Precursor routes to polyacetylene: The microstructure of the precursor polymers

W. J. Feast
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, UK

and M. J. Taylor and J. N. Winter
BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, UK
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In the synthesis of polyacetylene via precursor polymers it seems reasonable to assume that the morphology of the product will be dependent, at least to some extent, on that of the precursor. A full stereochemical analysis of precursor polymer structure requires the synthesis of a range of samples with different microstructures. Since this was not possible for the thermally unstable precursor polymers used for the synthesis of polyacetylene, we have conducted studies on the model system poly(7′,8′-bis(carboxymethyl)-bicyclo[2.2.2]octa-5′-ene-2′,3′-diyl)-1,2-ethenediyl. Infra-red and ^{13}C n.m.r. studies establish that this thermally stable analogue of polyacetylene precursors can be prepared with a range of vinylene stereochemistries although it was not possible to establish the details of microstructure completely. Monomers for the synthesis of polyacetylene precursor polymers are potentially bidentate ligands and might be expected to show unusual behaviour with some classes of metathesis catalyst; however, the monomer for this model study showed a conventional response to a range of metathesis catalysts.

(Keywords: metathesis; ring-opening; polyacetylene precursor; microstructure; ^{13}C n.m.r. spectroscopy)

INTRODUCTION

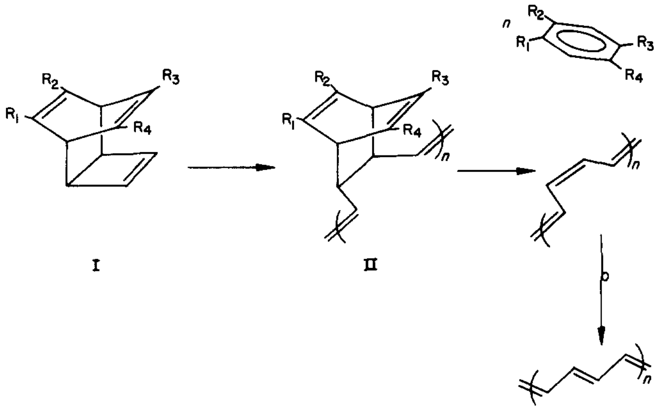
Most polymers are made directly from a monomer or a mixture of monomers. In some circumstances this approach is not effective and alternative strategies have to be adopted, the most familiar of which is the chemical conversion of an appropriate precursor. The earliest syntheses of polyacetylene via addition polymerization established that the material was intractable and air sensitive, and the observation that it could not be processed via either melt or solution methods probably deterred many would-be investigators. The studies of Shirakawa and co-workers[1] on the direct polymerization of acetylene at the interface between a concentrated catalyst solution and the gaseous monomer led to the production of films of polyacetylene and this represented a considerable advance which allowed the fascinating range of electrical properties of the material to be demonstrated and studied. However, the insolubility, infusibility, and lack of any effective means of regulating the polymer's morphology remained a serious inhibition to study of this superficially simple polymer.

A few years ago we reported an alternative synthesis of polyacetylene via a soluble precursor polymer[2], subsequently several variants and refinements of the original synthesis were also described[3,4]. This approach has a number of useful features which have been elaborated in a series of papers[5]. Perhaps the most significant consequence of this 'precursor polymer' approach is that it makes polyacetylene available in a very wide range of morphologies which can be selected and controlled in a reproducible manner. The consequences of this development in synthesis for the materials science of polyacetylene are considerable[6]; in this paper we address another aspect of this approach which might be expected to have some significance, namely the microstructure of the precursor polymer.

DISCUSSION

General considerations

The process which has become known as the Durham precursor route to polyacetylene is summarized in *Scheme 1*. In this process the monomer **I** undergoes metathesis ring-opening polymerization at the double bond of the cyclobutene ring to give the precursor polymer **II** which subsequently undergoes a thermal elimination reaction in which an aromatic unit is lost and polyacetylene is formed. The formation of polyacetylene from precursors **II** is a complicated process in which the first step is a symmetry-allowed elimination reaction which generates a *cis* double bond in the polymer backbone together with



Scheme 1 Durham precursor route to polyacetylene

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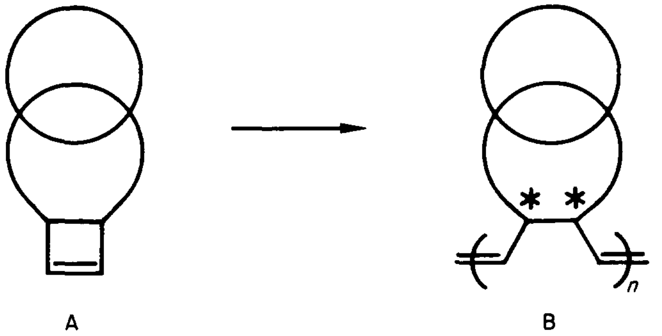
an aromatic molecule which is, of necessity, in close proximity to the newly formed double bond. In subsequent steps the *cis* double bond isomerizes to the more stable *trans* geometry and the eliminated aromatic molecule migrates through the sample and eventually evaporates. The precursor polymers **II** are soluble, and films are cast from solution prior to conversion to polyacetylene. The details of the microstructure of polymer **II** might reasonably be expected to have an influence on the conformation of the polymer in solution and its morphology in the cast film, which in turn may effect the nature of the final sample of polyacetylene obtained via a particular conversion protocol from a particular precursor polymer.

The monomer **I** can have several isomers depending on the substitution pattern. To simplify matters we shall consider only the cases where $R_1 = R_2$ and $R_3 = R_4$. The monomer then has a plane of symmetry and complications from head–tail, tail–tail and head–head placements along the chain are avoided. If R_1, R_2, R_3 and R_4 are different a further potential complication from syn/anti isomerism has to be considered but, in this study, we have used only isomerically pure monomers and as a result can simplify the stereochemical considerations to the generalized form shown in *Scheme 2*.



Scheme 2 Generalized scheme for ring opening polymerization of polycyclic monomers

Thus, ring-opening polymerization of the isomerically pure polycyclic monomer A at the cyclobutene double bond leads to polymer B. In the carbon atom sequence which constitutes the backbone of polymer B the vinylene units may have Z(*cis*, *c*) or E(*trans*, *t*) stereochemistry and the allylic carbons (*) are chiral and may have R or S stereochemistry. We can, following Ivin[7], define monomer assembly modes in terms of vinylene stereochemistry together with the chirality of the adjacent carbons; a double bond with adjacent carbons of opposite chirality defining a meso (m) dyad, whereas the same chirality defines a racemic (r) dyad. For polymer B (*Scheme 2*) there are therefore four assembly modes; *c*m, *c*r, *t*m and *t*r. An homopolymer with all meso assemblies is defined as isotactic and one with all racemic assemblies is defined as syndiotactic and there are four possible stereoregular homopolymers of A. There is a possibility of confusion between the nomenclature adopted for this kind of polymer and the more familiar nomenclature used for the stereochemically simpler polymers of monosubstituted ethylenes and *Figure 1* is included in order to help clarify the matter.

The actual outcome of a particular polymerization of the kind generalized in *Scheme 2* is a complicated function of a variety of factors including: the structure of the monomer, the nature of the catalyst and cocatalysts (if any), the solvent, the temperature, and the concentrations of the various components of the system. It might be expected that the nature of the transition metal centre of the catalyst would exert a dominant influence on the outcome of the process; however, at the current stage of development of understanding of metathesis ring-opening polymerization, while some trends appear to be discernible, no secure generalizations can be made. Thus, for example, the active catalysts generated from tungsten (VI) halides are often found to be non-discriminating giving rise to roughly 50:50 *cis*:*trans* vinylene content and atactic polymers. Nevertheless, it has been shown that tungsten based catalysts can initiate the ring-opening

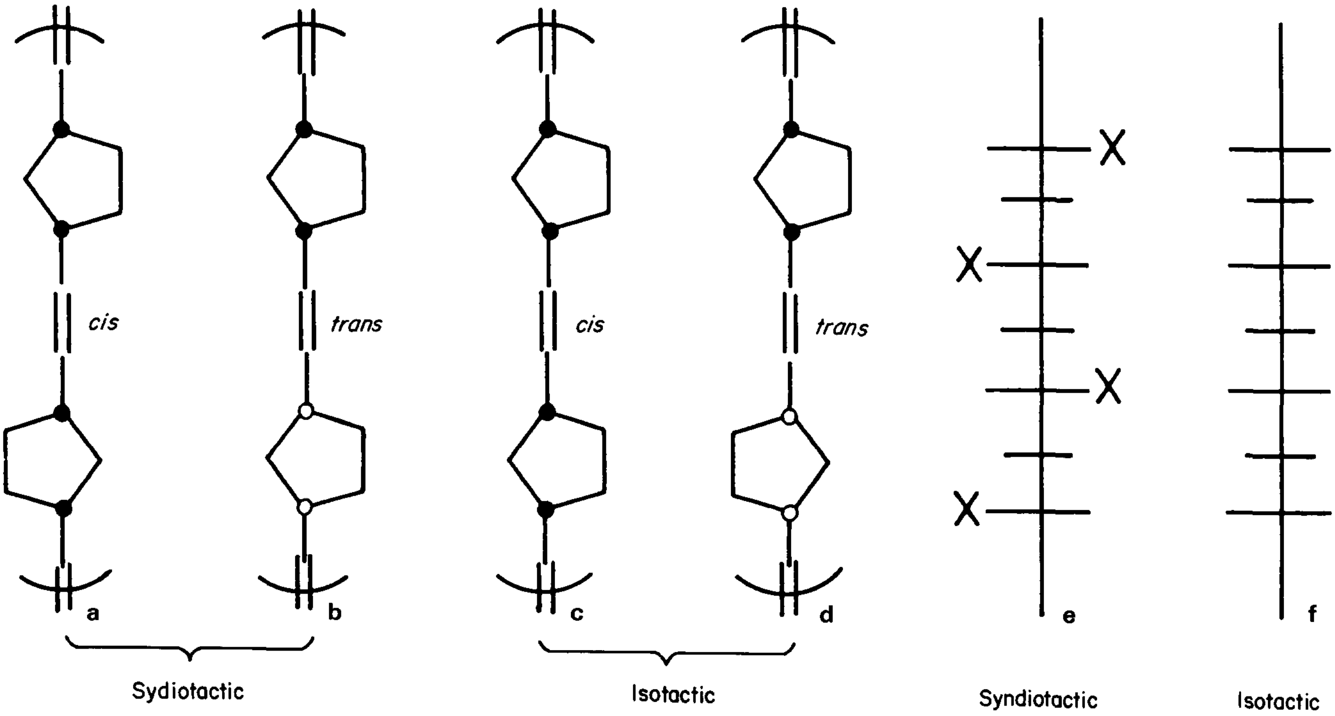


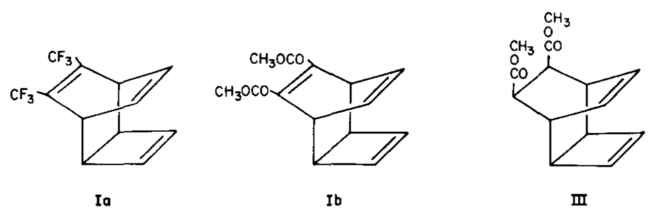
Figure 1 Extended chain conformations of polynorbornene (a→d) and head–tail polymers of monosubstituted ethylenes (e and f)

polymerization of a simple monomer like norbornene to give materials with vinylene contents ranging from high *cis* to high *trans*. Some of the less reactive catalysts appear to have a greater propensity for stereoregulation; for example, almost all polymerizations initiated by $ReCl_5$ lead to materials with a high *cis* vinylene content and, where details of microstructure have been established, to syndiotacticity. By contrast, $IrCl_3$, $RuCl_3$ and $OsCl_3$ based catalysts tend to generate a high percentage of *trans* double bonds with variable tacticity[7].

In practice, the analysis of the structures of polymers produced by ring-opening metathesis has relied heavily on two techniques. In many cases infra-red spectroscopy has been valuable in establishing the relative abundance of *cis* and *trans* vinylene units through an examination of the C–H out-of-plane bending modes. The most generally useful structural probe has been ^{13}C n.m.r.[7,8], which in favourable cases can lead to an absolute specification of the details of chain microstructure[9]. In the majority of cases, where an understanding of the relationship between spectra and microstructure has been established, it has been achieved by correlation of results from polymers prepared from one monomer using a range of catalysts which generate a variety of different microstructures.

Polyacetylene precursor polymers

The synthesis of polyacetylene via a precursor route which has received most attention is that which starts from 7,8-bis(trifluoromethyl)tricyclo-[$4.2.2.0^{2,5}$]-deca-3,7,9-triene (i.e. **Ia** of *Figure 2*) as the monomer. With this system it is to be expected, and inspection of simple molecular models makes it very clear, that in precursor polymer **II** the dyads based on *cis* vinylene units will be much more sterically constrained in either meso or racemic assembly mode than will those based on *trans* units; the consequences of the polarity of the trifluoromethyl groups are harder to assess. It seems reasonable to conclude that a precursor polymer with a high *cis* vinylene content will adopt a stiffer more tightly coiled conformation in solution, which will have consequences for the structure of the solution cast film and product polyacetylene. In practice it is difficult to study the details of the structure of such polymers since they have a limited stability at room temperature. However, we have observed that precursor polymers **II** ($R_1 = R_2 = CF_3$, $R_3 = R_4 = H$) produced using the $MoCl_5/(CH_3)_4Sn$ catalyst are invariably less soluble than analogous polymers produced using the $WCl_6/(CH_3)_4Sn$ system. These differences may be a consequence of the nature and extent of stereoregulation of this monomer by these two catalysts. Unfortunately the temperature and/or duration of reaction required to bring about polymerization with the catalysts which generally give high *cis* ($ReCl_5$) or high *trans* ($RuCl_3$, $OsCl_3$, $IrCl_3$) vinylene contents is such that attempts to prepare precursor polymers inevitably lead to highly coloured (partially converted) or insoluble products.



Ia Ib III

Figure 2 Structural relationship between the widely used monomer (**Ia**), the diester analogue (**Ib**) and the model diester monomer (**III**)

Choice of a model system

In order to try to gain some insights into the questions raised above we have studied a model system. It is known that the monomer **Ib** (*Figure 2*) undergoes the same sequence of reactions as the more widely studied trifluoromethyl substituted case **Ia**. The system is less attractive since the eliminated dimethylphthalate is less volatile than hexafluoroxylene and consequently less easily removed from the product polyacetylene. When the 7,8-double bond of the diester monomer **Ib** is saturated one of the possible products is readily available as isomerically pure compound[10] and this is the monomer we have used for our model studies, the structural relationships are illustrated in *Figure 2*. The polymer derived from the monomer **III** is stable and does not undergo elimination of a cyclohexadiene to yield polyacetylene; however, it is structurally a close relative of the diester polymer (**IIb**). The ester substituents in the model are situated far from the cyclobutene unit which undergoes ring opening polymerization and would not be expected to interfere with the assembly mechanism; this is the basis of our choice of this monomer for our model studies.

EXPERIMENTAL

Synthesis of cis-*7,8-bis(carboxymethyl)-endo-tricyclo [$4.2.2.0^{2,5}$]deca-3,9-syn diene (III)*

A solution of maleic anhydride (20.6 g) in freshly distilled 1,2-dichlorobenzene (100 ml) was heated to reflux under dry nitrogen, a solution of cyclooctatetraene (20.6 g) in dichlorobenzene (25 ml) was added dropwise. The mixture was refluxed for one hour, on cooling the 7,8-carboxylic acid anhydride of endo-tricyclo[$4.2.2.0^{2,5}$]-deca-3,7-syn-diene crystallized and was recovered by filtration, washed (diethyl ether), and dried (32.1 g, 80%). The white crystalline product was mixed with methanol (150 ml) and concentrated sulphuric acid (75 ml) and the mixture refluxed for one and a half hours, cooled to room temperature and poured onto crushed ice. The pale yellow solid which separated was recovered by filtration, dissolved in diethyl ether and this solution was washed with 5% aqueous sodium bicarbonate and then distilled water, dried and the solvent evaporated. The diester (**III**) was purified by two recrystallizations from n-hexane.

Polymerizations

General experimental procedures, purification of solvents, preparation of catalysts etc, have been described previously[11]. The molar ratio of monomer **III**:transition metal catalyst:co-catalyst (when used) was 100:1:2.

(A) Tungsten hexachloride was dissolved in chlorobenzene to give a 0.01 g ml^{-1} blue-black solution; tetramethyl tin (0.055 ml) was added to 8 ml of this solution and the resulting chestnut brown solution stirred at room temperature for 30 min. This aged catalyst solution was syringed into a stirred solution of monomer **III** (5.0 g) in chlorobenzene (11 ml); there was an immediate colour change to violet-black and the solution became viscous within 5 min. The mixture was stirred for one hour and the reaction was terminated by pouring the mixture into a solution of methanol (2 ml) in acetone (100 ml). The polymer was recovered by two reprecipitations from acetone into methanol, and then dried (24 h, room temperature, 10^{-3} mm Hg) to yield 4.55 g 91% of white polymer, sample A.

(B) Case A was repeated with the addition of 0.8 g oct-4-ene to the monomer solution before the addition of catalyst. The reaction mixture was precipitated into hexane (1000 ml). Catalyst residues which precipitated with the polymer were removed by the reprecipitation procedure described in A above, 0.2 g (4%) of polymer B were obtained. Evaporation of the hexane gave unreacted **III** (4.5 g).

(C) Case A was repeated replacing tungsten hexachloride by molybdenum pentachloride. The activated catalyst solution was pale orange-brown, a colour maintained throughout the reaction. The yield of polymer C was 4.9 g, 96%.

(D) Ruthenium trichloride trihydrate was dissolved in a 50/50 (V/V) mixture of ethanol and chlorobenzene to give deep red-brown solution, 0.01 g ml^{-1}. This catalyst solution (5 ml) and a 1.0 g ml^{-1} monomer solution (5 ml) in chlorobenzene were mixed and refluxed together for ten days to yield, after the recovery procedure described above, 0.6 g (12%) of polymer D. This sample was appreciably more easily dissolved in a variety of organic solvents than other samples.

(E) Following the same procedure as for D, but replacing ruthenium trichloride trihydrate by osmium trichloride and heating at 80°C for four days, gave polymer E (0.5 g, 10%).

Table 1 Molecular weight data for polymers A to F*

Polymer (catalyst metal)	A(W)	B(W)	C(Mo)	D(Ru)	E(Os)	F(Ti)
$\bar{M}_n$	100000	9000	63000	10000	19000	8000
$\bar{M}_w$	280000	18500	150000	14000	36000	15000

* Derived from g.p.c. data using a $10^{6\ 543}$ Å μ-styragel column set with i.r. and u.v. detectors, calibration with standard polystyrene samples and 'polystyrene equivalent' molecular weights are recorded in the Table

(F) 'Tebbe's Reagent', μ-chloro-μ-methylene bis(cyclopentadienyl) titanium dimethylaluminium was supplied as a solution in toluene which was diluted with chlorobenzene to 0.01 g ml^{-1}. The deep red catalyst solution was added to a solution of **III** (5 g) in chlorobenzene (8 ml); the mixture became very viscous within ten minutes at room temperature. The recovery procedure described above gave polymer F (4.5 g, 90%).

All samples A–F were white and soluble.

(G) Rhenium pentachloride in chlorobenzene (4.8 ml, 0.01 g ml^{-1}) was added to a solution of **III** (5 g) in chlorobenzene (1 ml), the mixture was heated to 70°C during which process it changed from green to brown. A very low yield (~1%) of pale green polymer G was recovered after the usual recovery procedure. It proved impossible to improve the yield or to obtain the product free from catalyst residues. The catalyst was shown to be active in the polymerization or norbornene and would also copolymerize **III** with norbornene.

RESULTS

Clearly the first point to establish is that the products A to F are in fact polymers formed by ring-opening at the cyclobutene ring. All these products were soluble and *Table 1* records the results of g.p.c. analyses which clearly demonstrate that all were polymers. The addition of oct-4-ene as a chain transfer agent, polymer B, had the desired effect of reducing the polymer molecular weight. Nearly all the samples gave symmetrical, relatively narrow distributions and there was little evidence of the skewed or multiple peaks, which would be expected for a mixture of linear and macrocyclic products.

The infra-red spectra of polymers A to F were recorded as thin films solvent cast onto KBr discs; a Perkin-Elmer 580 spectrophotometer was used. All the spectra were consistent with the expected metathesis polymer structure and a representative example (F) is recorded in *Figure 3*.

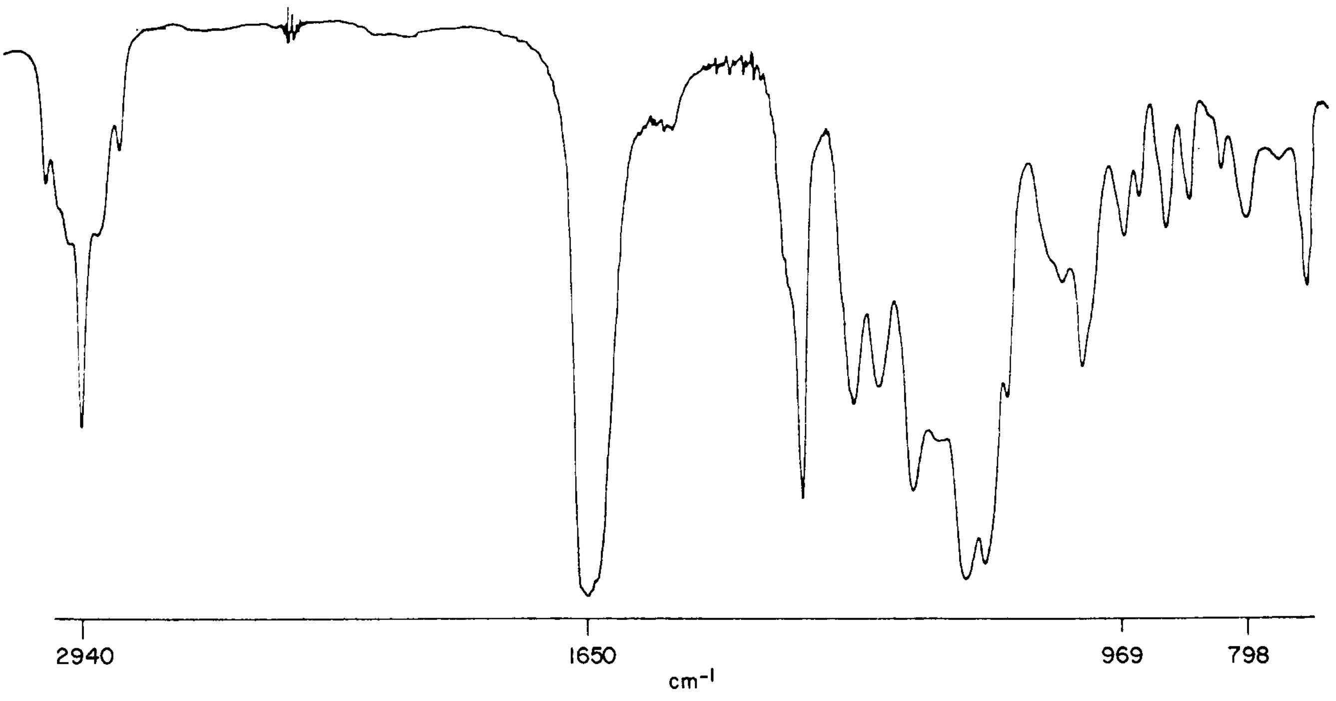


Figure 3 Infra-red spectrum of a thin film of polymer F

Spectra of samples A to F were virtually identical apart from differences in the relative intensities of absorption in the 1000 to 700 cm^{-1} region. Generally it is found that a *trans* vinylene unit displays an absorption at *ca.* 970 cm^{-1} and a *cis* vinylene unit shows a peak at *ca.* 730 cm^{-1}; the exact positions may be influenced by the environment. In this set of spectra the major differences between samples arose from bands at 969 cm^{-1} and 798 cm^{-1} which can be assigned to *trans* and *cis* vinylenes respectively. The peak at 969 cm^{-1} is in the 'normal' position whereas the 798 cm^{-1} peak assigned to the *cis* vinylene is at a significantly higher frequency than is usually observed. This may be a consequence of the steric stresses set up about a *cis* vinylene unit in these highly congested structures. Representative examples are recorded in *Figure 4* for polymers A(W), C(Mo) and D(Ru); it can be seen that, assuming the assignment is correct, the tungsten derived polymer A has significant contribution from both *cis* and *trans* vinylenes, whereas polymer C(Mo) has more *cis* than *trans* units and polymer D(Ru) has predominantly *trans* vinylene units. These results are consistent with the general trends observed for this set of catalysts in the ring-opening polymerization of a range of monomers[7]. It is also worth recording that the infra-red spectrum of the trace of polymer produced using $ReCl_5$ catalyst showed a strong band at 798 cm^{-1} with virtually no absorption at 969 cm^{-1}, indicating a high *cis* polymer in this case, which is again consistent with established trends. These observations lead to the conclusion that monomer **III** does not display any notably abnormal behaviour in its response to typical metathesis catalysts.

The most powerful probe of microstructure for this class of polymers has proved to be solution-phase high-field ^{13}C n.m.r. spectroscopy. Unfortunately, with polymers of the general structure **II** (*Scheme 1*), it has proved particularly difficult to obtain well resolved spectra. Indeed, the spectrum of the high *trans* polymer D derived from the $RuCl_3$ catalyst and shown in *Figure 5* represents the best resolved spectrum we have been able to obtain.

To try to gain some insight into the mechanism of line broadening for these polymers, an investigation of some relevant spectral parameters was undertaken. Values of the spin lattice relaxation times (T_1) are collected in *Table 2* for samples A, D and F.

Considering the wide variation in line width found in the spectra of these materials, the relaxation times for nuclei in analogous environments in different samples are very similar. For comparison, a typical solution of polyvinylchloride has ^{13}C T_1 values of 0.4 to 0.2 seconds, and linewidths sufficiently narrow (*ca.* 10 Hz) to resolve signals from stereochemically distinct environments.

Although the T_1 values do not reflect the broadness of resonances for these polymers, they do allow the calculation of quantitative acquisition parameters (*ca.* $5T_1$ recycle time between 90° pulses). Nuclear Overhauser effects can also distort ^{13}C resonance intensities[12] and to estimate the importance of this parameter, nOe enhancement factors, η, were measured for polymer A, and are collected in *Table 3*. It is clear that (i) η is not identical for all sites and (ii) η is not at the maximum expected for dipolar relaxation in the extreme narrowing limit $\eta_{max} = 1.99$).

Point (i) requires acquisition of data in the nOe suppressed mode to ensure quantitative reliability. Interpreting η for polymers is not trivial[13]. However, one

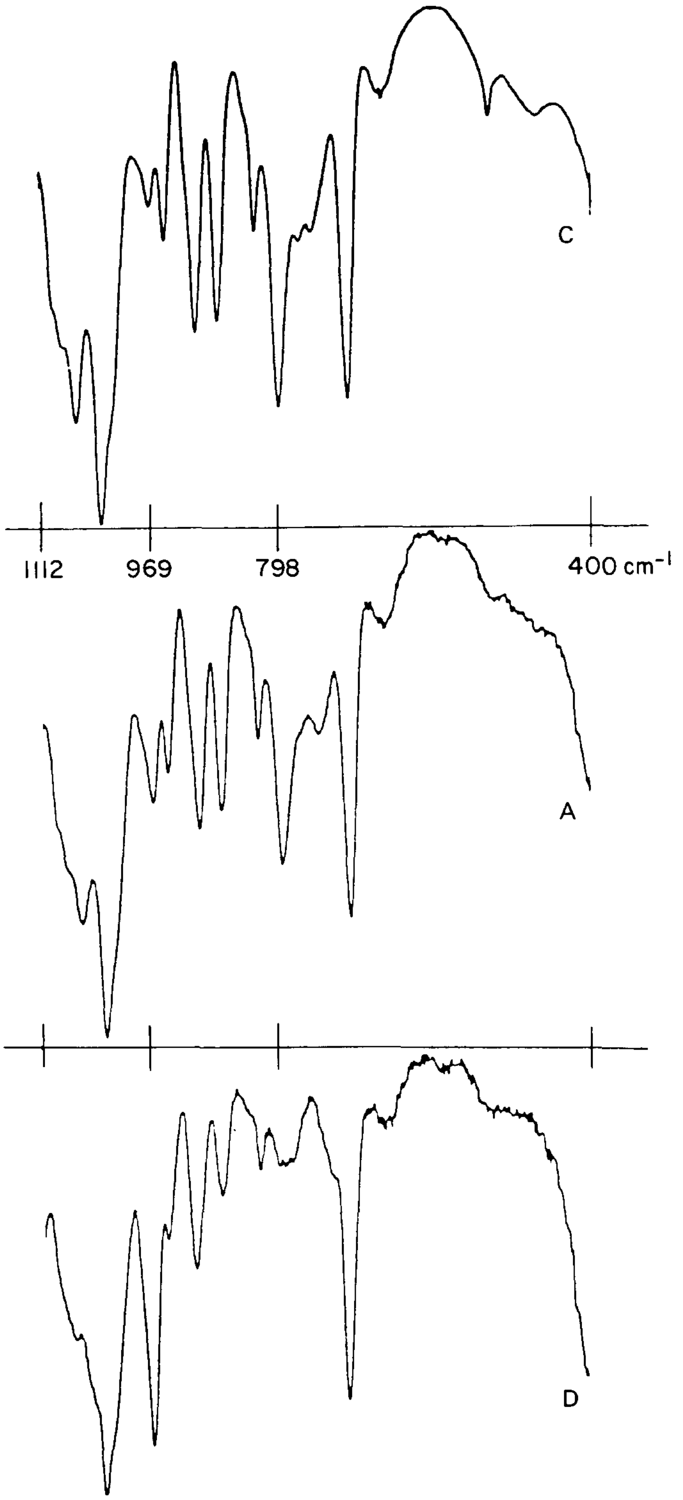


Figure 4 Infra-red spectra for polymers A, C and D in the out-of-plane CH bending region for *cis* and *trans* vinylene units

Table 2 ^{13}C spin lattice relaxation times (seconds)

Resonance	A (W)	F (Ti)	D (Ru)
a	2.8	3.8	2.5
b, c	0.2	0.2	0.2
d	0.9	1.2	0.8
e, f, g, h	0.2	0.3	0.2

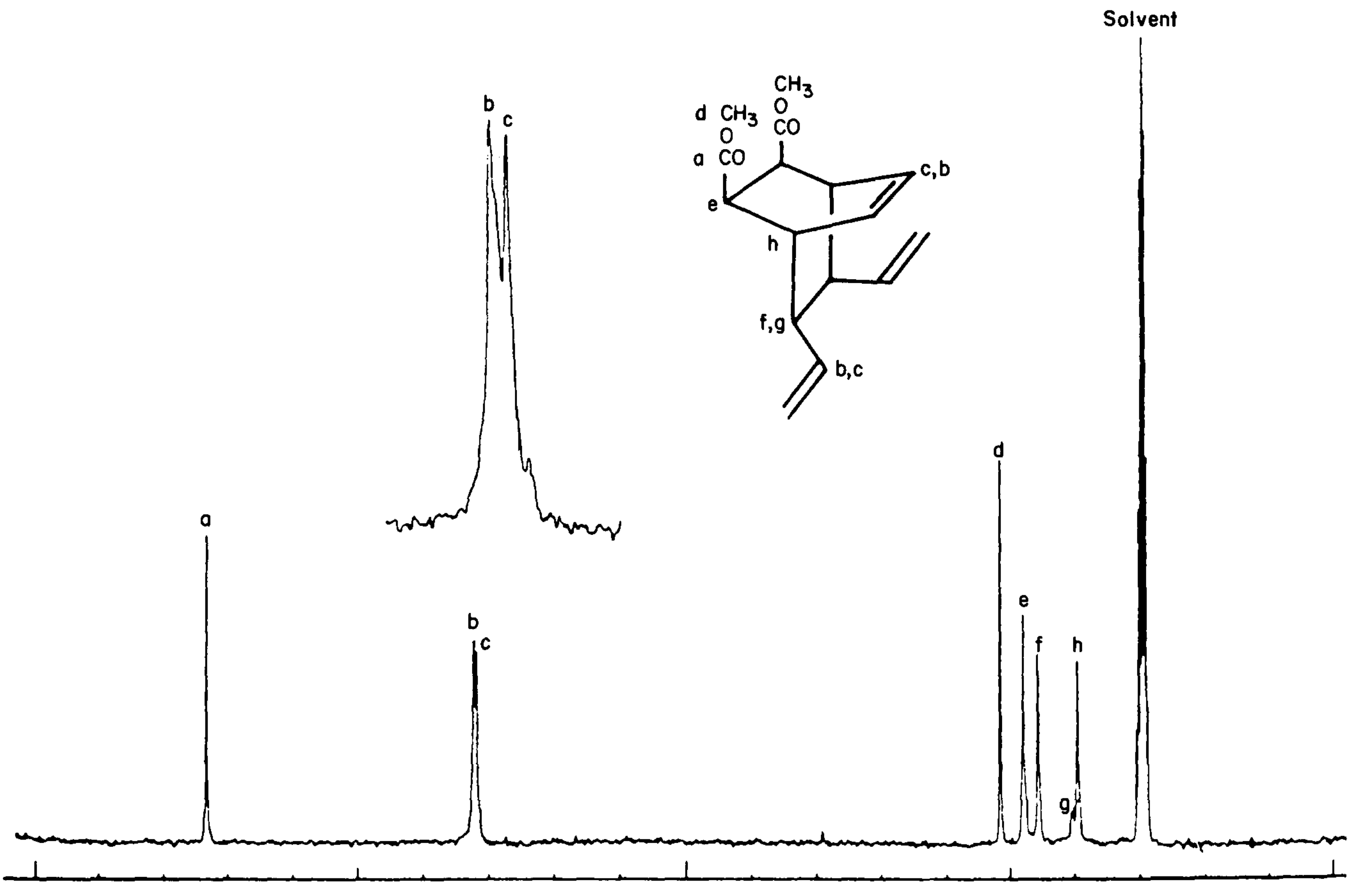


Figure 5 ^{13}C n.m.r. spectra of polymer D, recorded at 67.8 MHz in acetone solution

Table 3 Nuclear Overhauser enhancement factors 2, for sample A

Resonance	a	bc	d	ef	gh
η*	0.27	0.43	0.59	0.64	0.50

* $\eta=\frac{I-I_0}{I_0}$ I_0 = Intensity without nOe enhancement
I = Intensity with nOe enhancement

Table 4 Half-height widths, $\Delta\nu_{1/2}$, for polymer A (W catalyst)

(i) *Proton resonances*	$\Delta\nu_{1/2}$(Hz)	
Chemical shift	60 MHz	270 MHz
6.3	14.5	48.3
5.3	26.0	79.4

(ii) *Carbon resonances*	$\Delta\nu_{1/2}$(Hz)		
Resonance	50 MHz	67.8 MHz	100 MHz
a	25	24	30
b, c	105	145	235
d	25	24	25
e, f	52	81	125
g, h	105	153	250

factor which may cause a reduction of η from η_{max} is a long correlation time (slow motion)[12]. In such a situation, it is possible that the ^1H–^{13}C dipolar coupling will not be averaged to zero, and a short T_2 (wide line) results. The half height width of such a homogeneously broadened line should (iii) be independent of operating frequency, and (iv) be narrowed under certain circumstances if correlation times can be decreased.

An alternative explanation for the line broadening is that the polymer exhibits a range of chemical shifts for a given carbon site, i.e. the lines are heterogeneously broadened. In such a situation the half-height width will (v) be linearly dependent on the field, B_0, and (vi) not be sensitive to small changes in the correlation time.

To distinguish between points (iii) and (v), we have measured the half height widths for ^{13}C and ^1H resonances at a number of operating frequencies for sample A. The half height widths ($\Delta\nu_{1/2}$) of the two resolved olefinic resonances in the proton n.m.r. spectra are compared in *Table 4(i)*. Although the ratio of $\Delta\nu_{1/2}$ at the two fields is not as high as is required for a purely heterogeneously broadened line (4.5), the linewidths do increase by a factor of about three on going from 60 to 270 MHz. Values of $\Delta\nu_{1/2}$ for ^{13}C resonances are collected in *Table* 4(*ii*), and it is again evident that most increase markedly with the field, B_0. The value of $\Delta\nu_{1/2}$ for the quaternary (a) and methyl (d) resonances are not sensitive to the field as would be expected for groups well removed from the effects of *c*/*t* and m/r isomerism.

An attempt was made to decrease correlation times and therefore distinguish points (iv) and (vi), but the linewidths remained unaltered under variation of the following parameters: the temperature, which was varied from 300 to 400 K for A in DMSO-d_6 and from 240 to 300 K for both A and D in acetone-d_6; the viscosity, as solution concentrations of A in acetone-d_6 were increased from 0.2 to 1.0 g/ml; the average molecular weights, as $\bar{M}_n$ for A varied between 9000 and 100 000 polystyrene equivalents; and the nature of the solvents, including deuterated chloroform, acetone, benzene and DMSO.

Since the CH linewidths are field dependent, and there is no evidence that they can be reduced by decreasing correlation times, it is reasonable to assume that linewidths are principally determined by a distribution of environments for each carbon site. On this basis, we have attempted to interpret the observed, albeit broad resonances in terms of the expected stereochemistry of the polymer.

The assignments shown in *Figure 5* are made on the basis of comparisons with established systems and the requirement for internal consistency. The ester carbonyl (a) occurs at highest frequency 173.29 ppm, with its methyl (d) at 51.63 ppm; peaks b and c at 132.31 and 131.87 ppm can be assigned confidently to the vinylic carbons as indicated but it is not possible to say which is which. However, since we can assign this material as having a high *trans* vinylene content on the basis of the infra-red spectroscopic analyses and since one of the totally reliable features of ^{13}C n.m.r. assignments is that allylic carbon adjacent to *cis* vinylenes occurs *ca.* 5 ppm to lower frequency from those adjacent to *trans* vinylenes it is possible to assign peaks f(t) and g(c) as those due to the allylic carbons, as shown in *Figure 5*. The remaining assignments of e, α to the ester carbonyl, and the bridgehead carbon h follow straightforwardly on the basis of their relative shifts. This assignment is valuable for the interpretation of the other ^{13}C spectra which were considerably less well resolved; *Figure 6*, the spectrum of polymer A, provides a typical example and the peak assignments follow those elaborated above. Despite the relatively poor resolution for most of these spectra, it has proved possible to deduce some useful structure information from an analysis of the aliphatic carbon resonance region, *Figure 7*. It is clear that in these spectra the resolution will allow us to make deductions about the *cis*/*trans* vinylene content but that it is not sufficiently

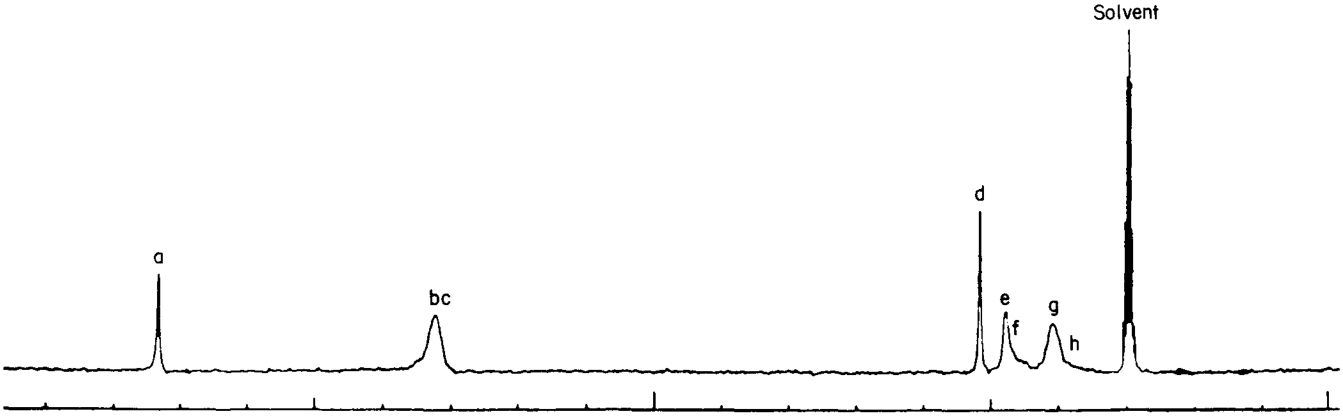


Figure 6 ^{13}C n.m.r. spectra of polymer A, recorded at 67.8 MHz in acetone solution

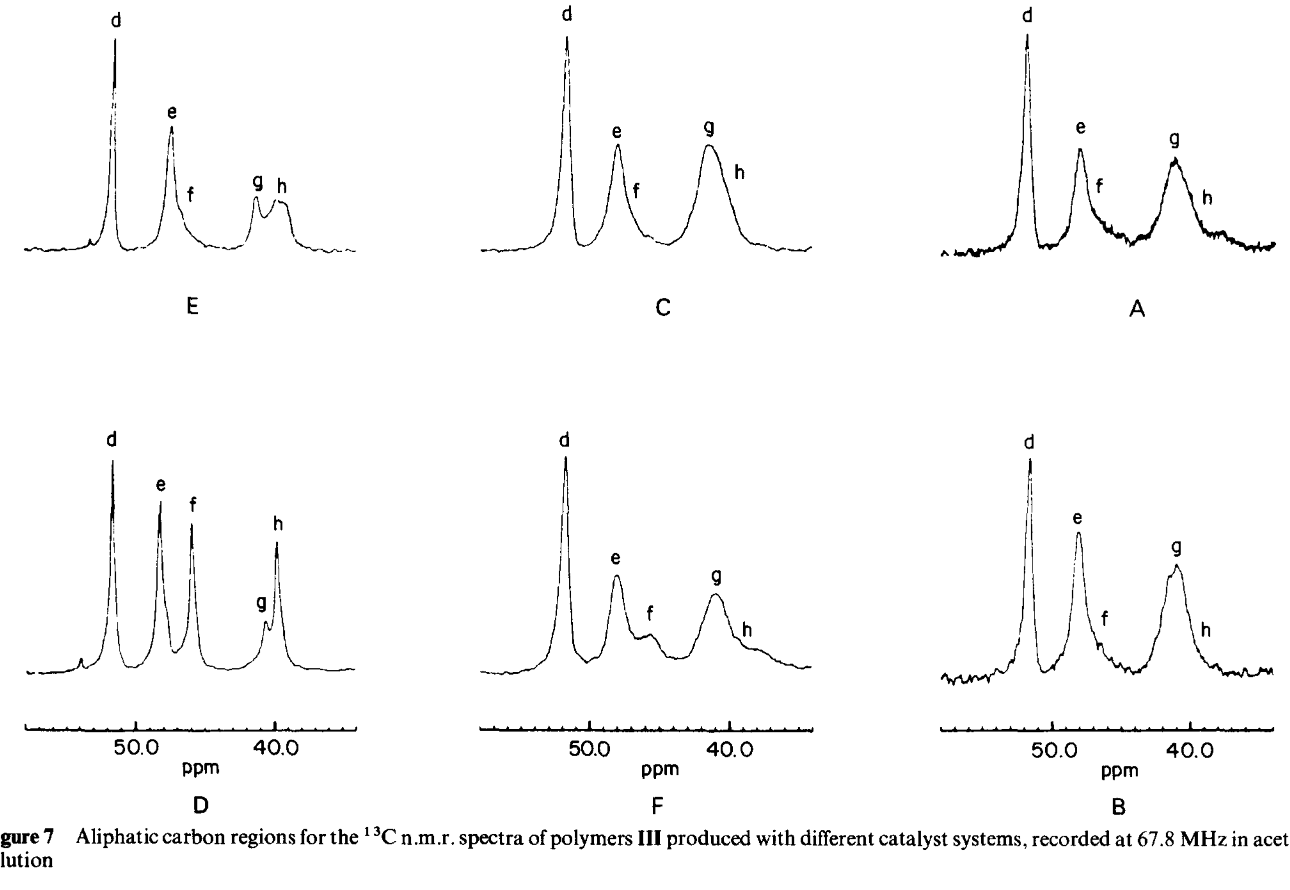


Figure 7 Aliphatic carbon regions for the ^{13}C n.m.r. spectra of polymers **III** produced with different catalyst systems, recorded at 67.8 MHz in acetone solution

good to see any meso/racemic effects[7]. The spectra were accumulated under conditions that assure each carbon gives the same spectral response and so the *cis/trans* ratios were calculated in the following way. The integrated intensity of peaks e to h inclusive were normalized to three carbons (one tertiary, one allylic and one bridgehead). One (a tertiary carbon) was then subtracted from the normalized intensity under the often unresolved e/f peak to give the relative intensity due to the allylic carbons adjacent to a *trans* vinylene. The results of this analysis, which can be regarded as quantitative, provided that intensity lost to the wings of the broadest lines is relatively insignificant, are collected in *Table 5*. They are in satisfactory agreement with the earlier results of an analysis of the infra-red spectra.

All the lines recorded in *Figure 7* are rather broad but the lines e to h broaden much more than d. As a general trend it seems that the g/h region broadens as the *cis* content increases. While this is inconvenient with respect to the use of ^{13}C n.m.r. as a structural probe; it may be taken as an indication of the considerable steric congestion about *cis*-dyads in these polymers which give rise to a multiplicity of environments which are slightly different from one another and account for this line broadening in *cis* sequences.

CONCLUSIONS

The above analysis of the spectral data for model polymers A to F derived from monomer **III** is self consistent. While the resolution of the ^{13}C n.m.r. spectra is poorer than normally observed for related systems this can be accounted for in terms of steric congestion which is most pronounced in *cis*-dyad sequences. It therefore appears that monomer **III**, and by implication monomers **Ib** and **Ic** for which **III** acts as a model, behaves as a normal monomer in metathesis ring-opening polymerization. It therefore seems likely that polyacetylene precursor polymers produced using $WCl_6/(CH_3)_4Sn$ catalysts will have (as has generally been assumed) a roughly 50:50 *cis:trans* vinylene composition and consequently the polyacetylene generated will have approximately 75% *cis* vinylene content at the moment of its formation, precursors derived from $MoCl_5/(CH_3)_4Sn$ will have a somewhat higher *cis* vinylene content (*ca.* 88%). The implications of these observations for the nature of the final polyacetylene are being explored and will be reported in due course.

Table 5 ^{13}C n.m.r. and i.r. at *trans* vinylene contacts for polymers A–F

Polymer sample (catalyst metal)	A(W)	B(W)	C(Mo)	D(Ru)	E(Os)	F(Ti)
Fraction of *trans* vinylene						
^{13}C n.m.r.	0.30	0.45	0.23	0.94	0.47	0.44
i.r.	low	medium	v. low	v. high	medium	medium

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