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Microstructural Studies of Poly(7-oxabicyclo[2.2.1]hept-2-ene) Derivatives Prepared from Selected Ruthenium Catalysts

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ABSTRACT: The microstructures of polymers prepared from ring-opening metathesis polymerization (ROMP) of 7-oxanorborene (7-oxabicyclo[2.2.1]hept-2-ene) (**3**), *endo*-5-(methoxymethyl)-7-oxanorbornene (**2**), and *exo,exo*-5,6-bis(methoxymethyl)-7-oxanorbornene (**1**) with four metathesis catalysts were studied by ^{1}H and ^{13}C NMR spectroscopy. Tacticities were determined by hydrogenation of the polymers (which removed double-bond isomerism) and also by ROMP of (*S*)-*endo*-5-(methoxymethyl)-7-oxanorbornene (**2S**)(which related head–tail isomerism with tacticity). Polymers prepared from $W(CH\text{-}t\text{-}Bu)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-diisopropylphenyl) (**6**) have all cis double bonds and are highly syndiotactic, while those from $RuCl_3{\cdot}3H_2O$ (**8**) and $[RuCl(\mu\text{-}Cl)(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$ ($C_{10}H_{16}$ = 2,7-dimethyloctadienediyl) (**9**) have a high trans double-bond content and are highly isotactic. Polymers prepared from $[Ru(H_2O)_6](tosylate)_2$ (**7**) exhibit roughly equal amounts of cis and trans double bonds that are randomly distributed in the polymer chain and are atactic. The apparent correlation between double-bond isomerism and tacticity for a classical hexacoordinated metal center is consistent with the model proposed by Ivin and co-workers.

Introduction

Ring-opening metathesis polymerization (ROMP) has been the subject of numerous studies since its discovery in the 1960s.[1] The process involves the [2+2] cycloaddition of metal–alkylidene species with a cyclic olefin to form a metallacyclobutane intermediate which subsequently undergoes ring opening to regenerate the metal–alkylidene species (Figure 1).[2a] The reaction is driven forward by the release of ring strain in the cyclic olefin. The recent emphasis has been on the synthesis of more versatile catalysts and the use of these catalysts to prepare polymers with interesting properties.[3]

Polymer properties depend on chemical composition (as determined by the monomers used), molecular weight, and microstructure.[4] Recently, some insights have been gained in controlling polymer properties through studies on the mechanism and kinetics of polymerization.[1b,5] New metal–alkylidene catalysts have been developed that are tolerant to certain functional groups in the monomer.[6] This enables the incorporation of non-carbon atoms into the polymer chain. Knowledge of reactivity ratios of various monomers is also being used to design block copolymers.[7] The role of Lewis bases (such as phosphines and amines) in changing the kinetics of initiation versus chain propagation has been clarified and thus allows precise control of the molecular weight and its distribution.[8] However, in spite of all these developments, limited progress has been made in elucidating the conditions that control polymer microstructure.[9]

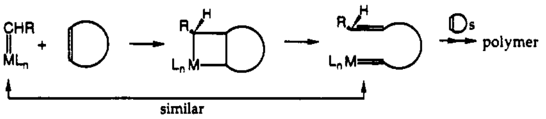
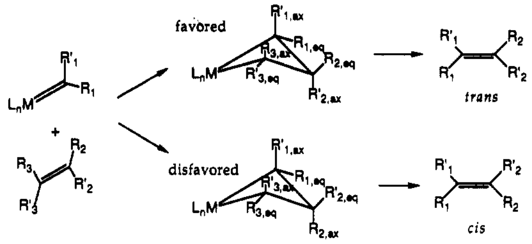


Figure 1. Ring-opening metathesis polymerization (ROMP) of cyclic olefins.



$R_1 = R_2 = R_3$ = alkyl group; $R'_1 = R'_2 = R'_3$ = hydrogen

Figure 2. 1,2-Interaction determining the stereochemistry of the product.

For example, the propensity of trans stereoselectivity in ROMP polymers has been postulated to be caused primarily by steric interaction of the substituents in the 1,2-position of a puckered metallacyclobutane intermediate (Figure 2).[10] Metallacyclobutane having (1,2)-(equatorial,equatorial) interaction exhibits less steric crowding and was presumed to be the favored intermediate, thus resulting in trans stereoselectivity. The role of the 1,3-substituent and the ligand substituent interactions on the stereoselectivity is unknown.

A different mechanism was proposed to account for the observed relation of cis–trans isomerism with tacticity in ring-opened polynorbornene.[2] The lability of the ligands on the metal is a key feature of the postulate. In each propagation step, a pseudooctahedral metal–carbene complex with nonlabile ligands can only produce one vacant site for olefin coordination. As seen from Figure 3, if the ligands around the metal are nonlabile and the rotation about the metal–carbene bond is slow, isotactic segments are produced whenever trans double bonds are produced. The same mechanism accounts for the relation of syndiotactic segments with cis double bonds.

In order to test these models, the precise identification of microstructures in a polymer is essential. NMR spectroscopy is currently the most powerful tool in microstructural assignments of polymers and has been used to determine the microstructure on polynorbornene derivatives.[11] In order to further test these models, a careful study of the microstructure of poly(7-oxanorbornene) derivatives prepared with a variety of catalysts has been carried out. The results of such a study can be compared with those of polynorbornene. The study with

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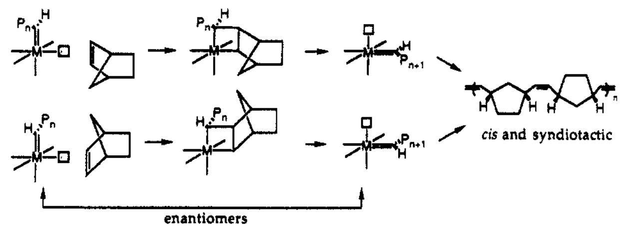
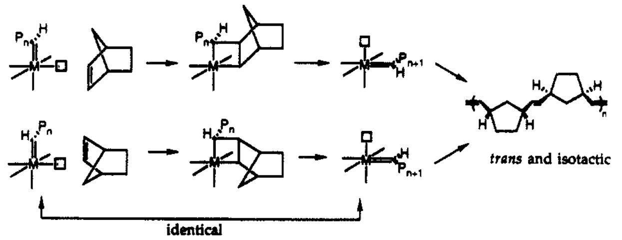


Rac dyads are formed whenever *cis* double bonds are formed.



Similarly, *meso* dyads are formed whenever *trans* double bonds are formed.

Figure 3. Proposed propagation mechanism for observed cis double bond association with syndiotacticity and trans double bond association with isotacticity in norbornene-type polymers prepared from classical ROMP catalysts.[2a] P_n = polymer chain, M = metal, □ = vacant site.

7-oxanorbornene allows a comparison of the late-transition-metal catalyst in aqueous media to more defined early catalysts. Norbornenes due to their insolubility in water can only be studied with early-transition-metal catalysts. The robustness of $[Ru(H_2O)_6](tosylate)_2$ in aqueous media, its tolerance of functional groups,[12] the symmetrical geometry around the metal center, and the facile substitution of aqua ligands with other ligands[13,14] make $[Ru(H_2O)_6](tosylate)_2$ an ideal system to study the effect of ligand lability on the stereochemistry of the polymer.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were acquired on a JEOL GX-400 (399.65-MHz ^1H), optical rotations measured on a Jasco DIP-181 digital polarimeter, IR spectra measured on a Perkin-Elmer 1600 Series FTIR, and polymer molecular weights on a gel permeation chromatography (GPC) column (American Polymer Standard; porosity, linear 10 μm, methylene chloride) on a Knauer differential refractometer relative to a polystyrene standard.

Materials and Methods. All manipulations of air- and/or moisture-sensitive compounds were carried out under argon using standard Schlenk and vacuum-line techniques. Argon was purified by passing through columns of activated BASF RS-11 (Chemalog) oxygen scavenger and Linde 4A molecular sieves. Solids were weighed in a drybox equipped with a MO-40-1 purification train. Solvents were purified as follows: benzene, tetrahydrofuran, and toluene were distilled from sodium benzophenone ketyl into solvent flasks equipped with Teflon screw-type valves; chlorobenzene, chloroform, and dichloromethane were distilled from calcium hydride under vacuum into small Schlenk flasks and subsequently freeze–pump–thaw degassed. Absolute ethanol was used directly from a new bottle without further drying.

$RuCl_3{\cdot}3H_2O$ (8; Johnson-Matthey), $RhCl(PPh_3)_3$ (Aldrich), *p*-toluenesulfonhydrazide (Aldrich) were obtained commercially and used directly without further purification. Catalysts 6, 7, and 9 were prepared by previously reported procedures.[15-17] Monomers 1 and 3 were prepared by previously reported procedures.[12b,18] (*R*,*S*)-*endo*-7-Oxanorbornene-5-carboxylic acid and (*R*)-(+)- and (*S*)-(−)-*endo*-7-oxanorbornene-5-carboxylic acid were prepared from previously reported procedures with the following modification.[19]

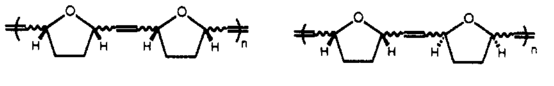


Figure 4. Meso–rac isomerism. The labels are noninterchangeable (mr ≠ rm).

(*R*,*S*)-*endo*-7-Oxanorbornene-5-carboxylic Acid. Acrylic acid (21.6 g, 0.3 mol), furan (40.8 g, 0.6 mol), and hydroquinone (0.1 g) were stirred under Ar for 90 days. From 32 g of the mixture (ca. 50% conversion), (*R*,*S*)-*endo*-7-oxanorbornene-5-carboxylic acid, (*R*,*S*)-*exo*-7-oxanorbornene-5-carboxylic acid, and unreacted acrylic acid were separated by silica gel flash chromatography using 1:2 hexane–diethyl ether (done in 4-g increments).

Endo Isomer. ^1H NMR ($CDCl_3$): δ 6.45 (d), 6.44 (d), 5.18 (d), 5.03 (d), 3.15 (qn), 2.11 (ddd), 1.55 (dd). ^{13}C NMR ($CDCl_3$): δ 177.97 (C_7), 137.18 (C_3), 132.62 (C_2), 79.05 (C_4), 78.62 (C_1), 42.76 (C_5), 28.38 (C_6). **Exo Isomer.** ^1H NMR ($CDCl_3$): δ 6.41 (d), 6.35 (d), 5.21 (s), 5.10 (d), 2.47 (dd), 2.15 (dt), 1.60 (dd). ^{13}C NMR ($CDCl_3$): δ 179.50 (C_7), 137.16 (C_3), 134.49 (C_2), 80.92 (C_4), 78.02 (C_1), 42.63 (C_5), 29.21 (C_7).

(*R*)-(+)-*endo*-7-Oxanorbornene-5-carboxylic Acid.[19] A total of 1.7 g of white solid (*R*,*S*)-*endo*-7-oxanorbornene-5-carboxylic acid (12.3 mmol) was dissolved in a minimum amount of absolute ethanol. (*S*)-(−)-α-Methylbenzylamine (1.49 g, 12.3 mmol) was added. The resultant salt was recrystallized four times in hot ethanol, redissolved in water, and finally passed through a cation ion-exchange resin (Dowex 50X2-400 previously treated with HCl and rinsed until Cl^- free). The product was obtained by pumping off the solvent under vacuum. $[\alpha]^{22}_D$ = 98.7 in EtOH. Optical purity = 89%. An analogous procedure was followed for (*S*)-(−)-*endo*-7-oxanorbornene-5-carboxylic acid using (*R*)-(+)-α-methylbenzylamine.

(*S*)-*endo*-5-(Methoxymethyl)-7-oxanorbornene (2S). $LiAlH_4$ (0.25 g, 6.69 mmol) in THF (5 mL) was added to a stirred solution of (*R*)-(+)-*endo*-7-oxanorbornene-5-carboxylic acid (1 g, 7.14 mmol) in THF. After the mixture had been heated to 60 °C for 10 h, water was added and the salts were filtered off. The filtrate was dried with $MgSO_4$, and the solvent rotovapped off. The product 7-oxanorbornene-5-carbinol was redissolved in THF, and NaH (0.2 g) was added. Iodomethane (0.5 mL) was syringed into the solution and the mixture stirred for 3 h. Water was added, followed by a copious amount of ether. After the salts were filtered off and the filtrate was dried with $MgSO_4$, the solvent was rotovapped off. The crude product was purified via Kugelrohr at 50 °C (0.01 mmHg). After redrying with NaH, the product was vacuum distilled into a Schlenk tube. Total yield: 40–61%. **2R** is prepared in a similar manner. ^1H NMR ($CDCl_3$): δ 6.35 (dd), 6.23 (dd), 4.97 (d), 4.91 (d), 3.29 (m), 3.27 (s), 2.48 (qn), 1.97 (ddd), 0.66 (dd). ^{13}C NMR ($CDCl_3$): δ 136.27 (C_3), 132.32 (C_2), 79.54 (C_4), 78.23 (C_1), 75.32 (C_7), 37.75 (C_5), 27.95 (C_6). For comparison, the (*R*,*S*)-exo isomer, synthesized in a similar manner, has the following NMR values. ^1H NMR ($CDCl_3$): δ 6.28 (s, 2 H), 4.91 (d), 4.81 (s), 3.35 (m), 3.34 (s), 1.80 (m), 1.35 (dd), 1.21 (m). ^{13}C NMR($CDCl_3$): δ 135.72 (C_3), 134.93 (C_2), 79.45 (C_4), 77.74 (C_1), 75.66 (C_7), 58.78 (C_8), 37.94 (C_5), 28.45 (C_6).

General Procedure for Polymerization Using $W(CH\text{-}t\text{-}Bu)(NAr)(OCMe(CF_3)_2)_2$ ($Ar = 2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$) (6). Monomer (1.26 mmol, degassed and NaH dried) was added to a −40 °C solution of 6 (20 mg, 0.0252 mmol) in toluene (2 mL). The solution was gradually warmed to room temperature. After 1.5 h, wet acetone (2 mL) was added to the reaction mixture. Polymer was obtained by pumping off the solvent or by adding the reaction mixture to pentane. Yield: 40–75%.

General Procedure for Polymerization Using $[Ru(H_2O)_6](tosylate)_2$ (7). Monomer (0.3 mmol, degassed) was added to a stirred solution of 7 (3.5 mg, 0.0063 mmol) in previously degassed water (0.5 mL) under Ar. These immiscible liquids were stirred vigorously and heated to 50 °C. White solid polymer can be detected within a minute. After an hour, the polymer was dissolved in 50 mL of ethanol, reprecipitated in 200 mL of 0.02 M Na_2EDTA/water, and dried overnight under vacuum. Yield: quantitative.

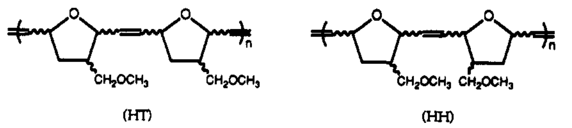


Figure 5. Head-tail isomerism. Labels are non-interchangeable (HT ≠ TH).

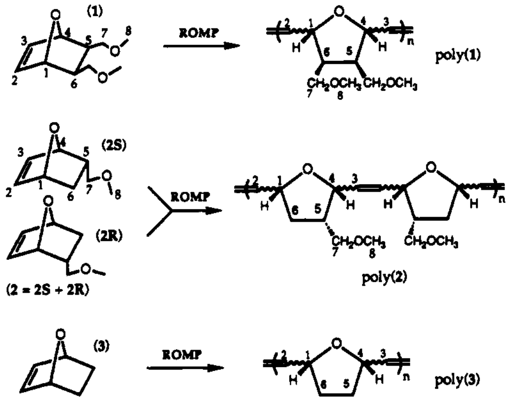


Figure 6. Ring-opening metathesis polymerization of 7-oxanorbornene monomers.

General Procedure for Polymerization Using RuCl$_3$·3H$_2$O (8). In a typical experiment, a stirred solution of 8 (33 mg, 0.126 mmol) in chlorobenzene (1.5 mL) and absolute ethanol (1 mL) was degassed. Monomer (5.79 mmol, degassed) was added to this solution which was then heated to 50 °C for 30 h. The resultant viscous solution was poured into ethanol and centrifuged, and the liquid portion was precipitated into water. Typical yield: 48%.

General Procedure for Polymerization Using [RuCl(μ-Cl)(η^3:η^3-C$_{10}$H$_{16}$)]$_2$ (C$_{10}$H$_{16}$ = 2,7-Dimethyloctadienediyl) (9). Monomer (0.3 mmol, degassed) was added to a stirred solution of 9 (3.8 mg, 0.00617 mmol) in CH$_2$Cl$_2$ (0.15 mL) and then heated to 50 °C for 12–24 h. The viscous solution was then filtered through silica gel. The polymer was obtained by pumping off the solvent. Yield: ca. 70%.

General Procedure for Hydrogenation of Polymer Using *p*-Toluenesulfonhydrazide. The polymer (0.8 g, 4.34 mmol in double bond) was dissolved in hot xylene (30 mL, 60 °C). TsNHNH$_2$ (4.63 g, 24.9 mmol) was added, and the solution, gradually heated to 110 °C and maintained for 3 h. The hot solution was decanted and cooled. Xylene was distilled off under vacuum. Polymer was isolated using silica gel flash chromatography in THF/ligroin.

Hydrogenation of Poly(*exo,exo*-5,6-bis(methoxymethyl)-7-oxanorbornene) with RhCl(PPh$_3$)$_3$/H$_2$. In the drybox, RhCl-

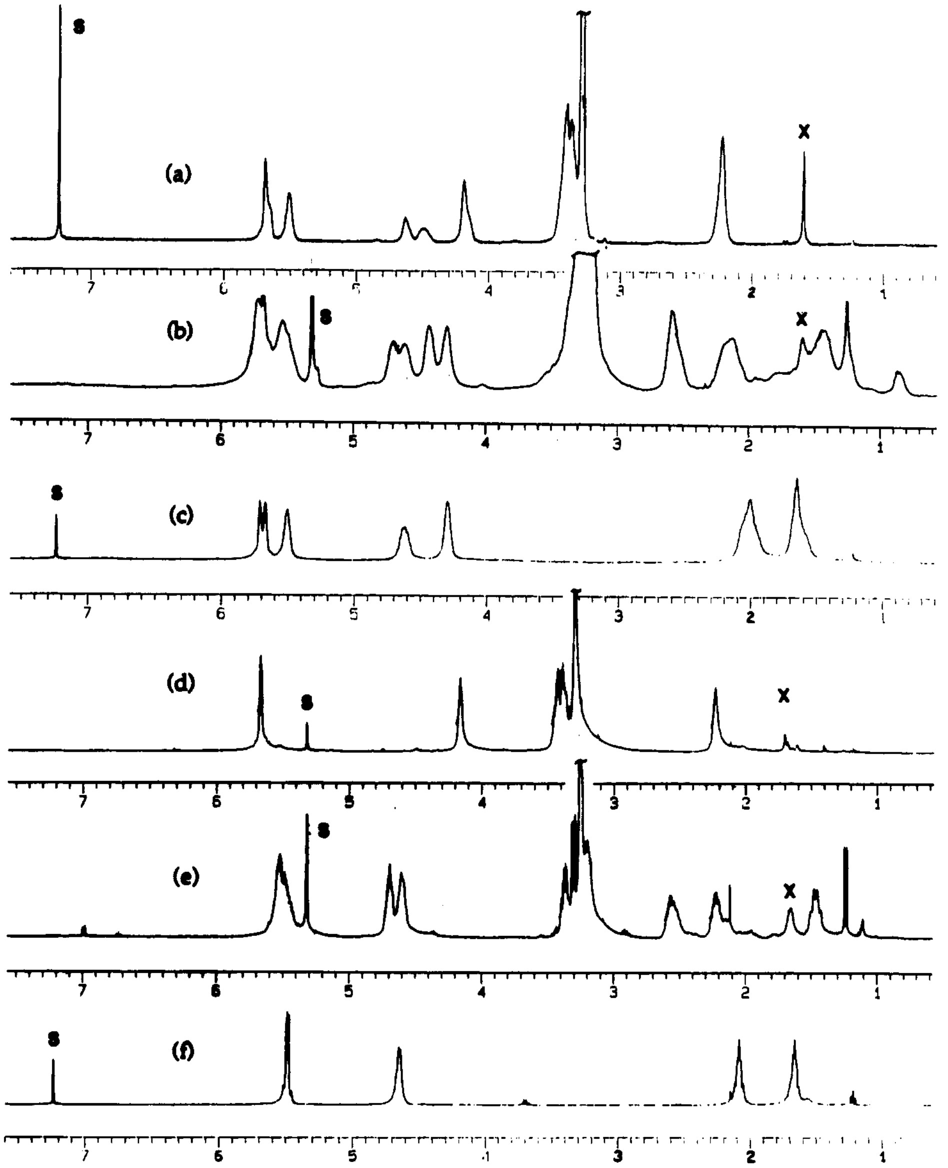


Figure 7. ^{1}H NMR spectra of (a) poly(1), (b) poly(2), and (c) poly(3) prepared from [Ru(H$_2$O)$_6$](tosylate)$_2$. ^{1}H NMR spectra of these polymers using catalysts 6, 8, and 9 are similar to those above except they are much simpler in appearance due to the absence of particular microstructures (e.g., (d) poly(1) using 9; (e) poly(2) using 6; (f) poly(3) using 6). Peak assignments in poly(2) are deduced from ^{1}H–^{1}H COSY. See Table I for peak assignments. X = water. S = solvent.

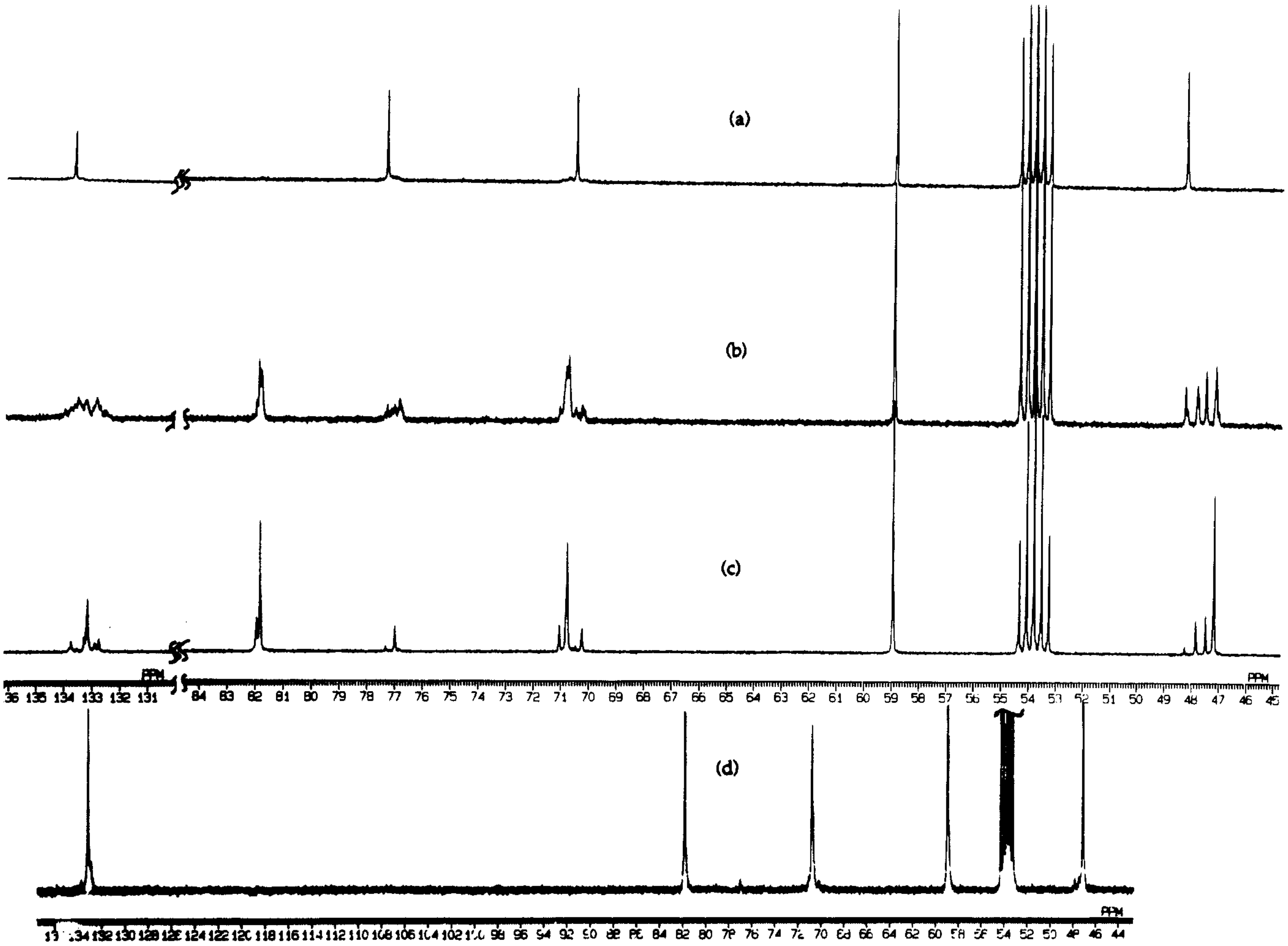


Figure 8. ^{13}C NMR spectra of poly(1). Spectra a–d correspond to poly(1) prepared using catalysts 6–9, respectively. d does not have the same scale as the others. See Table III for peak assignments.

$(PPh_3)_3$ was added to a solution of polymer in toluene in a Fisher–Porter bottle. Nitrogen gas was pumped off from the bottle, and the bottle was repressurized with hydrogen gas (40 psi). The solution was heated to 50 °C for 8 h and then filtered through silica gel. The product was isolated by pumping off solvent.

Results and Discussion

The microstructure of a norbornene-type polymer depends on the relationship between adjacent chain units. The simplest isomeric relationships between two units (diads) in a polymer are usually divided into the following types:[20] 1. cis (c)–trans (t) isomerism for the double bond in the diad; 2. meso (m) (i.e., isotactic)–racemic (r) (i.e., syndiotactic) relationship of the two tetrahydrofuran rings of the diad (Figure 4); 3. head (H)–tail (T) isomerism for the substituent in one ring of the diad relative to the second ring (Figure 5). This isomerism exists only if the norbornene-type monomer possesses C_1 symmetry. The diad is labeled as (HH), (HT), (TH), or (TT) depending on whether the substituent in one ring of the diad is near (head) or far (tail) from the second ring of the diad, and vice versa.

Similar types of isomerism exist for triads and higher order *n*-ads. In each *n*-ad, the total number of possible isomers increases geometrically with *n*.[20]

When monomers 1–3 were polymerized (Figure 6), the number and position of ^1H and ^{13}C NMR peaks for each polymer were found to be dependent on the ROMP catalyst used (Figure 7). These differences are correlated to the microstructure variation in the polymers (vide infra).

Table I
^1H NMR Assignments for Poly(1), Poly(2), and Poly(3) in $CDCl_3$ or CD_2Cl_2

polymer	chemical shift (ppm)	H no. (type)	peak assignment
poly(1)	5.69–5.65	2,3 (olefin)	trans
	5.52–5.50	2,3 (olefin)	cis
	4.63–4.50	1,4 (bridgehead)	cis
	4.19–4.16	1,4 (bridgehead)	trans
	3.42 and 3.37	7 (methylene)	insensitive
	3.29	8 (methyl)	insensitive
	2.23	5,6 (ring)	insensitive
poly(2)	5.73	2 (olefin)	trans, tail
	5.69	3 (olefin)	trans, tail
	5.52	2 (olefin)	cis, tail
	5.49	3 (olefin)	cis, head
	4.69	4 (bridgehead)	cis, head
	4.60	1 (bridgehead)	cis, tail
	4.43	4 (bridgehead)	trans, head
	4.30	1 (bridgehead)	trans, tail
	3.39–3.30	7 (methylene)	insensitive
	3.26	8 (methyl)	insensitive
	2.56	5 (ring)	insensitive
	2.22	6 (exo, ring)	exo
	1.48	6 (endo, ring)	endo
poly(3)	5.71–5.67	2,3 (olefin)	trans
	5.51–5.48	2,3 (olefin)	cis
	4.62	1,4 (bridgehead)	cis
	4.30	1.4 (bridgehead)	trans
	2.04	5,6 (exo, ring)	exo
	1.66	5,6 (endo, ring)	endo

Olefin and Bridgehead Proton and Carbon NMR Resonances Gave the Cis to Trans Content of the Polymer. Aside from IR spectroscopy, the cis to trans

Table II
Percent of Double Bonds in Poly(1) That Are Trans[a]

catalyst	$H_{2,3}$ (olefin)	$H_{1,4}$ (bridgehead)	$C_{1,4}$ (bridgehead)	$C_{5,6}$ (ring)	C_7 (methylene)
6	3	3	not integ[b]	not integ[b]	not integ[b]
7	59	58	58	57	not integ[b]
8	84	85	84	83	85
9	96	96	not integ[b]	not integ[b]	not integ[b]

[a] Value as determined by the integration of the NMR peak areas of particular proton and carbon nuclei. [b] Signal to noise ratio in the spectra not acceptable (see Figure 8).

double bond content in the polymer can be determined by integration of the ^{1}H NMR peaks of olefin and allyl protons. The ^{1}H NMR peak of a trans olefin proton in a disubstituted alkene is always downfield from that of a cis olefin proton, while that of a bridgehead proton one carbon removed from a trans double bond was upfield from that of a cis double bond (Table I).[21,22] Some of these resonances have futher splittings not arising from spin-spin couplings. Unfortunately, these splittings within the cis-trans isomerism resonances, that may be due to meso-rac isomerism, are too poorly resolved to make definite assignments. On the basis of ^{1}H NMR, the double bonds in poly(1) prepared with the tungsten catalyst 6 were cis, those from the ruthenium catalysts 8 and 9 were highly trans (85% and 96% of double bond are trans, respectively), and those from the ruthenium catalyst 7 were roughly equal amounts of cis and trans (Table II). Similar trends are observed for poly(2) and poly(3) prepared using these catalysts (Figure 7).

^{13}C NMR spectra of the polymers provide another method for determining the cis-trans ratio of the double bonds. Chemical shifts of carbons α to a trans double bond generally occur 4-5 ppm downfield from those of cis double bonds.[22] This observation also holds for poly(1), poly(2), and poly(3). The bridgehead carbons of poly(1) exhibit two major clusters around 81.8 and 77.3 ppm, arising from trans and cis diads, respectively (Figure 8). Evaluation of the areas under these peaks yielded the same cis-trans double bond ratio as obtained from ^{1}H NMR spectra (Table II). For poly(3), the bridgehead carbon allylic to a trans double bond resonated at 79.5 ppm, while that to a cis double bond appeared at 75.3 ppm. For poly(2), the chemical shift of the bridgehead carbon was further resolved into four peaks instead of two due to head-tail isomerism caused by the methoxymethyl substituent. The bridgehead carbons C_4 and C_1 of the trans diad occurred at 80.7 and 79.4 ppm, about 4.0 and 4.5 ppm downfield from C_4 and C_1 of the cis diad (76.7 and 74.9 ppm, respectively).

Ring (or Bridge) Carbon and Methylene Carbon NMR Peaks Allowed Determination of Cis and Trans Blockiness (Degree of Clustering of Cis or Trans Double Bonds) of the Ring-Opened Polymer. In contrast with some of the carbons in poly(1) wherein only two peaks corresponding to cis-trans isomerism of the double bond in the diad were observed, the remaining ring carbon C_5 in poly(1) had four identifiable chemical shifts (48.3, 47.9, 47.5, 47.2 ppm) (Figure 8). The same held for methylene carbon C_7 (71.1, 70.8, 70.5, 70.2 ppm). Since poly(1) cannot exhibit head-tail isomerism because of the symmetric nature of the monomer, these peaks are either due to diads sensitive to both cis-trans and meso-rac isomerisms or due to triads that are sensitive to only one type of isomerism. The former case would give rise to quadruple peaks corresponding to (cr), (cm), (tr), and (tm). The latter case also gives rise to quadruple peaks [(cc), (ct), (tc), (tt)] or [(rr), (rm), (mr), (mm)] depending on which type of isomerism the said carbon was sensitive to. This ambiguity as to whether the resonances observed are the result of general sensitivity to all types of diad configurations or just to a selective sensitivity to certain triad configurations was resolved by hydrogenating poly(1), which removes cis-trans isomerism. The meso-rac ratio in the polymer remains unaffected since meso-rac isomerism was determined by the stereochemistry of the bridgehead carbons. Regardless of which catalyst was used to synthesize poly(1), upon hydrogenation, hydrogenated poly(1) exhibits double peaks for carbons C_2 (former olefin), C_1 (bridgehead), and C_5 (ring) (Figure 9). These double resonances must be due to meso and rac diads. Thus, none of the original poly(1)s synthesized using different catalysts were completely tactic. This result, combined with the previous observation (Figure 8) that both pure *cis*-poly(1) made from tungsten catalyst 6 and high *trans*-poly(1) made from ruthenium catalyst 9 show a *single* ring carbon C_5 NMR peak, implies that quadruple resonances cannot result from meso-rac isomerism. In other words, the quadruple resonances arise from (cc, ct, tc, tt) triads and not from (cr, cm, tr, tm) diads nor (rr, rm, mr, mm) triads. This conclusion was not totally surprising. Related studies using polynorbornene also show that the remaining ring carbon C_5 of polynorbornene was sensitive to cis-trans isomerism of triads only, the chemical shift difference arising from meso-rac isomerism being too small to be observed.[23]

Thus, the lone peak at 48.3 ppm (Figure 8) of poly(1) using tungsten catalyst 6 was (cc) (Table III). The predominant peak with 47.2 ppm for poly(1) by ruthenium catalysts 8 and 9 was (tt). The remaining two peaks of equal intensity at 47.9 and 47.5 ppm that are also present in poly(1) using ruthenium catalyst 7 are (ct) and (tc). The resonances of methylene carbon are assigned similarly. Internal consistency of the assignments was also found when the necessary interdependent relationships of higher *n*-ads to lower *n*-ads are used. The (cc + ct)/(tc + tt) ratio calculated by integrating the remaining ring carbon C_5 or methylene carbon was equal to the cis-trans ratio calculated by integrating ^{13}C or ^{1}H bridgehead peaks (Table II).[24]

Stereochemistry of Higher *n*-Ads ($n > 2$) Can Be Observed by Carbon NMR but Can Only Be Partially Assigned. The presence of at least six resolvable resonances coming from olefin carbons in poly(1) and poly(3) implies that the carbon was sensitive either to tetrads of cis-trans isomerism or to the combined effects of triads of cis-trans and diads of meso-rac isomerism, both of which give rise to eight possible resonances. Occasionally, the former was invoked even though the olefinic carbons in adjacent double bonds are at least four or five bonds away.[20] Without any other experimental data available, these resonances cannot be assigned unambiguously. It can only be noted that cis-trans *n*-ads occurred in two distinct regions. For poly(1), cis olefin carbons resonate in the region 133.8-133.3 ppm while trans olefin carbons resonate from 133.1 to 132.7 ppm (Table III). Similarly, for poly(3), cis olefin carbons resonate from 133.1 to 132.7 ppm while trans olefin carbons resonate from 132.5 to 132.1 ppm.

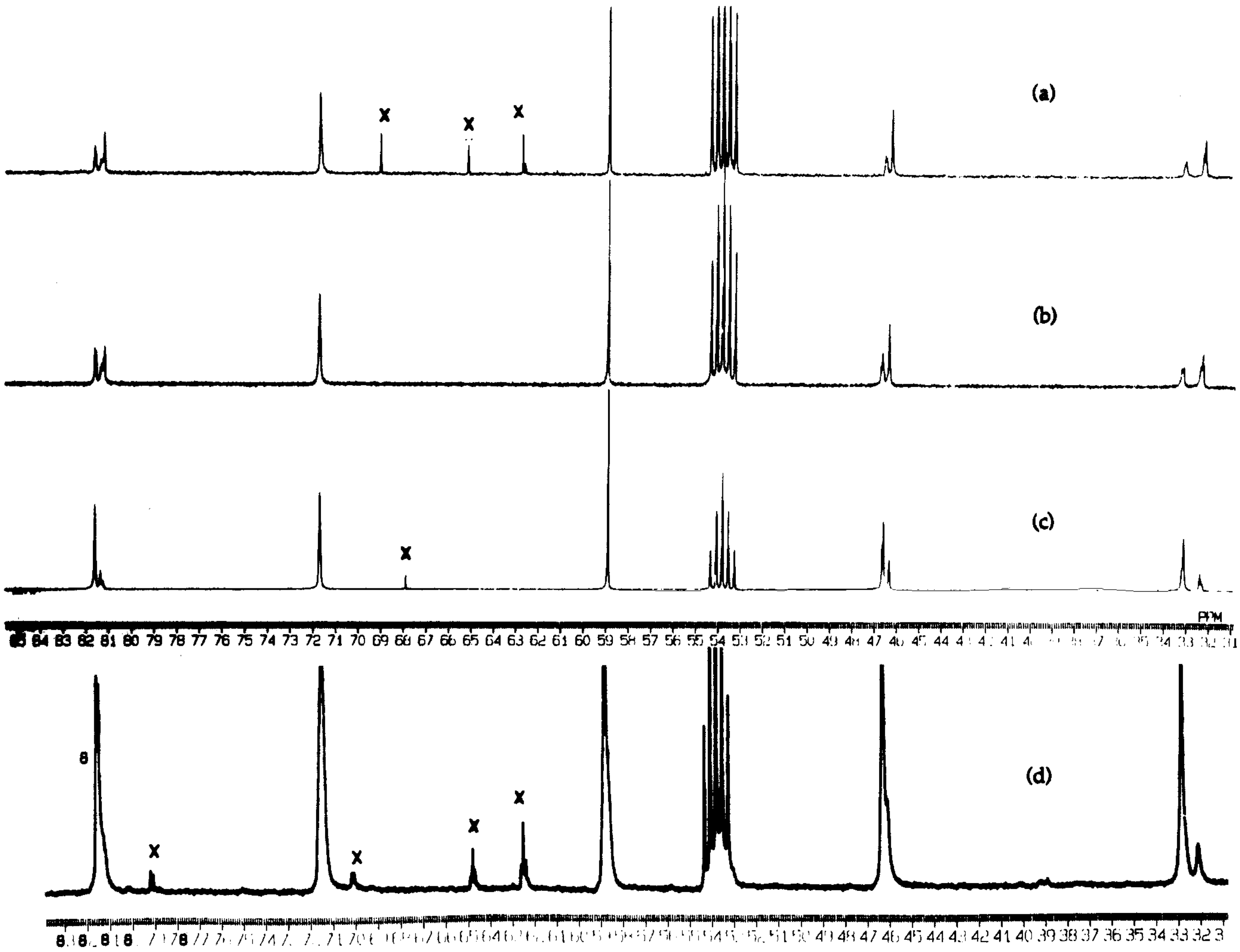


Figure 9. ^{13}C NMR spectra of hydrogenated poly(1). Spectra a–d correspond to hydrogenated poly(1) prepared using catalysts 6–9, respectively. *p*-Toluenesulfonhydrazide is used to hydrogenate poly(1). X = impurities. See Table V for peak assignments.

Table III
^{13}C NMR Assignments for Poly(1) in CD_2Cl_2

chemical shift (ppm)	C no. (type)	peak assignment
133.8	2,3 (olefin)	"cis"
133.7	2,3 (olefin)	ccc
133.5	2,3 (olefin)	"cis"
133.3	2,3 (olefin)	"cis"
133.1	2,3 (olefin)	ttt
132.9	2,3 (olefin)	"trans"
132.7	2,3 (olefin)	"trans"
82.0	1,4 (bridgehead)	tc
81.8	1,4 (bridgehead)	tt
77.3	1,4 (bridgehead)	cc
77.0–76.9	1,4 (bridgehead)	ct
71.1	7 (methylene)	tc
70.8	7 (methylene)	tt
70.5	7 (methylene)	ct
70.2	7 (methylene)	cc
48.3	5,6 (ring)	cc
47.9	5,6 (ring)	ct
47.5	(5,6 ring)	tc
47.2	5,6 (ring)	tt
59.0	8 (methyl)	insensitive

Hydrogenated ROMP Polymer Provided a Way To Determine the Meso to Rac Content of the Original ROMP Polymer. Definitive Peak Assignments of Hydrogenated Poly(1) Achieved by Using Enantiomerically Pure Monomer 2S. Assignment of the two ^{13}C NMR peaks arising for each type of carbon of the hydrogenated poly(1) to meso or rac is achieved by knowing that the tacticity of poly(1) can be deduced using an enantiomerically pure monomer 2S. When an enantiomerically pure monomer of C_1 symmetry was polymerized with a ROMP catalyst, (HT) and (TH) diads can only give rise to a meso diad, while (HH) and (TT) diads can only give rise to a rac diad (Figure 10).[25] Provided that differences in ^{13}C NMR chemical shifts for head–tail diads are large enough to be resolved, meso–rac isomerism can thus be determined indirectly by examining head–tail isomerism in the polymer. The pendant methoxymethyl group attached to the ring carbon C_5 of 2S was too far from the double bond to favor the existence of one diad isomer over the other.[26]

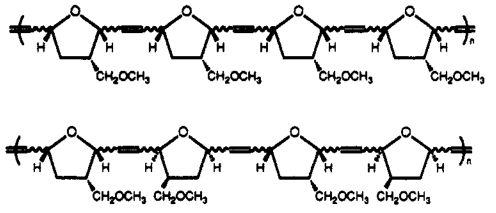


Figure 10. (HT) and (TH) can only correspond to meso (top diagram) and (HH) and (TT) to rac (bottom diagram) for polymers prepared from ROMP of enantiomerically pure 7-oxanorbornene-type monomers possessing a C_1 symmetry. The monomer used above is 2S.

Since meso–rac isomerism for (7–oxanorbornene)-type polymer cannot be determined directly by ^{13}C NMR due to the absence of resolvable peak splittings, the theoretical number of olefin resonances arising from the combination of cis–trans and head–tail isomerism in poly(2) is 8 for diads and 32 for triads; poly(2S) theoretically also gives 8 for diads and 32 for triads. Any further reduction in the

Table IV
Theoretical Number of ^{13}C NMR Resonances for the Olefinic Carbon of the Polymer[f]

n-ads	polymer	A[a]	B[b]	C[c]	D[d]	E[e]
diads	poly(2)	16	8	4	8	4
	poly(2S)	8	8	4	2	2
triads	poly(2)	128	32	8	32	8
	poly(2S)	32	32	8	4	2

[a] A = all types of microstructures arising from the three different types of isomerisms can be resolved by ^{13}C NMR. [b] B = cis–trans and head–tail isomerisms resolvable but not meso–rac isomerism. [c] C = same as B with the added condition that the double bonds in the polymer are either all cis or all trans. [d] D = same as B with the added condition that the polymer is tactic. [e] E = both conditions in C and D are fulfilled simultaneously. [f] For diads ((c,t), (m,r), (HH, HT, TH, TT)) and for triads ((cc, ct, tc, tt), (mm, mr, rm, rr), (HHH, HHT, HTH, THH, HTT, THT, TTH, TTT)). Note that HHT ≠ THH.

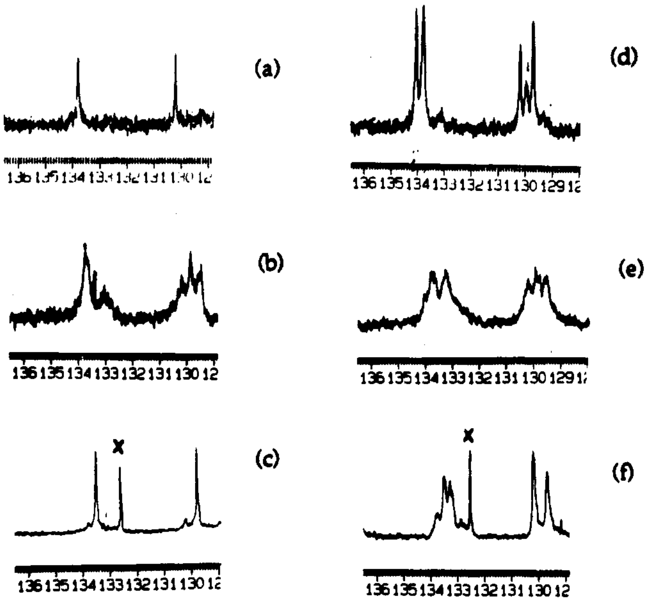


Figure 11. ^{13}C NMR spectra of the olefin region of poly(2) and poly(2S). Spectra a–c correspond to poly(2S) prepared using catalysts 6, 7, and 9, respectively. Spectra d–f correspond to poly(2) prepared using catalysts 6, 7, and 9, respectively. X = starting monomer.

number of peaks observed implies either an absence of certain microstructure or that the resonances are again not well separated enough to show unique chemical shifts. An example of the former case is pure *cis*- or *trans*-poly(2) which theoretically gives 4 (diad isomer) and 8 (triad isomer) olefin resonances and pure *cis*- or *trans*-poly(2S) which gives 4 (diad) and 8 (triad) resonances (Table IV). A cis and at the same time tactic poly(2) gives 4 (diad) and 8 (triad), while tactic *cis*-poly(2S) gives 2 (diad) and 2 (triad). Note that only if the polymer has a high degree of microstructural order is the number of olefin resonances arising from the polymer prepared from ROMP of (*R*,*S*) monomer different from that of the (*S*) monomer, as was possible in the case of poly(2) and poly(2S).

Since tungsten catalyst 6 gives cis polymer while ruthenium catalyst 9 gives trans polymer, the spectra are simplified by reducing the theoretical allowable number of resonances. Using catalyst 6, the olefinic carbons of poly(2) show four predominant peaks at 134.0, 133.8, 130.2, and 129.7 ppm while those from poly(2S) only give rise to two peaks at 133.8 and 130.2 ppm (Figure 11). This difference in the number of peaks observed must only be from head–tail isomerism. The exact assignment of the two peaks with 133.8 and 130.2 ppm to cisTT and cisHH in poly(2S) and to the additional two at 134.0 and 129.7 ppm to cisTH and cisHT in poly(2) was by analogy with polynorbornene that has a pendant substituent at ring carbon C_5—which always shows the same ordering of chemical shifts for the isomeric olefin carbons.[27] Therefore, poly(2S) was a predominant (TT) and (HH) polymer, implying that the larger peak in the double peak splittings in the ^{13}C spectrum of hydrogenated poly(1) using 6 is rac (Table V and Figure 11). Consequently, the original poly(1) synthesized using catalyst 6 is a cis, highly syndiotactic polymer.

Table V
^{13}C NMR Assignments for Hydrogenated Poly(1) in CD_2Cl_2

chemical shift (ppm)	C no. (type)	peak assignment
81.63–81.58	1,4 (bridgehead)	meso
81.37–81.19	1,4 (bridgehead)	rac
71.74	7 (methylene)	insensitive
58.92	8 (methyl)	insensitive
46.74–46.63	5,6 (ring)	meso
46.44–46.35	5,6 (ring)	rac
33.22–33.16	2,3 (post-olefin)	meso
32.39–32.29	2,3 (post-olefin)	rac

For poly(2) prepared using catalyst 9, four peaks are discernible at 133.5, 133.3, 130.2, and 129.7 ppm, while that from poly(2S) has only two peaks at 133.5 and 129.8 ppm. By similar reasoning, the four peaks from poly(2) are assigned as transTH, transTT, transHH, and transHT, respectively. Hence, polymers from 9 were high-trans, highly isotactic. The high-trans nature of polymers obtained from ROMP of cyclic monomers was a general feature observed for late-transition metal with chloro ligands in nonaqueous solvents.[28] However, the meso content of these norbornene-derivative polymers ranges from 50% (atactic) to 66%, as opposed to at least 75% meso for 7-oxanorbornene derivatives.[27b,c]

Using the above assignments, polymers prepared using 7 as catalyst showed no cis or trans preference and were also atactic. The cis and trans double bonds along the backbone of poly(1) are also randomly distributed, as the area under ^{13}C NMR triads (cc × tt)/(ct × tc) gives a value of 1.2.[29] Consequently, labile symmetrical ligand spheres result in total scrambling of all stereochemistry in the polymer.

In this limited survey of catalysts, there exists a correlation between tacticity and double-bond isomerism in poly(7-oxanorbornene) derivatives. Meso diads are associated with trans diads, and rac diads with cis diads. Whether this correlation is the result of the proposed propagation mechanism for classical catalysts (Figure 3) or other factors is not understood at this point. Certainly, the chloro ligands in catalyst 8 and the allyl ligands in catalyst 9 are essentially inert, whereas the aqua ligands of catalyst 7 are relatively labile.[13,30] On the basis of the model, the observation that catalyst 7 gave the most atactic polymer among the ruthenium catalysts studied implies that the aqua ligand dissociation rate is comparable to the polymer propagation rates. The kinetics of dissociation of various ligands and olefins on the metal center are currently being investigated.

Conclusion

Poly(7-oxanorbornene) derivatives prepared from classical hexacoordinated ruthenium catalysts exhibit a trans tendency if chloro ligands in nonaqueous media are employed. These polymers also exhibit high isotacticity.

In the cases where $[Ru(H_2O)_6](tosylate)_2$ was used as catalyst, the polymers obtained had no preference for trans geometry nor for particular tacticity. This presumably arises from the lability of the aqua ligands which allow several potential coordination sites for the incoming olefin and a complete loss of stereochemical memory after each propagation step.

An apparent correlation exists between tacticity and double-bond isomerism whereby meso diads are associated with trans double bonds and rac diads with cis double bonds. Whether this correlation is a consequence of ligand stereochemistry around the metal center remains unanswered until the chain propagating ruthenium–carbene species in the reaction can be identified.

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