Determination of the tacticities of ring-opened metathesis polymers of symmetrical 5,6-disubstituted derivatives of norbornene and norbornadiene from the ^{13}C NMR spectra of their hydrogenated derivatives

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Abstract

Ring-opened metathesis polymers were made from 5,6-di-exo-(carbomethoxy)-norbornene and 5,6-di-(carbomethoxy)-norbornadiene using a variety of catalysts and their ^{13}C NMR spectra analyzed in detail. These polymers were then fully hydrogenated using diimine and found by ^{13}C NMR analysis to give with complete selectivity the same saturated derivative. This permitted the tacticities to be assigned in detail and the consistency of the analysis further checked with respect to the m (meso) and r (racemic) line orders identified for all the precursor polymers. While $OsCl_3$/phenylacetylene as catalyst gave high cis syndiotactic polymers $OsCl_3$ by itself formed high trans atactic material; $RuCl_3$ afforded the corresponding trans polymer with a substantial isotactic bias. By way of contrast $MoCl_5/Me_4Sn$ in dioxan is an excellent catalyst for the synthesis of all cis isotactic poly-5, 6-di-(carbomethoxy)-norbornadiene. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Tacticity; Metathesis polymerization; Hydrogenation; Symmetrical monomers

1. Introduction

The tacticities of ring-opened metathesis polymers of norbornene and norbornadiene cannot be determined directly using ^{13}C NMR spectroscopy as there is no line splitting due to m and r dyads [1]. Symmetrically substituted polymers made from the 5,6-di-X-derivatives of those monomers **1**, **2** and **3** (Scheme 1) present a similar problem in that although all cis polymers have been made [2] and the cis resonances show fine structure due to ring dyads, there is no way of making an unambiguous assignment

of the various lines or determining the line order, i.e., $\delta_{mm} > \delta_{mr,rm} > \delta_{rr}$ or, $\delta_{rr} > \delta_{rm,mr} > \delta_{mm}$ [3]. This problem arises because there is an intramolecular plane of symmetry bisecting not only all of these monomers but also the repeating unit in the polymer.

Even if there is no intramolecular plane of symmetry as for (±)-5, 5-dimethyl [4] and (±)-5,6-endo-exo-dimethylnorbornene [5], or (±)-3-methylcyclobutene [6] an exactly analogous problem arises. Now the intermolecular plane of symmetry between enantiomers in the racemic mixtures precludes absolute assignments of the m or r components of the lines from cis and trans dyads. However by polymerizing the re-

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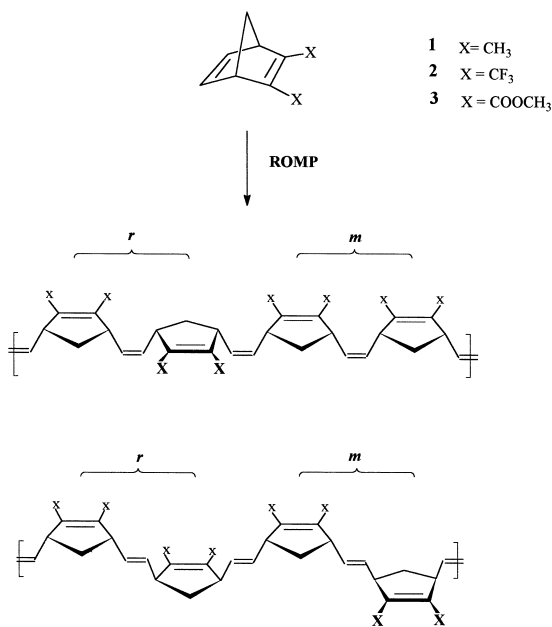
Scheme 1.

solved monomers [4] we are able to determine the exact nature of the tacticity of the dyads; a range of catalysts may then be characterized according to their ability to produce tactic polymer. Thus $ReCl_5$ [1] and $OsCl_3/PhCCH$ [7] consistently give high cis syndiotactic polymers, whereas $RuCl_3$ [1] catalyses formation of high trans mainly atactic polymers. Recently we have found that the C^7 and $C^{5,6}$ resonances in fully hydrogenated poly(norbornene) and poly-(norbornadiene), **4**, are m/r resolved. Since $ReCl_5$ and $OsCl_3/PhCCH$ catalysts also gave high cis polymers from these prototype monomers, whereas $RuCl_3$ gave all trans material, these initiators were used as standards to establish that the line order is $\delta_{mm} > \delta_{mr, rm} > \delta_{rr}$ for C^7 and $\delta_r > \delta_m$ for $C^{5,6}$ [7].
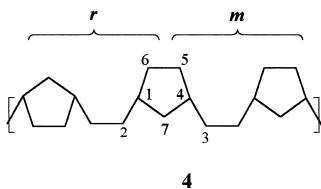
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Structures as in Scheme 1 remained a problem however, but in a very elegant analysis

O'Dell et al. [3] removed the plane of symmetry by changing the ester substituent in **3** to the chiral (-)methyl analog and then applied COSY ^1H NMR spectroscopy. They were then able to distinguish directly isotacticity and syndiotacticity for all cis and all trans polymers and to show that the cc C^7 line order is $\delta_{mm} > \delta_{mr, rm} > \delta_{rr}$, i.e., the same as that for polymer **4**. However poly(**1**), poly(**2**), and poly(**3**), where the plane of symmetry cannot be removed in such a way still present the problem of tacticity assignment.

Since we had found the hydrogenation method to be very valuable in this respect and very easily used we decided to check the conclusions of O'Dell et al. [3] by applying it to poly(**3**) and then to extend it to poly(**1**) and poly(**2**). This report shows that the final goal has been achieved with complete success. Three monomers were chosen for investigation, 5,6-di-exo-(carbomethoxy)norbornene, **5**, 5,6-diendo-(carbomethoxy)norbornene, **6** and 5,6-di-(carbomethoxy)-norbornadiene, **3**. Polymers of all of these were made using a variety of catalysts and hydrogenated using diimine;
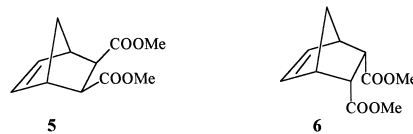
fully hydrogenated materials and their precursors were analyzed in detail by ^{13}C NMR. The success of the method for the diene polymers requires that the C-5 ring double bond either remains unhydrogenated or is fully, symmetrically and selectively, hydrogenated. If the latter can be achieved the consistency of all the tacticity assignments, as well as catalyst behaviour, is subject to a multiple check.

2. Experimental

2.1. Materials and instrumentation

GPR grade solvents were used throughout. Dioxan and THF were distilled from CaH_2 and

chlorobenzene from P_2O_5 before use and diethyl ether was dried over sodium wire, otherwise solvents were used as received. The metal salts $OsCl_3 \cdot 3H_2O$ (Fluka), $RuCl_3 \cdot nH_2O$ (Aldrich), WCl_6 (Aldrich), $MoCl_5$ (Aldrich) and the cocatalysts Me_4Sn (Aldrich) and phenylacetylene (Aldrich) were also used as received.

The monomers, 5,6-exo-(dicarbomethoxy)-norbornene, **5**, and 5,6-endo-(dimethyl)-norbornene, **6**, were synthesised from the respective anhydride precursors in an acid catalysed esterification reaction [8]. 5,6-di-(carbomethoxy)norbornadiene, **3**, was prepared by a Diels/Alder synthesis [9].

$^{13}C\{^1H\}$ NMR spectra were obtained at 125 MHz on a GE, GN Omega 500 spectrometer. Polymer samples were dissolved in an appropriate solvent, either $(CD_3)_2CO$ or $CDCl_3$ with TMS as an internal standard.

2.2. Polymerization procedures

Polymers were prepared according to the procedures outlined below. Although dry solvents were used no particular attempt was made to carry out the reactions anaerobically. Yields of all polymers were of the order of 70%.

2.2.1. $OsCl_3 \cdot 3 H_2O$ and $RuCl_3 \cdot nH_2O$

The metal halide (15 mg) was dissolved in industrial alcohol (1.5 ml) and to this was added the monomer (500 mg) dissolved in chlorobenzene (1.5 ml). The reaction was allowed to proceed in a Carius tube at 70°C for 48 h.

2.2.2. $OsCl_3 \cdot nH_2O$ / phenylacetylene

Osmium trichloride hydrate (15 mg) and phenylacetylene (100 mg) were dissolved in THF (2 ml). After an induction period of 1 h at 20°C the monomer (500 mg), dissolved in THF (2 ml) was added and allowed to react at room temperature for 48 h.

2.2.3. WCl_6 / Me_4Sn and $MoCl_5$ / Me_4Sn in dioxan solvent

A solution of dioxan (0.7 ml) in chlorobenzene (2 ml) was added to the metal halide (100 mg) followed by tetramethyl tin (4 drops). After a 2-min induction at 20°C the monomer (500 mg), dissolved in chlorobenzene (1.5 ml) was added and reaction allowed to proceed for 24 h at room temperature.

2.2.4. $MoCl_5$ / Me_4Sn / Et_2O

A solution of diethyl ether (0.7 ml) in chlorobenzene (2 ml) was added to the metal halide (100 mg) followed by tetramethyl tin (4 drops). After a 2-min induction at 20°C the monomer (500 mg), dissolved in chlorobenzene (1.5 ml) was added and reaction allowed to proceed for 24 h at room temperature.

2.2.5. WCl_6 / Me_4Sn and $MoCl_5$ / Me_4Sn

To a suspension of the metal halide (100 mg) in chlorobenzene (2 ml) was added tetramethyl tin (IV) (4 drops). After a 2-min induction at 20°C the monomer (500 mg), dissolved in chlorobenzene (1.5 ml) was added and the reaction allowed to proceed for 24 h at room temperature.

2.3. Hydrogenation of polymers

Typically, polymer (100 mg) was dissolved in xylene (10 ml) and *p*-toluenesulphonhydrazide (2 g) was added, the solution was stirred with heating at 120°C for 2 h [10]. After cooling, the reaction mixture was poured into methanol (50 ml) and the precipitated polymer, after several washings with methanol, was retrieved by filtration or centrifugation as appropriate.

3. Results and discussion

Metathesis polymerization of 5,6-di-(carbomethoxy)-norbornadiene, **3**, was carried out using the high trans directing $RuCl_3$ and $OsCl_3$ and the high cis directing $OsCl_3$/phenylacetylene and $MoCl_5$/Me_4Sn/dioxan catalyst systems. Here, and in other cases, the main resonances were easily distinguished using

DEPT spectroscopy and the trans or cis nature of the polymer was determined from the relative intensity of the $C^{1,4}$ signals; the trans $C^{1,4}$ signal in the spectra of this type of polymer is invariably about 5 ppm downfield from the $C^{1,4}$ cis signal [1].

The high trans polymers prepared from $OsCl_3$ ($\sigma_c = 0.10$) and $RuCl_3$ ($\sigma_c = 0.06$) yielded very similar spectra as expected (Fig. 1a and b) with the low intensity cis lines in each exhibiting fine structure which must be due to tacticity, the trans C^7 line also showing some minor splitting of the order of 0.1 ppm. The signals in these spectra were assigned as follows: OCH_3 (m and r) 51.9 ppm, trans $C^{1,4}$, 49.1 ppm; cis $C^{1,4}$ (multiplet cc, ct and m/r splitting) 44.2 ppm; C^7 tc, 38.0 ppm and C^7 tt, centered at 37.8 ppm. The high cis polymers ($\sigma_c = 0.83$)
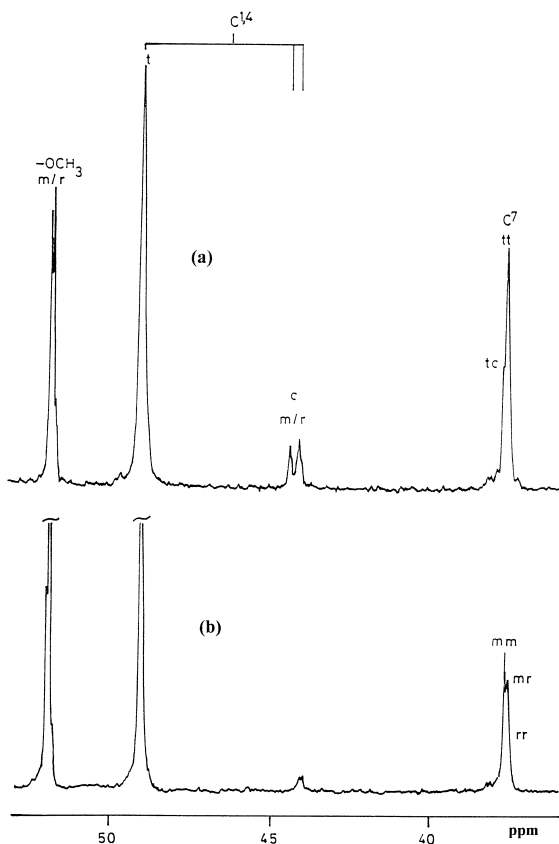

Fig. 1. ^{13}C NMR spectra of poly(**3**) prepared using, (a) the OsCl$_3$ catalyst, $\sigma_c = 0.10$ and (b) the RuCl$_3$ catalyst, $\sigma_c = 0.06$.
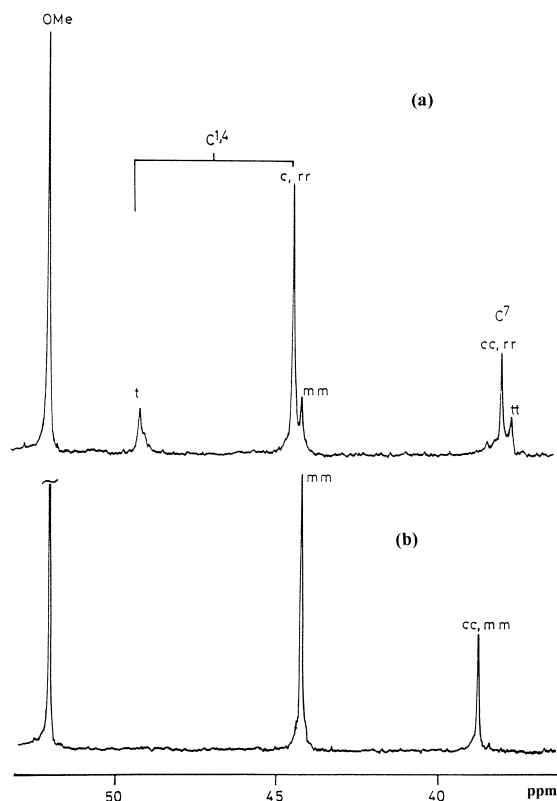

Fig. 2. ^{13}C NMR spectra of poly(**3**) prepared using, (a) the OsCl$_3$/phenylacetylene catalyst, $\sigma_c = 0.83$ and (b) the MoCl$_5$/Me$_4$Sn/dioxan catalyst, $\sigma_c = 1.00$.
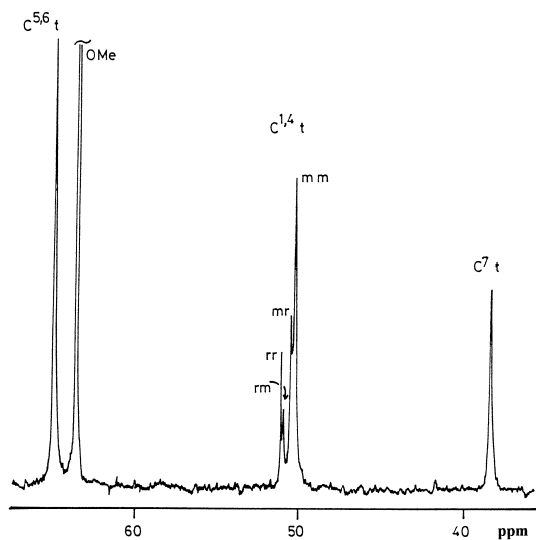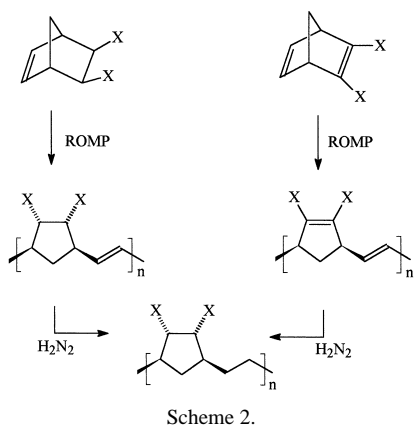

Fig. 3. The ^{13}C NMR spectrum of poly(**5**) prepared using the RuCl$_3$ catalyst.

Scheme 2.

formed from the $OsCl_3$/phenylacetylene catalyst, known to generate syndiotactic biased polymers with other monomers [7], yielded a ^{13}C NMR spectrum (Fig. 2a) which allowed the cis resonances to be tentatively assigned as follows: cis $C^{1,4}$ r, 44.3 ppm; cis $C^{1,4}$ m, 44.0 ppm; C^7 cc, rr, 37.9 ppm and C^7 tt, 37.8 ppm. On the basis of these two assignments the signals in the spectrum of the polymer formed from the $MoCl_5$/Me_4Sn/dioxan catalyst (Fig. 2b; $\sigma_c = 1.00$) were assigned as: cis $C^{1,4}$ m, 44.0 ppm; C^7 cc, mm, 38.7 ppm. In these high cis polymers the signals from the methyl ester
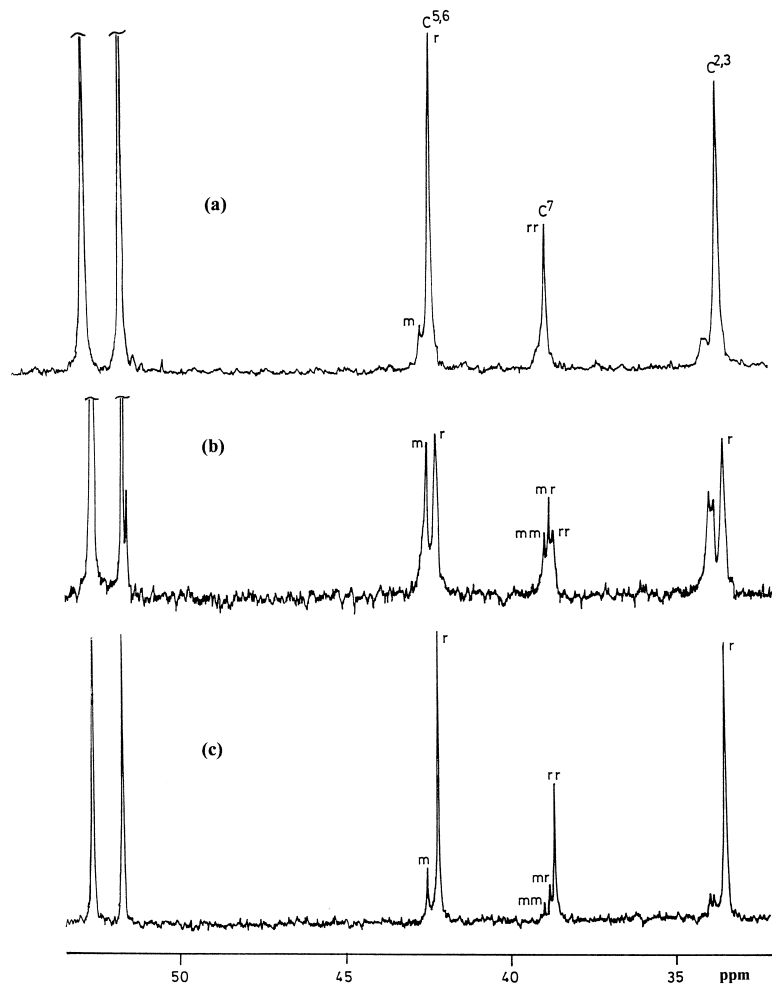

Fig. 4. ^{13}C NMR spectra of hydrogenated polymers derived from (a), poly(**3**) prepared using the $OsCl_3$/phenylacetylene catalyst, (b), poly(**3**) prepared using the $OsCl_3$ catalyst and (c) poly(**5**) prepared using the $OsCl_3$ catalyst.

groups occur at 51.9 ppm in each spectrum and is unaffected by tacticity, $C^{2,3}$ olefinic signals at approximately 131 ppm and $C^{5,6}$ olefinic signals at approximately 142 ppm were not sufficiently resolved for a meaningful analysis.

High trans polymers ($\sigma_c = 0.01$) were also formed from **5** using the $RuCl_3$ catalyst (Fig. 3) and here the $C^{1,4}$ signal is extensively split by tacticity ($C^{1,4}$ rr, rm, mr, and mm) the polymer having an isotactic bias in addition to being quite stereoblocky, i.e., mm/mr · rr/rm = 6.0. By way of contrast a family of high cis poly-

mers ($\sigma_c = 0.86$) was formed from **5** using $OsCl_3$, Fig. 3b; signals were assigned as: C^7 tt, 39.2 ppm; C^7 ct, 40.0 ppm; C^7 cc and cis $C^{1,4}$, 40.8 ppm (overlapping); trans $C^{1,4}$ r, 45.2 ppm; trans $C^{1,4}$ m, 45.5 ppm; cis and trans OCH_3, 51.8 ppm; trans $C^{5,6}$, 52.5 ppm; cis $C^{5,6}$, 53.2 ppm; $C^{2,3}$, 132.1 ppm.

The ^{13}C NMR spectra of hydrogenated poly(**3**) formed with the $MoCl_5/Me_4Sn/di$-oxan catalyst was very simple and since no olefinic signals were present in the spectrum it was apparent that the diimine reagent had not
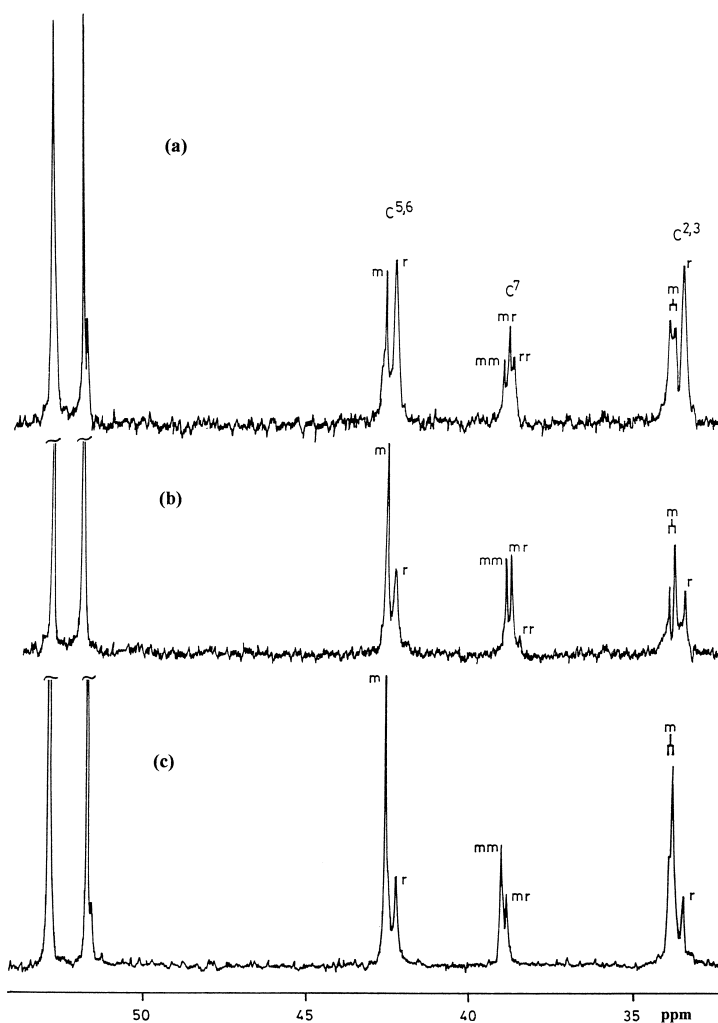

Fig. 5. ^{13}C NMR spectra of hydrogenated polymers derived from (a), poly(**3**) prepared using the $OsCl_3$ catalyst (same spectrum as Fig. 4a for comparison), (b), poly(**3**) prepared using the $RuCl_3$ catalyst and (c) poly(**5**) prepared using the $RuCl_3$ catalyst.

only hydrogenated both double bonds but had attacked regiospecifically at one face of the C-5 ring double bond; attack at both faces would have yielded spectra showing both cisoid and transoid C-5 rings. However it remained to be determined which of the two available faces had been attacked. This was accomplished by comparing the spectra obtained for the hydrogenated derivatives of all the poly(**3**) samples discussed above with those of the hydrogenated poly(**5**) which must necessarily have a transoid repeating unit (Scheme 2).

This is done in Figs. 4 and 5 which show that all the signals in the spectrum of hydrogenated poly(**5**) coincide exactly with those in the spectrum of hydrogenated poly(**3**), proven further by mixing polymer samples and then analyzing again by ^{13}C NMR. Therefore poly(**6**) was not investigated as it was not essential for the main purpose of the investigation. It was thus apparent that hydrogenation of poly(**3**) was occurring with complete selectivity at the most sterically hindered face of the C-5 ring double bond. This could be rationalized by considering the energetics of the hydrogenation process. Hydrogenation at the unhindered face leads to a high energy cisoid product in which all ring substituents are on the same face and is less energetically favorable than the transoid isomer.

Once ^{13}C NMR lines for poly(**3**) were identified the lines for the corresponding fully hydrogenated polymer were assigned, using ^{13}C/^{1}H HETCOR, to be: C^{2,3} r, 33.4 ppm; C^{2,3} mr,

33.8 ppm; C^{2,3} mm, 33.9 ppm; C^{7} mm, 38.6 ppm; C^{7} mr/rm, 38.75 ppm; C^{7} rr, 38.9 ppm; C^{1,4} r, 42.1 ppm; C^{1,4} m, 42.4 ppm; OCH$_3$, 51.7 ppm; C^{5,6}, 52.6 ppm. This information was then applied to the analysis of the spectra of hydrogenated poly(**3**) and hence the assignment of the resonances for poly(**3**) completely confirmed by this additional check. The results are summarized in Table 1.

4. Conclusion

The sequence of chemical shifts, or line order, for the C^{7} triplet in all the hydrogenated polymers, including that of the prototypal poly(norbornene), has been shown to be; $\delta_{mm} > \delta_{mr,rm} > \delta_{rr}$. The same is also true for both the C^{7} cc and C^{7} tt resonances in high cis and high trans polymers respectively before hydrogenation, although a strong asymmetry in the very large chemical shifts $\delta_{mm} \leftarrow \rightarrow \delta_{mr(rm)} \leftarrow \rightarrow \delta_{rr}$ for C^{7} cc is noted. This seems to be a general feature for diene polymers of the type shown in Scheme 1 as it is also observed [11] with X = CF$_3$ and is most likely due to long-range conformational effects [7]. However our analysis is completely consistent with that carried out by Schrock et al. [11] who found that there is a systematic change from production of all cis syndio to all cis isotactic polymer of 5,6-di(carbomethoxy)-norbornadiene, **3**, merely by changing the nature of the alkoxy ligand in their well-defined [Mo] = (carbene) initiators. The observation here that conventional Mo-based catalysts have been induced to produce all cis isotactic polymer is therefore very gratifying because it shows that a general principle operates in controlling cis isotacticity and that this is not simply due to specific factors which are peculiar to Schrock's initiators.

By way of contrast the same MoCl$_5$-/SnR$_4$/dioxan catalyst also produces almost all cis poly(norbornene) which on hydrogenation was found to have only a very slight isotactic

Table 1
Microstructure of polymers formed from **3** and **5**

Monomer	Catalyst	σ_c[a]	Tacticity
3	RuCl$_3$	0.06	isotactic bias
3	OsCl$_3$	0.01	atactic
3	MoCl$_5$/Me$_4$Sn	0.87	isotactic bias
3	MoCl$_5$/Me$_4$Sn/dioxan	1.00	all isotactic
3	WCl$_6$/Me$_4$Sn/dioxan	0.66	syndiotactic bias
3	OsCl$_3$/phenylacetylene	0.83	syndiotactic bias
5	RuCl$_3$	0.01	isotactic bias[b]
5	OsCl$_3$	0.76	atactic

[a]Fraction of cis double bonds in polymer before hydrogenation.
[b]Polymer was stereoblocky (see text).

bias [10]. A $WCl_6/SnR_4/dioxan$ catalyst behaved in an exactly analogous manner. These results are further evidence for the general view that the prototypes, norbornene and norbornadiene, are less prone to yield tactic polymers than the corresponding derivatives.

The C^7 cc and C^7 tt line orders shown here are the inverse of those assigned in earlier work [12] so claims [3,12] that all trans syndiotactic polymers have been made from **2** and **3** are suspect. It is much more likely that these polymers have an isotactic bias or are atactic. For example, the same Schrock initiator which produces all trans atactic polymer from 5, 6-endo,exo-dimethylnorbornene [5] is most unlikely to make all trans syndiotactic poly(**3**) [12]. Furthermore in all our extensive studies using conventional catalysts we have yet to record a high trans polymer with a substantial syndiotactic bias.

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