3$, $IrCl_3$, and $ReCl_5$. The only product which displays evidence indicative of stereoregulation is that derived from $ReCl_5$.

INTRODUCTION

The background and motivation for this work was set out in the introduction to the first paper of this series(2). The initial objectives being to investigate the polymerizability of a range of fluorinated monomers with a variety of initiator systems, and to establish the microstructure of the polymers produced by analysis of their infra-red and nmr spectra, particularly the high field ^{13}C-nmr spectra. The variety and complexity of microstructures possible as a consequence of metathesis ring opening polymerization of polycyclic alkenes is considerable(3), and in an attempt to simplify the analytical task we started our investigation with symmetrically substituted derivatives of bicyclo[2.2.1]hepta-2,5-diene since the use of such systems eliminated potential complications due to exo/endo isomerism and head-head, tail-tail, and head-tail placements(2,4). In this paper we describe our examination of the polymerization of the racemic monomer 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene (I), and a comparison of the results obtained with those reported previously(2) for the related symmetrical monomer, 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (II).



Scheme 1

EXPERIMENTAL

The monomer for this work was prepared and purified by the methods described previously(5). General experimental techniques, polymerization procedure, and equipment details have also been documented in earlier papers in this series. Table 1 records the experimental details for the polymerizations. The polymers were purified prior to analysis by successive reprecipitation from acetone into methanol, and could be solvent cast to give colourless transparent films.

Table 1. Polymerization of 2-Trifluoromethylbicyclo[2.2.1]hepta-2,5-diene(I)

Catalyst	Co-catalyst	Molar ratio Cat.: Co-cat.: I	Solvent[a] (ml)	Temp.[b] (^oC)	Time (hrs.)	Yield[c] %
$MoCl_5$	Me_4Sn	1 : 2 : 200	C, 7	RT	5 mins.	50
WCl_6	Me_4Sn	1 2 : 200	C, 4.6	RT	5 mins.	~90
$OsCl_3$	None	1 : 0 : 150	CE, 0.3	40	2½	25
$RuCl_3$	None	1 : 0 : 150	CE, 0.14	40	65	5
$IrCl_3$	CF_3COOH	1 : 5 : 200	CE, 1.5	40	48	25
$ReCl_5$	None	1 : 0 : 200	C, 0.3	60	48	7

[a] C - chlorobenzene, CE - 1:1 (vol. for vol.) mixture of chlorobenzene and ethanol.

[b] RT - room temperature, roughly 15 ± 5^{o}C. The polymerization was notably exothermic, no monitor of temperature was placed in the reaction vessel.

[c] After re-precipitation and drying under vacuum for at least 24 hrs.

RESULTS AND DISCUSSION

The first point that emerges from this study is that it is possible to polymerize monomer I with a wider range of metathesis catalysts than monomer II. Table 1 lists six different catalysts based on the chlorides of W,Mo,Ru,Ir,Os and Re all of which were successfully used to polymerize I; by contrast II was not polymerized in any of several attempts with Ir, Os or Re based catalysts. While it is admittedly risky to read too much into a failure to achieve reaction this observation implies that replacing one of the trifluoromethyl groups in II by hydrogen has the effect of increasing the monomer's susceptibility, even though the substituents concerned are quite remote from the double bond undergoing reaction.

The fact that the polymerization of I with metathesis catalysts leads to the production of polymers of overall structure III (scheme 1) was established in an earlier study(5); the questions at issue here are concerned with the geometry of the vinylene units in the polymer chain and the details of microstructure.

The infra-red spectra of these polymers (see figure 1) are, as expected, dominated by the intense absorptions between 1350 and 1100cm^{-1} associated with the trifluoromethyl group: although these bands are consistent with the expected structure no structurally useful information could be deduced from them nor from the C-H or C=C stretching absorptions in the 3000 and 1650cm^{-1} regions respectively. However, the absorptions characteristic of out-of-plane vinylic C-H bending are well resolved and can be assigned with some confidence. The band arising from the C-H at C-3 (scheme 1 III) should have roughly the same intensity relative to the absorptions due to the trifluoromethyl groups in all the samples and the band at 860cm satisfies this condition; by contrast the out-of-plane bending modes for the vinylene C-H bonds should occur with variable intensities dependant on the relative concentrations of cis and trans geometries, and the bands at 970(trans) and 720cm^{-1} (cis) satisfy this requirement. It was something of a surprise to find that five of the six infra-red spectra of these polymers were virtually superimposable all displaying significant absorptions at both 970 and 720 cm^{-1}, the exception was the spectrum of the polymer prepared using $ReCl_5$ initiator in which the 970cm^{-1} band

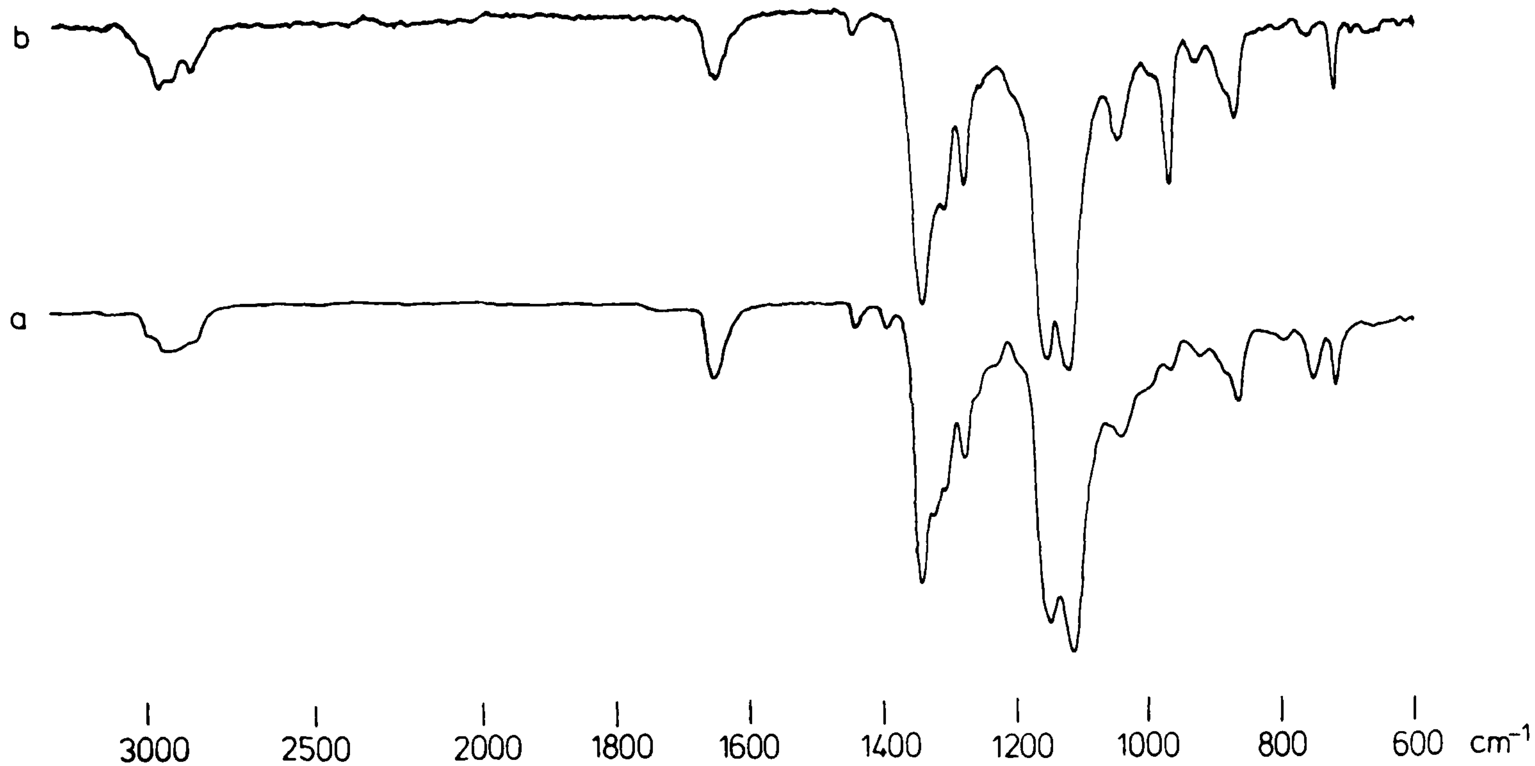


Figure 1. Infra-red spectra of thin films poly(2-trifluoromethyl-1,4-cyclopent-2-enylene vinylene), a) $ReCl_5$ initiation b) $MoCl_5/(CH_3)_4Sn$ initiation.

had almost vanished. The spectra of polymers derived via $ReCl_5$ and $MoCl_5/(CH_3)_4Sn$ initiation are shown in Figure 1 to illustrate the features discussed above.

The conclusion from this examination of infra-red spectra is that $ReCl_5$ initiation gives rise to a polymer with a high cis vinylene content, which is consistent with other polymerizations initiated by this compound(3,6), whereas all the other initiators give significant proportions of both cis and trans vinylenes, this last observation is something of a surprise since $IrCl_3$, $RuCl_3$, and $OsCl_3$ have all shown a marked tendency to give polymers with a high trans vinylene content with a variety of related monomers(3,6).

Examination of the ^{13}C nmr spectra confirmed the overall conclusions drawn from the analysis of the infra-red spectra in that, although there were some variations in both the quality (S/N) and in the detail of resolved fine structure, the overall appearance of the spectra was the same for all the polymers except that prepared via $ReCl_5$ initiation. The spectra recorded for polymers obtained via $OsCl_3$ and $ReCl_5$ initiation are reproduced in Figures 2 and 3 respectively.

In Figure 2 the DEPT spectra distinguish the quaternary carbons and those carrying one and two hydrogens and make the assignment of resonances as shown in the figure fairly straightforward. Thus, the resonance at lowest field (140.4ppm) is assigned to C-3 and its broadness is taken as evidence that it represents the sum of signals from several non-equivalent environments; the poorly resolved quartet centered at 135.9ppm is assigned to C-2 with J $\sim$30Hz; the multiplet between 133.3 and 131.7ppm arises from the different vinylene carbon environments, and the quartet of doublets centered at 123.2ppm with Jq=270Hz indicates that the trifluoromethyl groups are

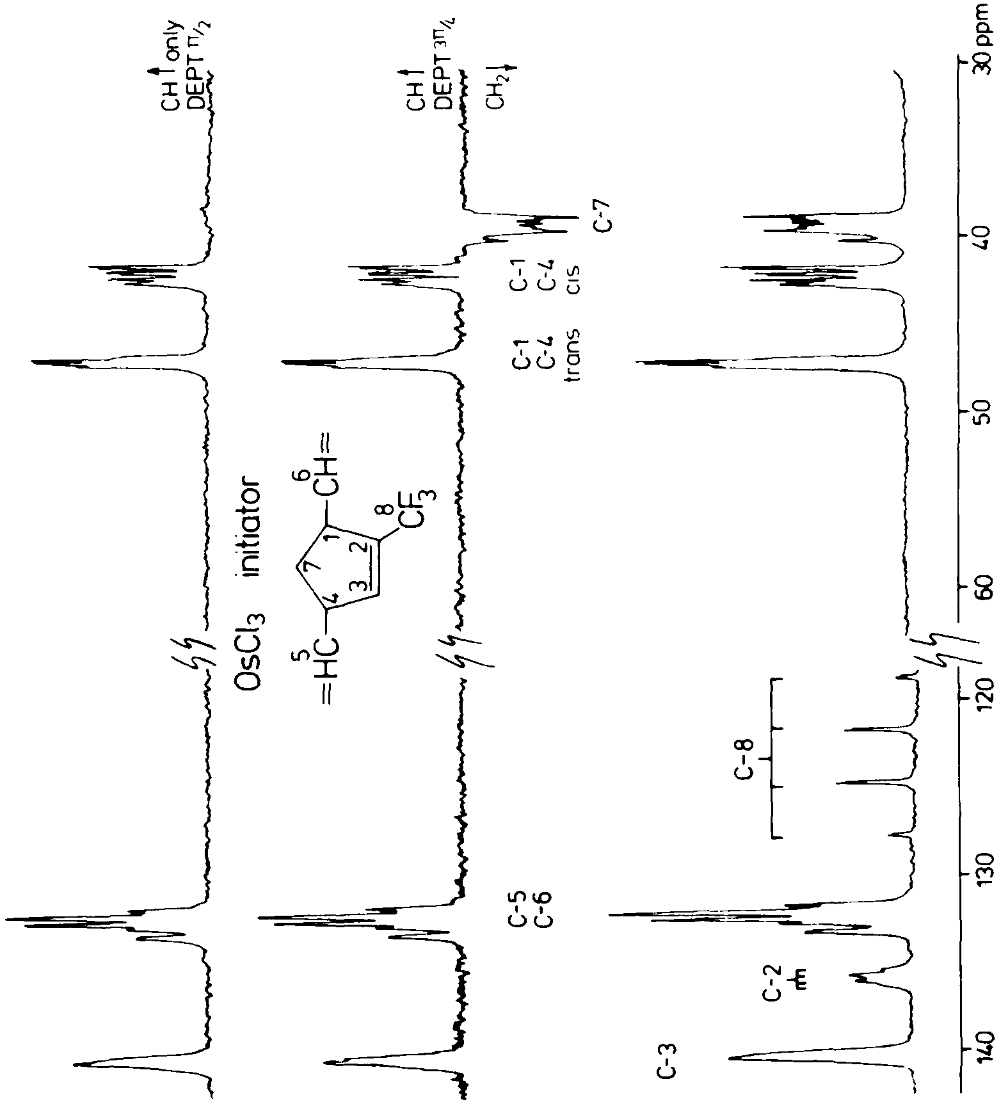


Figure 2. [13]C-nmr spectra for poly(2-trifluoromethyl-1,4-cyclopent-2-enylene vinylene) prepared using $OsCl_3$ initiation, recorded at 90.56MHz, $(CD_3)_2CO$ solution, TMS internal reference.

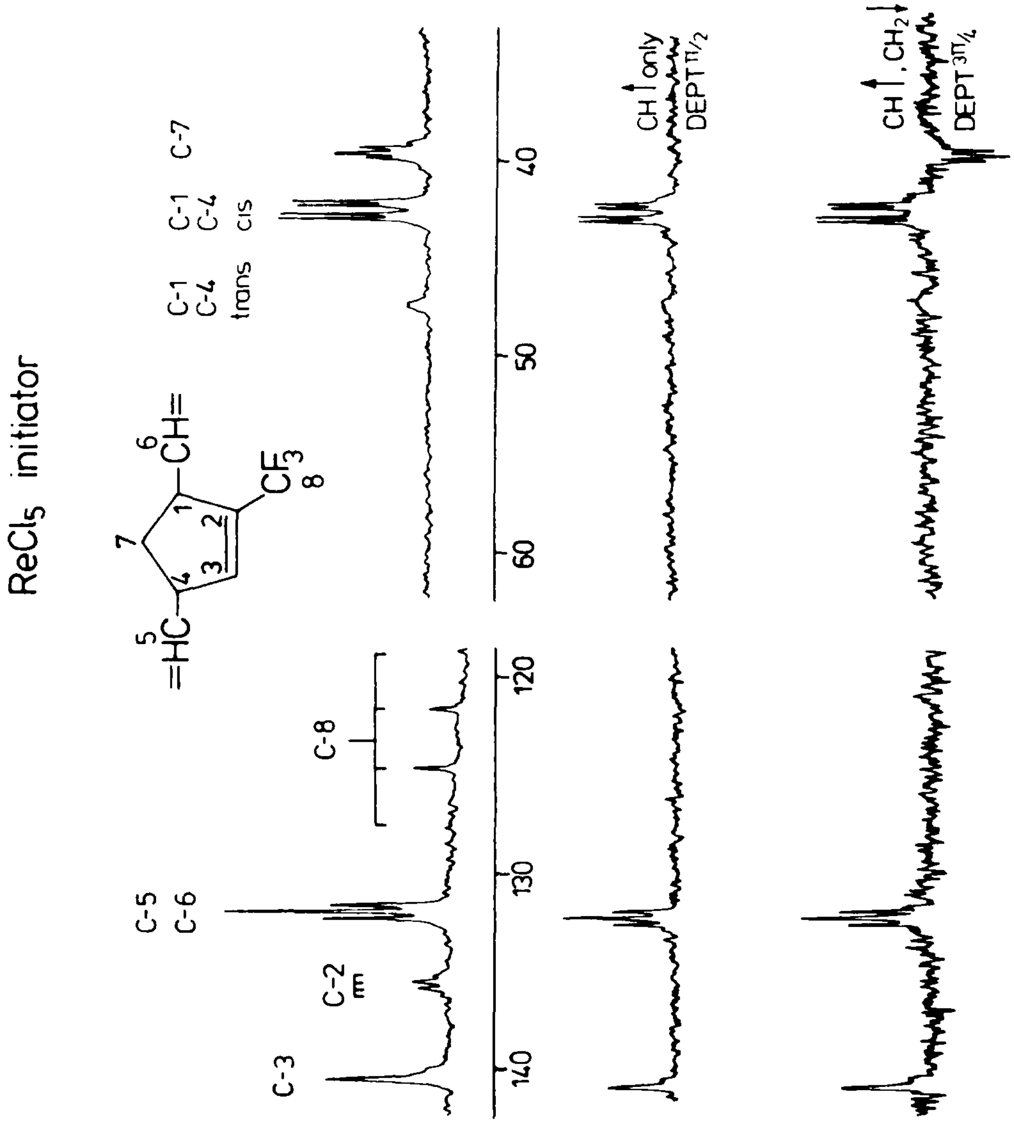


Figure 3 ^{13}C-nmr spectra for poly(2-trifluoromethyl-1,4-cyclopent-2-enylene vinylene) prepared using $ReCl_5$ initiation, recorded at 90.56MHz, $(CD_3)_2CO$ solution, TMS internal reference.

found in at least two non-equivalent environments in this polymer. In the higher field region of the spectrum the resonances due to the allylic methine units are distinguished from the methylene resonances by the DEPT spectra, and the mulitplet between 41.8 and 42.8ppm can be confidently assigned to allylic carbons adjacent to a cis vinylene, with that between 47.2 and 47.5ppm due to allylic carbons adjacent to a trans vinylene(2). The multiplicities of these resonances has so far defied detailed interpretation but demonstrates that this and the related polymers derived from W,Mo,Ru and Ir initiation all have both cis and trans vinylenes in the backbone. The proportions of cis vinylene units can be calculated from the relative intensities of the allylic carbon multiplets and the values are recorded in Table 2, along with the analogous values for polymers derived from II.

Table 2. Fraction of Cis Vinylenes (σ_C) for Samples of Poly(2-trifluoromethyl-1,4-cyclopent-2-enylene vinylene)

Catalyst	σ_C (calculated from allylic carbon signals)	
	I	II
$MoCl_5/Me_4Sn$	0.30	0.13
WCl_6/Me_4Sn	0.48	0.48
$OsCl_3$	0.45	no polymer
$RuCl_3$	0.44	0.28
$IrCl_3$	0.46	no polymer
$ReCl_5$	0.86	no polymer

The data presented in Table 2 indicate that the more readily polymerized monomer I also displays a lower stereoselectivity in polymerization with a variety of catalysts; thus, the very active catalyst system $WCl_6/(CH_3)_4Sn$ does not appear to discriminate between I and II giving roughly equal proportions of cis and trans vinylenes, whereas $MoCl_5/(CH_3)_4Sn$ and $RuCl_3$ both give a higher selectivity with II than with I, and the Os, Ir, and Re chlorides fail to polymerize II at all.

The spectrum of the polymer produced via $ReCl_5$ initiation (Figure 3) was much simpler than those obtained from all the other samples, although unfortunately the yield of this polymerization was extremely low. The more selective ReCl initiator gives a polymer with a high proportion of cis vinylenes (σ_c 0.86). At low field the C-8 and C-2 resonances are easily identified with the aid of the DEPT spectrum. The C-3 vinylene carbon resonance appears at lowest field and is considerably sharper than in the spectrum of the $OsCl_3$ derived polymer, indicating an increased structural homogeneity. The carbon signals C-5 and C-6 appear as three lines in the approximate ratio 1:2:1; the polymer has a high cis vinylene content and these lines are provisionally assigned to the TH,TT,HH, and HT environments, where the middle peak represents coincidence of two environments. At high field the resonance for the allylic carbons adjacent to cis double bonds consists of two sets of two signals at 42.95 and 42.26ppm, and 42.70 and 42.04ppm. This assignment is based on the fact that the total intensity of the C-4 resonance must equal the intensity of the C-1 signal; the higher field signal in each pair has a lower intensity than the low field signal. The C-7 resonance appears as three lines in the approximate ratio 1:2:1; these signals are assigned to the HH,HT,TH and TT effects from adjacent rings with the middle signal again representing chemical shift equivalence of two environments. It is possible that the observed resolution of the carbon resonances could be attributed to m/r effects in an all HHTT or all HT polymer. However, when resolution due to m/r effects has been observed previously(3,6) it was usually in the HH vinylene carbon environment. It seems unlikely that m/r resolution would be observed for all signals, and therefore it is highly probable that this high cis polymer has an approximately equal distribution of HH,HT,TH and TT assembly modes and with all m or all r dyads. It is, however, impossible to determine unambiguously which is the case on the basis of the available data. The fact that the HH and HT signals for C-1, and the TT and TH signals for C-4 have slightly different intensities suggests there may be a small degree of HHTT or HT bias in the polymer. In those cases where unambiguous proof is available(3,7) $ReCl_5$ initiation of ring opening polymerization of substituted norbornenes leads to a cis-syndiotactic microstructure, so these observations are not inconsistent with related literature data. It was not possible to derive any detailed analysis of the multiplicities observed in the spectra of other samples. It does appear, however, that in the other samples the number of resolved lines is higher than would be expected for highly stereoregular polymers and therefore that these materials were probably atactic.

CONCLUSIONS

The racemic monomer 2-trifluoromethylbicyclo[2.2.1]hepta-2,5-diene is more readily polymerized by metathesis ring opening than its 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene analogue. Five of the six initiator systems investigated appeared to give largely atactic products, the sixth ($ReCl_5$) gives a polymer with a high cis vinylene content and, although there appears to be a mixture of head-head-tail-tail and head-tail monomer placements, it is possible that the cis sequences have a high level of tacticity.

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