Probing the Stereoselectivity of the Ruthenium-Catalyzed Ring-Opening Metathesis Polymerization of Norbornene and Norbornadiene Diesters

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ABSTRACT: The ring-opening metathesis polymerization (ROMP) of two optically active 2,3-dicarboalkoxynorbornadienes derived from (*S*)-(−)-2-methyl-1-butanol and (*R*)-(−)-2-butanol were carried out in the presence of the $[RuCl_2(p\text{-cymene})]_2$ catalyst precursor activated by trimethylsilyldiazomethane (TMSD). ^1H and ^{13}C NMR analyses showed that a high degree of stereoregularity was achieved, and homonuclear proton−proton COSY spectroscopy indicated that the major trans fractions of the polymers were most likely isotactic, while the minor cis fractions were syndiotactic. Ring-opened metathesis polymers were also made from 2,3-dicarbomethoxynorbornadiene and *exo,exo*-2,3-dicarbomethoxy-5-norbornene. They were hydrogenated into the corresponding polynorbornanes using diimide. The NMR spectra of the reduced materials confirmed that the unsaturated parent polymers had an all-trans highly isotactic microstructure. A tentative mechanism involving arene loss, carbene formation, and monomer chelation is proposed to account for the observed stereoselectivities.

Introduction

Thanks to the development of well-defined tungsten-, molybdenum-, and ruthenium-based initiator systems, the ring-opening metathesis polymerization (ROMP) of cyclic olefins has become a powerful tool for the preparation of synthetic macromolecules with narrow polydispersities and regular architectures.[1,2] The progressive move from early multicomponent Ziegler-type catalytic systems based on transition-metal halides to rationally designed preformed metallacarbene complexes dramatically improved the control over the polymer molecular weight and microstructure.[3] The precise factors that govern the outcome of a ROMP reaction in terms of stereochemistry remain, however, poorly understood. In particular the influence of the catalyst on the polymer tacticity is scarcely documented. Most literature reports focus on the double bond stereochemistry in the ROM polymers (expressed by a cis/trans ratio), but the more complex microstructural features (among which the meso and racemic dyad splitting) are frequently overlooked. Yet, the determination and the interpretation of tacticity are key steps to ultimately control the bulk properties—and hence the practical and commercial values—of many polymeric materials.[4] The problem is not trivial, though. The vast majority of metathesis polymers are obtained from norbornene (bicyclo[2.2.1]hept-2-ene) and its derivatives. Upon ring-opening, these monomers afford a chain of cyclopentenylevinylene repeating units whose mode of linking gives rise to two independent types of isomerism (Figure 1). The first and foremost differentiation comes from the cis or trans configuration of the exocyclic double bonds. The second stereochemical variation arises from the fact that the two allylic bridgehead carbon atoms in norbornene are chiral and possess opposite configurations. In the polymer chain, these pairs of methine carbon atoms can therefore adopt two regular arrangements: $(-RS-RS-)_n$ is constituted of meso dyads and corresponds to an isotactic sequence, while $(-RS-SR-)_n$ comprises racemic dyads and affords a syndiotactic segment. A third kind of microstructural ordering occurs if the norbornene is unsymmetrically substituted. In this case, the substituents in successive units of the polymer backbone may be oriented head-to-tail (HT), tail-to-head (TH), tail-to-tail (TT), or head-to-head (HH), leading to a grand total of 16 possible dyads.

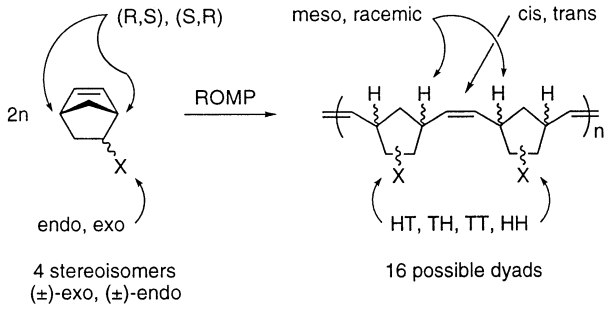

Figure 1. Possible microstructural variations in polymers formed by ring-opening metathesis polymerization of norbornene derivatives.

Systematic investigations on tacticity in ROMP reactions were first carried out in the late seventies by Ivin and Rooney.[5] Since then, research in the field has largely benefited from the developments and the availability of high resolution NMR spectrometers. The advent of well-defined initiators that afford highly stereoregular polymers has also contributed to ease the spectral assignments by providing highly tactic samples instead of ill-defined, atactic materials. Four methods have been used so far for the determination of tacticity in the ROMP of norbornene and its derivatives. The first method, pioneered in Belfast, consists of polymerizing single enantiomers of unsymmetrically substituted norbornenes and determining (mostly by ^{13}C NMR spectroscopy) whether the polymers have a HT (meso) or HH/TT (racemic) bias.[6−9] The second method designed by Schrock at M.I.T. is essentially an extension of the

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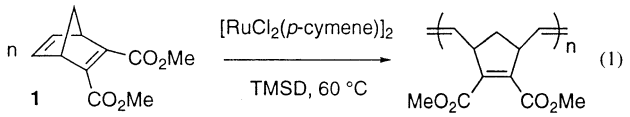
first, in which 2D NMR techniques were applied to probe the tacticity of poly-5,6-disubstituted norbornadiene derivatives containing optically active groups in their side chains.[10] The third method is based on the comparison of the ^{13}C NMR spectra obtained for polymers derived from prochiral monomers and those recorded for closely related chiral species. Thus, it is an indirect method which has been particularly successful when combined to a double bond hydrogenation.[11−13] The fourth and last method is more specific and has been applied to the sole case of poly[2,3-bis(trifluoromethyl)norbornadiene]. Because this polymer contains highly dipolar repeating units, the relaxed susceptibility and dielectric constant above T_g can be measured and correlated with the relative orientations of the neighboring dipoles in the polymer chains.[14]

In 1999, we showed that the ROMP of 2,3-difunctionalized norbornadienes and their 7-oxa analogues catalyzed by $[RuCl_2(p\text{-cymene})]_2$ (*p*-cymene is 1-isopropyl-4-methylbenzene) in the presence of trimethylsilyldiazomethane (TMSD) yielded high-trans, highly tactic polymers.[15] 2,3-Dicarbomethoxynorbornadiene (**1**) served as a test monomer to investigate the influence of the various experimental parameters and an all-trans, highly tactic (>79%) polymer was obtained under a wide variety of conditions (eq 1). The procedure was successfully applied to various other 2,3-dicarboalkoxynorbornadienes, benzonorbornadiene, and their 7-oxa analogues.[15] An important question which remained unanswered at that time was whether the trans polymer chains prepared had an iso- or a syndiotactic bias. Because neither the monomers nor the catalysts used in this study were optically active, direct NMR methods could not be employed to argue for a given tacticity of the polymers formed.



(1)

In this article, we describe the preparation and the polymerization of enantiomerically pure norbornadiene diesters in order to carry out an absolute determination of tacticity. Additional ROMP experiments with 2,3-dicarbomethoxynorbornenes and -norbornadiene followed by hydrogenation of the unsaturated polymers are also reported, as they allow an indirect confirmation of the tacticity assignments and provide further insight into the reaction mechanism.

Results

Polymerization of Optically Active 2,3-Dicarboalkoxynorbornadienes. Four regular primary structures are possible for the ROM polymers of 2,3-disubstituted norbornadienes bearing identical substituents. If these substituents are achiral, as in poly(2,3-dicarbomethoxynorbornadiene), symmetry operations render the olefinic protons equivalent in any given configuration. Conversely, if the substituents contain optically active groups (X*), the symmetry is broken and two sets of nonequivalent olefinic protons (H_A and H_B) can be distinguished (Figure 2). In the isotactic polymers (either cis or trans) these nonequivalent protons are divided up between both sides of all the exocyclic double bonds. Therefore, they are related by a ^3J coupling constant that can be detected by ^1H NMR correlation

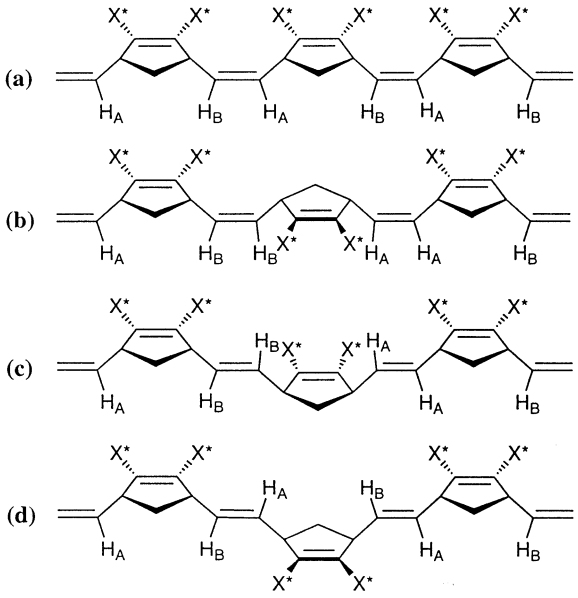
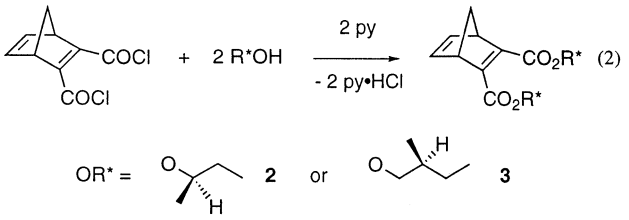


Figure 2. Four possible regular structures of poly(2,3-disubstituted norbornadienes) bearing optically active substituents: (a) cis, isotactic; (b) cis, syndiotactic; (c) trans, syndiotactic; (d) trans, isotactic.

spectroscopy provided that its magnitude is sufficient. In the case of a syndiotactic arrangement (either cis or trans), two types of symmetrically substituted double bonds alternate in the polymer chain. Thus, two olefinic proton resonances should also be visible in the NMR spectra, but they are no longer coupled to each other.

The presence or the absence of coupling cross-peaks in homonuclear ^1H COSY spectra was first investigated to probe the tacticity in the ROMP of enantiomerically pure 2,3-dicarboalkoxynorbornadienes by Schrock and co-workers.[10] Well-characterized molybdenum-alkylidene complexes served as initiators and the (−)-pantolactonyl and (−)-menthyl groups provided the chiral centers in the side chains. These alkoxy groups were deemed too bulky to afford highly stereoregular polymers with our catalytic system based on the $[RuCl_2(p\text{-cymene})]_2$ dimer activated by TMSD. Indeed, our previous work on the ruthenium-catalyzed ROMP of 2,3-dicarbomethoxy-, ethoxy-, isopropoxy-, and *tert*-butoxynorbornadienes and their 7-oxa analogues had shown that an increase in the alkyl substituent size led to a rapid decrease of the polymer trans content and tacticity.[15] We feared that the five- or six-membered cycloalkoxy groups used by Schrock et al. would hinder the coordination of the monomer to the catalytic center, thus leading to polymers with intermediate cis/trans and meso/racemic contents unsuitable for a straightforward determination of tacticity. Hence, we selected two alcohols from the chiral pool that were as simple and linear as possible to serve as ester substituents, namely (*R*)-(−)-2-butanol and (*S*)-(−)-2-methyl-1-butanol. The corresponding norbornadiene monomers **2** and **3** were obtained by reaction with 2,5-norbornadiene-2,3-dicarboxylic acid dichloride in the presence of pyridine (eq 2). They were purified by column chromatography and subjected to ROMP using the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalytic system under standard conditions (6 h reaction in THF at 60 °C). Poly(**2**) and poly(**3**) were first precipitated from methanol, then dissolved again in chloroform, and passed through a short plug of alumina to remove the ruthenium impuri-

ties. The solvents were evaporated, and the residues were dried overnight under high vacuum prior to NMR analysis in $CDCl_3$.



The cis/trans ratio of the double bonds in the unsaturated backbone of the polymers was deduced from their ^{1}H NMR spectra. For poly(**2**), a value of 16/84 was obtained by integrating the cis and trans olefinic proton resonances at 5.51 and 5.39 ppm, respectively. In the case of poly(**3**), the cis and trans =CH− signals were located at 5.45 and 5.40 ppm, respectively. They were in a 18/82 ratio. In both cases, the cis and trans resonances consisted of slightly broadened singlets and the assignment of the *upfield* line to the trans environment was driven by analogy with the sequence observed for other poly(dicarboalkoxynorbornadienes) previously studied, with the notable exception of poly(**1**), whose trans olefinic signal lies *downfield* from that of the cis one.[15] Another significant feature in the ^{1}H NMR spectra of poly(**2**) and poly(**3**) is the presence of only one resonance for the methine protons adjacent to the double bonds at 3.48 or 3.50 ppm, respectively. Thus, the allylic hydrogens remain unaffected by the cis or trans nature of the neighboring exocyclic C=C bonds, a situation already encountered with poly(2,3-dicarbo-*tert*-butoxynorbornadiene)[15] that prevents internal cross-checking of the cis/trans ratio. Yet, the high-trans bias of poly(**2**) and poly(**3**) prepared with the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalytic system is unambiguous and further supported by ^{13}C NMR data (vide infra). It is also in good agreement with the 15/85 cis/trans ratio determined for poly(2,3-dicarboisopropoxynorbornadiene) prepared under the same experimental conditions.[15] This did not come as a surprise for poly(**2**), whose side chain is the immediate superior homologue of the isopropyl group and also comprises a methyl branch next to the ester link. It is slightly more unexpected for poly(**3**), where the ramification is more distant from the carboxy group and should therefore have a less pronounced influence on the steric hindrance around the metal catalytic center.

Despite the fact that neither poly(**2**) nor poly(**3**) was fully trans, their ^{1}H homonuclear correlation spectra provided valuable information about their tacticity. The olefinic region of the 400 MHz COSY spectrum of poly(**2**) clearly showed the presence of intense cross-peaks between the main upfield trans protons H_A and H_B, while the minor downfield cis resonances did not give any off-diagonal peaks (Figure 3). A similar 2D spectrum was obtained with poly(**3**) (not represented). On the basis of the coupling patterns summarized above (cf. Figure 2), one can therefore infer that the cis fraction of both polymers is syndiotactic while the trans fraction is most likely isotactic. However, because an atactic polymer also contains isotactic dyads that produce cross-peaks, the degree of tacticity of the trans fraction cannot be determined solely on the basis of the COSY spectrum.

The full ^{13}C{^{1}H} NMR spectrum of poly(**2**) is depicted in Figure 4. Most peaks displayed a fine structure which

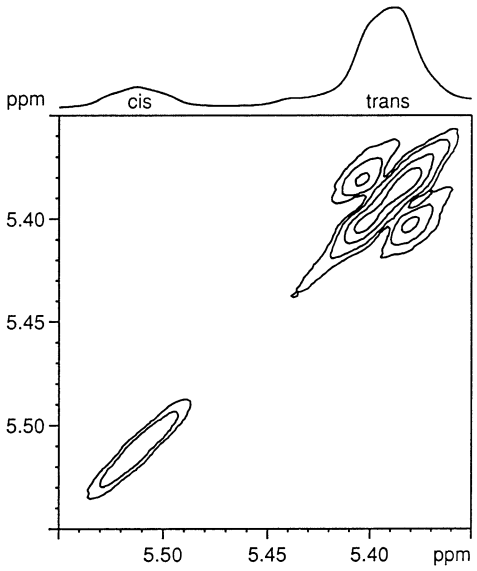


Figure 3. 400.132 MHz ^{1}H COSY spectrum of 84% *trans*-poly(**2**) in $CDCl_3$ showing the olefinic proton region.

is illustrated in insets for $C_{1,4}$, $C_{2,3}$, and C_7.[16] In the unsymmetrical monomer **2**, the presence of the (*R*)-1-methylpropoxy groups led to a diastereoisomeric splitting of $C_{2,3}$, $C_{5,6}$, C_7, and C=O that all appeared as sets of two close lines of equal intensities in proton-decoupled ^{13}C NMR analysis (see the Experimental Section for assignments). Such a 1:1 splitting is also clearly visible for $C_{1,4}$, $C_{5,6}$, and the trans contribution of $C_{2,3}$ in the corresponding polymer. Other chemical shift differences for each type of carbon atoms arose from the cis/trans and meso/racemic distributions induced by the opening of the norbornadiene-unsubstituted double bond. These effects were most prominent in the $C_{1,4}$ resonances of poly(**2**). Indeed, the allylic carbons adjacent to a cis double bond gave a neat doublet centered at 48.6 ppm, while the same methine groups in a trans environment gave a more complex signal around 49.5 ppm. The fine structure of this peak is due to the contributions of different types of dyads. However, the emergence of a rather well-shaped doublet strongly suggests that the polymer is highly tactic. Integration of the cis and trans components of $C_{1,4}$ gave a 16/84 area ratio, identical to the value obtained from the olefinic protons. The downfield position of the trans lines compared to their cis counterparts agreed with literature data gathered for metathesis polymers,[4] as well as linear alkenes.[17] The olefinic carbons in a trans environment were also deshielded relative to their cis equivalents, as evidenced from the 17/83 intensity ratio measured for the $C_{2,3}$ resonances located at 131.8 and 132.4 ppm, respectively. In this case, a distorted doublet was still observed for the major trans part of the signal while the minor cis one gave a broad singlet. Only one resonance was observed for C_7 at 37.6 ppm, consistent with poly(**2**) being highly tactic. Yet, a tenuous shoulder was present on the upfield face of the peak.

In monomer **3**, the stereogenic centers in the alkoxy side chains were further separated from the chiral norbornadiene bicyclic unit by an additional methylene group, as compared with monomer **2**. This extra spacer was sufficient to suppress all the diastereoisomeric splittings observed in **2**. Thus, only single lines were visible in the ^{13}C{^{1}H} NMR spectrum of diester **3** for $C_{1,4}$, $C_{2,3}$, $C_{5,6}$, C_7, and C=O (see the Experimental

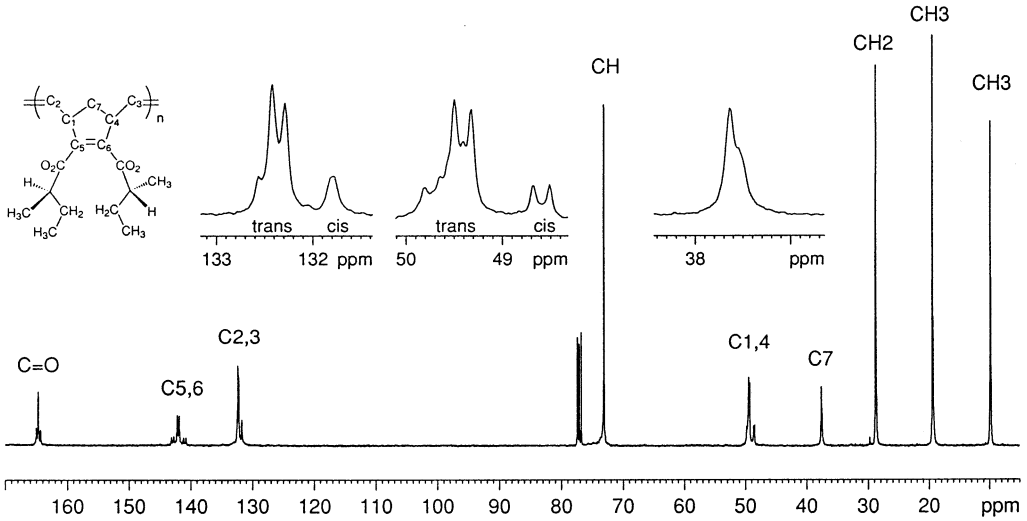


Figure 4. Full 100.613 MHz ^{13}C NMR spectrum in $CDCl_3$ of 84% *trans*-poly(**2**) prepared using as catalyst $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD.

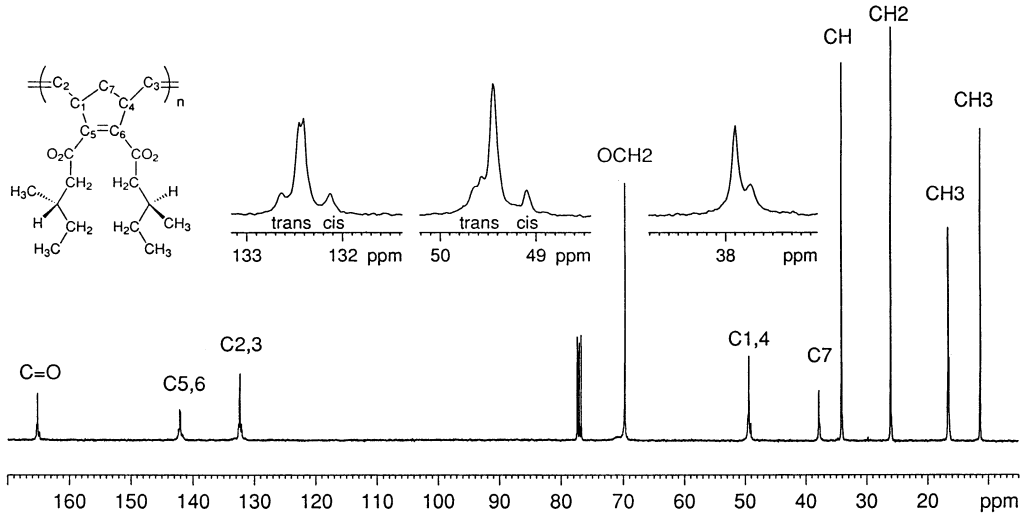


Figure 5. Full 100.613 MHz ^{13}C NMR spectrum in $CDCl_3$ of 82% *trans*-poly(**3**) prepared using as catalyst $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD.

Section for assignments).[16] A similar simplification occurred in the carbon NMR spectrum of poly(**3**) compared to poly(**2**). A close look at the fine structures of the $C_{1,4}$ and $C_{2,3}$ peaks depicted in Figure 5 clearly showed that the doublets present in Figure 4 had now disappeared. A tentative distinction between the minor cis singlets located upfield from the major trans multiplets is proposed in the graphical insets. Integration of the cis and trans regions led to area ratios of 12/88 and 15/85, respectively, for the allylic and olefinic carbons of poly(**3**), in moderate agreement with the 18/82 value obtained by ^1H NMR analysis. Finally, the resonance associated with C_7 and located at 37.9 ppm comprised a distinct shoulder to lower frequency. Deconvolution and integration of the two components of this signal indicated that they were in a 74/26 ratio.

Polymerization of 2,3-Dicarbomethoxynorbornenes. To further probe the stereoselectivity of our ruthenium catalytic system, we have applied it to the ROMP of norbornene 2,3-dimethyl esters. Whereas the corresponding norbornadiene derivative (**1**) existed as a single meso form, three diastereoisomeric compounds are now available for the norbornene skeleton, depending on the relative orientations of the two carboxylate groups. The *exo,exo*- and the *endo,endo*-2,3-dicarbomethoxy-5-norbornenes (**4** and **5**, respectively) are achiral due to the presence of a symmetry plane in these molecules. Their ROM polymerization gives rise to cis/trans and meso/racemic isomerism like that of **1**. The *endo,exo*-diester (**6**) lacks symmetry and exists as a pair of enantiomers. Its polymerization is expected to yield head-to-tail, tail-to-head, and head-to-head sequences in addition to the aforementioned possibilities. If a single enantiomer is used instead of the racemic mixture, a direct tacticity determination can be performed by ^1H COSY spectroscopy.[10]

Monomers **4**, **5**, and **6** (racemate) were reacted with the $[RuCl_2(p\text{-cymene})]_2$ catalyst precursor activated by TMSD under standard experimental conditions. After 6 h at 60 °C, the reaction media were poured in a large volume of methanol to precipitate the polymers formed. Only minute amounts of macromolecular products (ca. 1% yield) were obtained with the endo,endo and endo,-exo starting materials **5** and **6**, whereas the exo,exo derivative **4** afforded a modest 33% isolated yield of poly(2,3-dicarbomethoxynorbornene) (eqs 3−5). Although unsatisfactory for preparative purpose, this output was sufficient to fully characterize poly(**4**) by NMR spectroscopy. Since the main objective of this study was to determine the polymer microstructure, no

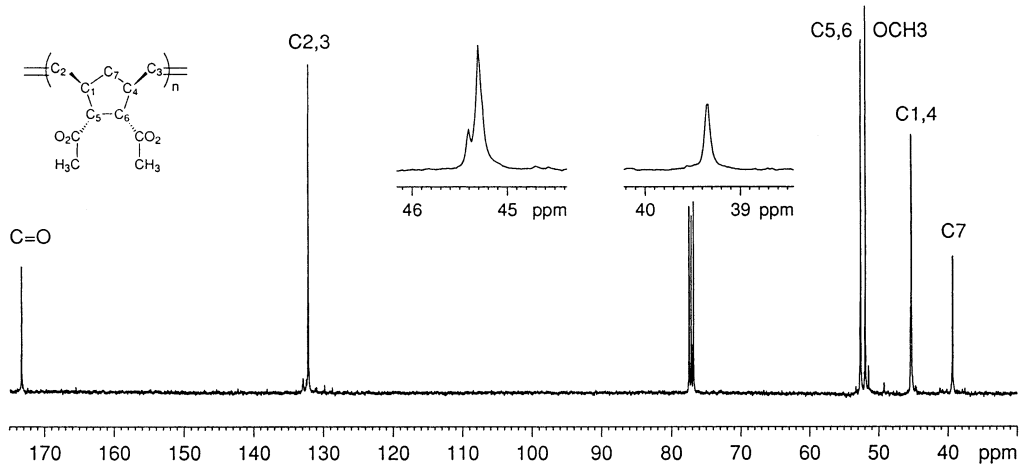
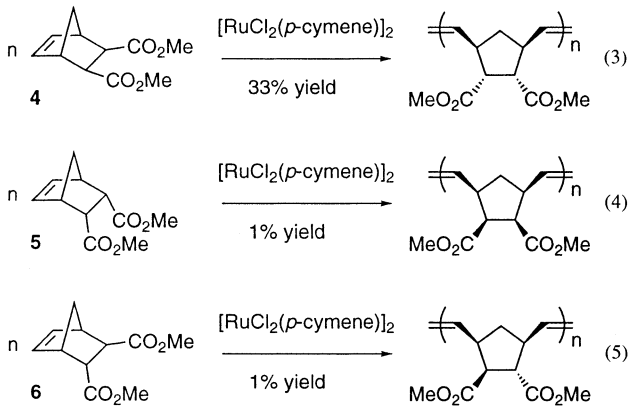


Figure 6. Full 100.613 MHz ^{13}C NMR spectrum in $CDCl_3$ of *all-trans*-poly(**4**) prepared using as catalyst $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD.

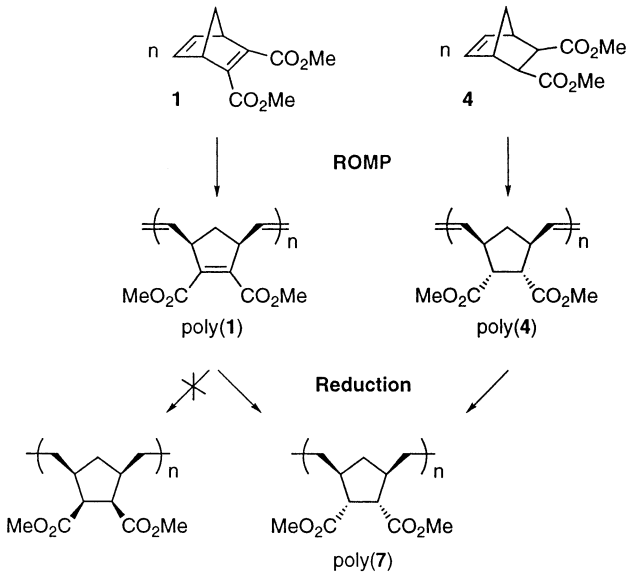
attempts were made at optimizing the reaction conditions to improve the yield.



Various authors have already noted that an endo-substituted norbornene is generally much less reactive than the corresponding exo isomer toward ring-opening metathesis.[1,18,19] The initiation and propagation rate constants for the polymerization of mono- and dicarbomethoxynorbornenes catalyzed by a tungsten-cyclopentylidene complex were deduced from NMR measurements in CD_2Cl_2 at 25 °C. The values obtained for the initiation step with monomers **4**, **5**, and **6** (expressed in 10^{-3} L mol^{-1} s^{-1}) follow the order $k_{i\,exo,exo}$ (40) > $k_{i\,exo,endo}$ (25) > $k_{i\,endo,endo}$ (5), while the propagation rate constants are similar for all three isomers ($k_p = (3-6) \times 10^{-3}$ L mol^{-1} s^{-1}).[20] Differences in steric interactions between the substituents around the five-membered ring have been invoked to explain the lower reactivity of *endo*-5-norbornene-2,3-dicarboxylic anhydride compared to its exo isomer when going from monomer to polymer.[21] A similar argument holds true for the dicarbomethoxy esters: poly(**5**) has its four carbon atoms substituting the ring in a cis relationship, a situation sterically less favorable than those encountered in poly(**6**), which has three substituents cis to each other, and in poly(**4**), where two pairs of substituents are in a trans relationship (see eqs 3−5). Chelation of the metal center by the monomer carboxylate groups may also significantly influence the outcome of the polymerization, thereby explaining why the position and the orientation of the ester substituents are so important. Indeed, Kanaoka and Grubbs attributed the inhibition of their $RuCl_2(PR_3)_2(=CH-CH=CPh_2)$ catalysts (R = phenyl or cyclohexyl) by *endo,endo*-2,3-dicarboethoxy-5-norbornene to the chelation of the metallic active sites by the carbonyl groups in the endo positions.[19] In our case, the coordination of the monomer to the catalyst is also believed to play a significant role in the ROMP process, but it was not possible to determine whether this phenomenon or the steric factors were responsible for the observed reactivities (or the lack thereof) of monomers **4**, **5**, and **6**.

The ^1H and ^{13}C NMR spectra of poly(**4**) were recorded in $CDCl_3$ and assigned by comparison with literature data.[13,18,22,23] They clearly showed that an all-trans polymer was formed under the experimental conditions adopted. Only one type of olefinic hydrogens was visible in the proton spectrum at 5.41 ppm, corresponding to a trans environment. The carbon spectrum also gave unequivocal evidence of a high stereoregularity (see Figure 6). Six out of the seven different types of carbon atoms in the repeating unit resonated as sharp singlets. For example, the signal of C_7 at 39.3 ppm is enlarged in Figure 6. On the basis of the extensive NMR data compiled for poly(**4**) by Ivin and Rooney,[13,22,23] it was assigned to a methylene group surrounded by two trans double bonds. Other environments for C_7 in which the neighboring alkenes have cis/trans or cis/cis configurations lead to peaks centered around 40.0 or 40.8 ppm, respectively. Their absence confirms the all-trans nature of our polymer sample. Only for $C_{1,4}$ was a tacticity splitting visible by NMR (see inset in Figure 6). The high sensitivity of allylic carbon atoms to structural variations was already pointed out for poly(2,3-dicarboalkoxynorbornadienes) and their 7-oxa analogues.[15] In the case of *high-trans*-poly(**4**), it is known that the $C_{1,4}$ signal is extensively split by meso/racemic tacticity at the triad level. Up to four lines can be distinguished, corresponding to the *rr*, *rm*, *mr*, or *mm* junctions, and their chemical shifts were found to follow the sequence $\delta_{rr} > \delta_{rm} > \delta_{mr} > \delta_{mm}$.[13] Only two overlapping peaks were detected at 45.3 and 45.4 ppm for *all-trans*-poly(**4**) prepared using the $[RuCl_2(p\text{-cymene})]_2$ catalytic system. Deconvolution and integration of these signals indicated that a 87% tacticity was achieved. The fact that the major component of the signal resonated upfield from the minor one suggests that the polymer has a strong isotactic (*m* or *mm*) bias.

Scheme 1



The minute amounts of poly(**5**) and poly(**6**) formed under the influence of our standard catalytic system were also subjected to NMR analysis. ^{1}H spectroscopy gave very broad signals, while ^{13}C spectra contained numerous peaks for each type of carbon atoms, indicative of a complex and atactic microstructure. No further attempts at characterizing these polymers were made.

Hydrogenation of Poly(2,3-Dicarbomethoxynorbornadiene) and Poly(2,3-Dicarbomethoxynorbornene). Thanks to the efforts of the Belfast school, the reduction of polynorbornenes and polynorbornadienes into the corresponding polynorbornanes has emerged as a powerful tool for the structural elucidation of unsaturated ROM polymers.[4,12] The tacticity of the hydrogenated products is directly related to that of the parent materials, because the relative configurations of the chiral carbon atoms C_1 and C_4 in the main chain are established during the metathesis reaction and remain unaffected by hydrogenation (Scheme 1). The removal of the double bonds suppresses the cis/trans isomerism and often leads to enhanced splittings in the NMR signals, due to the sole effect of meso or racemic environments. As a consequence, the ^{13}C NMR spectra of reduced polymers usually show well-resolved fine structures that can be assigned to tacticity only. To provide unambiguous results, the method requires that high-cis or high-trans polymers are used as starting materials. When polymers with an intermediate cis/trans content are hydrogenated, it becomes impossible to determine whether each type of double bond was associated with a given tacticity (e.g., cis-syndiotactic and trans-isotactic) or a random atactic chain was present. This limitation is, however, not a concern in the present study since the samples of unsaturated poly(**1**) and poly(**4**) prepared with the $[RuCl_2(p\text{-cymene})]_2$ catalyst precursor activated by TMSD are all-trans.

The reductions were carried out with diimide (NH═NH) generated in situ by heating an excess of *p*-toluenesulfonyl hydrazide in *m*-xylene at 120 °C. This reagent is frequently employed to achieve the rapid and quantitative hydrogenation of unsaturated polymers obtained by ROMP[11,24−26] or by other processes[27−29] under mild conditions. The reaction proceeds via a synchronous concerted pericyclic transfer mechanism and results in the highly selective *cis*-addition of two hydrogen atoms across a substrate olefinic bond.[30] Polar double bonds and aromatic rings remain inert.[31] In the specific case of poly(**1**), Rooney and co-workers have shown that diimide fully reduces both the exo- and the endocyclic C═C double bonds (the latter being symmetrically substituted by the same two polar carboxy groups fits within the nonpolar category) and leaves the ester groups unaffected. Furthermore, hydrogen insertion occurs stereospecifically on the sterically *most* hindered face of the cyclopentene ring unit to afford the *least* encumbered, thermodynamically more stable, transoid product poly(**7**) (see Scheme 1).[13] As already discussed for monomers **4**−**6** (see previous section and eqs 3−5), simple steric considerations can be invoked to explain the preferential formation of this isomer instead of the more crowded all-cis derivative that would result from an attack on the least hindered side of the endocyclic double bond. Accordingly, the saturated polymers prepared from poly(2,3-dicarbomethoxynorbornadiene) and from the *exo,exo*-isomer of poly(2,3-dicarbomethoxy-5-norbornene) share a common stereochemical filiation that allows a direct comparison of their respective NMR spectra.

Two samples of poly(**7**) were obtained in 73 and 31% yield, respectively, by hydrogenation of *all-trans*-poly(**1**) and *all-trans*-poly(**4**). Although we have no rigorous explanation for the yield discrepancy between the two reactions, we noticed that 100 mg of *all-trans*-poly(**1**) readily dissolved in 10 mL of hot *m*-xylene, whereas a similar amount of *all-trans*-poly(**4**) required 20 mL of *m*-xylene and 2 h of heating at 120 °C to afford an almost clear solution. Degradation of the polynorbornene upon prolonged heating and/or incomplete precipitation of the reduced polynorbornane in a solvent mixture enriched in *m*-xylene could be invoked to justify the loss of high molecular weight product, but we did not look into the workup filtrate for mass balance.

The two saturated polymers were first analyzed by ^{1}H NMR spectroscopy at 400 MHz. All their alkyl groups resonated as rather broad singlets. No fine structure and no tacticity splitting were visible. The main feature of the proton spectra was the absence of any signal in the olefinic region that confirmed the occurrence of a complete reduction of all the exocyclic C═C double bonds. ^{13}C NMR spectra revealed more information about the polymer microstructures. Carbon atoms linked to the ester groups (C═O, OCH_3, and $C_{5,6}$) appeared as sharp singlets in poly(**7**), as in poly(**1**) and poly(**4**). Thus, a stereoselective *cis*-addition of hydrogen atoms on the endocyclic double bonds of poly(norbornadiene-2,3-diester) does not cause new tacticity splittings in the corresponding polynorbornene or polynorbornane. On the other hand, the reduction of the exocyclic trans junctions led to significant changes in the chemical shifts of the neighboring carbon atoms. Indeed, the peaks of $C_{1,4}$, $C_{2,3}$, and C_7 in poly(**7**) displayed enhanced, well-resolved fine structures compared to their equivalents in poly(**1**) or poly(**4**) (see Figure 7).[16] The various components of each signal could be assigned to a specific tacticity by following the line orders determined by Rooney et al. at the diad ($\delta_m > \delta_r$) or triad ($\delta_{mm} > \delta_{mr} > \delta_{rr}$) level.[13] In both samples, the lines corresponding to a meso arrangement were the most intense. It can therefore be concluded that the fully hydrogenated derivatives had an isotactic bias and that the parent unsaturated polymers had an *all-trans highly isotactic* structure.

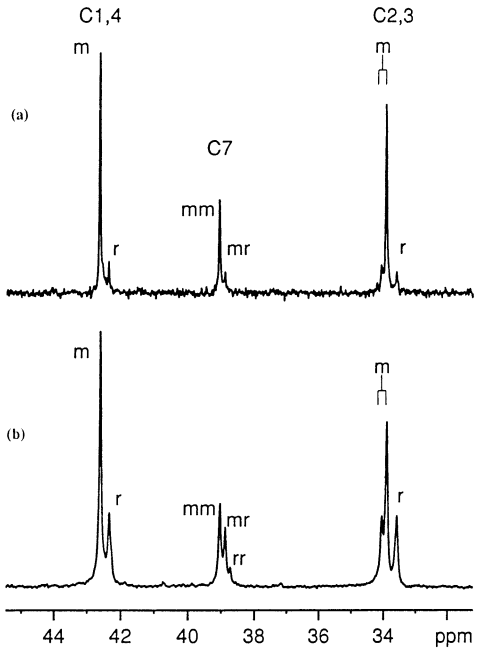


Figure 7. 100.613 MHz ^{13}C NMR spectra in $CDCl_3$ of hydrogenated polymers poly(**7**) derived from (a) *all-trans*-poly(**1**) and (b) *all-trans*-poly(**4**) prepared using as catalyst $[RuCl_2(p\text{-cymene})]_2$ in the presence of TMSD.

Although 2,3-dicarbomethoxynorbornadiene **1** and the *exo*,*exo*-norbornene diester **4** behaved in like manner toward our ruthenium catalytic system, the extent of stereocontrol slightly changed with the exact nature of the monomer. A visual inspection of the spectra depicted in Figure 7 revealed that a higher degree of tacticity was achieved after polymerization and hydrogenation of the norbornadiene diester. Deconvolution and integration of the various NMR signals helped quantify this observation. For the polynorbornane derived from poly(**1**), the average meso/racemic ratio calculated from the $C_{1,4}$ and $C_{2,3}$ peaks reached 91/9, whereas the sample prepared from poly(**4**) gave a 72/28 value. It should be pointed out that there is a significant discrepancy between these figures and those put forward for the precursor poly(**1**) (79/21, deduced from the two overlapping lines of C_7)[15] and poly(**4**) (87/13, deduced from the two overlapping lines of $C_{1,4}$; see previous section). Because ^{13}C NMR spectra were recorded using standard proton-decoupled sequences and not the gated-decoupled mode, integrals cannot be rigorously compared even between carbon atoms in closely related environments. Hence, the numerical data should be handled with care, but the conclusion that a high isotactic bias was achieved remains valid.

Discussion

Numerous catalytic systems based on transition-metal species have been devised for the ROMP of norbornene and norbornadiene diesters. 2,3-Dicarbomethoxynorbornadiene (**1**) is one of the most widely studied representative of this class of monomers, and a significant amount of data is available in the literature concerning the microstructure of its polymers.[1] The trans content and the tacticity bias of seven samples of poly(**1**) prepared using various catalyst precursors based on ruthenium, molybdenum, tungsten, and osmium are listed in Table 1. These initiators can be roughly separated into two categories. The first one groups together "classical" systems where the active catalytic species are formed in situ by a reaction between a simple transition-metal halide salt or complex and a cocatalyst (which may be the monomer itself). The $[RuCl_2(p\text{-cymene})]_2$ dimer activated by TMSD belongs to this category. The second one comprises the Grubbs benzylidene complex $RuCl_2(=CHPh)(PCy_3)_2$ and another well-defined molybdenum−alkylidene catalyst proposed by Schrock. Both species contain a preformed metal−carbene moiety and could be isolated in a high state of purity. Compared to the multicomponent systems, they allow a better control of the initiation and propagation kinetics, leading to polymers with a narrow polydispersity index (as low as 1.04 in the most favorable case)[32] and predictable molecular weights. In terms of microstructure control, however, they are not superior to the active species generated in situ. As shown in Table 1, the most stereoregular samples of *all-cis*- or *all-trans*-poly(**1**) were obtained with poorly defined molybdenum- and ruthenium-based catalytic systems, respectively. In both cases, a very high isotactic bias was attained. To the best of our knowledge, the corresponding syndiotactic materials have not been described yet. Only in the case of 2,3-bis(trifluoromethyl)norbornadiene was the formation of a high-cis (95%), highly syndiotactic (77%) polymer reported.[32]

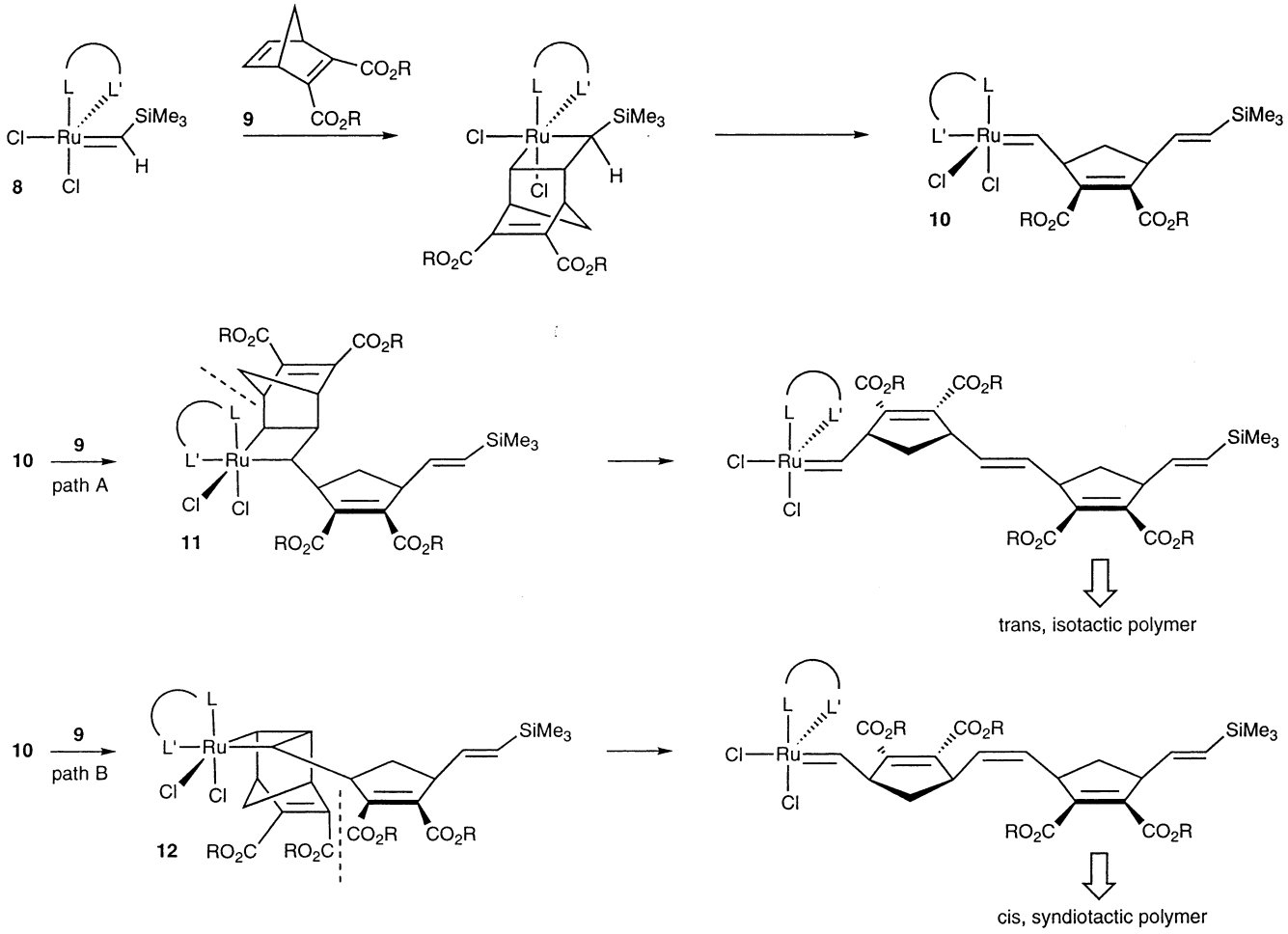
When working on their well-defined initiators of the type $Mo(NAr)(=CHCMe_2Ph)(OR)_2$ Schrock et al. were able to rationalize the cis/trans and meso/racemic distributions observed in the polymerization of norbornene and norbornadiene derivatives based on stereochemical and kinetic considerations.[10,32,34] In the case of the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalytic system, such an interpretation of tacticity at the molecular level is thwarted by the elusive nature of the initiating and propagating species. Because only minute amounts of active catalysts are generated in situ from a complex mixture of monomer and precursors, it is extremely difficult to seize the exact ligand distribution around the metal center. It can be assumed, nevertheless, that activation of the ruthenium dimer by TMSD proceeds via arene loss and carbene formation. The intermediacy of a monometallic ruthenium trimethylsilylvinylidene species $[Ru]=CHSiMe_3$ was evidenced by NMR spectroscopy in a related system based on $RuCl_2(arene)(PR_3)$ complexes,[35] while the thermal displacement of the *p*-cymene ligand was supported by NMR observations[35] and DSC measurements.[36] Recent work from this laboratory has shown that visible light also triggered the decoordination of the arene ligand when stable N-heterocyclic carbene ligands were present on the ruthenium atom.[37] Control experiments carried out with monomer **1** and the $[RuCl_2(p\text{-cymene})]_2$ dimer activated by TMSD revealed, however, that only thermal and no photochemical effects were operative in the present system. Chelation of a monomer is believed to make up for the departure of the η^6 arene ligand from the ruthenium coordination sphere. Indeed, the data already acquired for 2,3-dicarboalkoxynorbornadienes and their 7-oxa analogues strongly suggested that ester coordination to the metal center was of prime importance and resulted in highly ordered transition states, thereby explaining the high stereoselectivities observed.[15]

The results gathered in this study further substantiate our analysis. The fact that trans double bond formation is associated with isotacticity and that the

Table 1. Microstructures of Poly(2,3-Dicarbomethoxynorbornadiene) Prepared Using Various Catalytic Systems

catalytic system	% trans	tacticity bias	ref
$MoCl_5/Me_4Sn$/dioxan	0	isotactic	13
$Mo(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(=CHCMe_2Ph)[OC(CF_3)_3]_2$	1	isotactic	32
$OsCl_3 \bullet xH_2O$/phenylacetylene	17	syndiotactic	13
WCl_6/Me_4Sn/dioxan	44	syndiotactic	13
$RuCl_2(=CHPh)(PCy_3)_2$	89	isotactic	33
$RuCl3 \bullet xH_2O$	96	isotactic	13
$[RuCl_2(p\text{-cymene})]_2$/TMSD	100	isotactic	this work

Scheme 2



minor cis fractions of poly(**2**) and poly(**3**) are syndiotactic indicates that the basic ROMP mechanism postulated by Ivin and Rooney is compatible with our system. In this model, the sole interaction of the monomer with a chiral metal center accounts for the tacticity control (enantiomorphic sites model).[5a,38] Additional effects involving the last formed double bond adjacent to the metal center are also possibly operative. They were invoked for polymers whose trans junctions tended to be atactic (chain-end model)[38,39] but can be omitted here. Thus, we tentatively propose the reaction pathways depicted in Scheme 2 to account for the observed stereoselectivities in the ruthenium-catalyzed ROMP of a generic norbornadiene-2,3-diester, **9**. As discussed above, the exact nature of the initiator is unknown, but theoretical structure **8** constitutes a reasonable surrogate to start with. This 16-electron active species stems from the $[RuCl_2(p\text{-cymene})]_2$ precursor by activation with TMSD and arene release followed by chelation of a monomer (symbolized by L−L′). So far, all our attempts to provide spectroscopic evidence for the interaction of the diester functions with the metal center in a η^4-bidentate fashion remain inconclusive. Various experimental results strongly suggest, however, that ester coordination to the metal center is of prime importance to achieve high catalytic efficiencies. If ester coordination is hindered or impossible, both the polymer yield and stereoregularity are altered. This has been observed in a previous work when tricyclohexylphosphine was added to the reaction mixture or when various nonester 2,3-difunctionalized norbornadienes and unsubstituted norbornadiene itself were polymerized.[15] The results obtained with monomers **2** and **3** in the present study confirm that the steric bulk of the alkoxy substituents of norbornadiene-2,3-diesters significantly affects the polymer trans content and tacticity. The difference of behavior between the three diastereoisomeric 2,3-dicarbomethoxy-5-norbornene **4**, **5**, and **6** is also indicative of the role played by the ester groups and their relative orientations.

The subsistence of a vacant coordination site allows the possible addition of a second monomer unit cis to

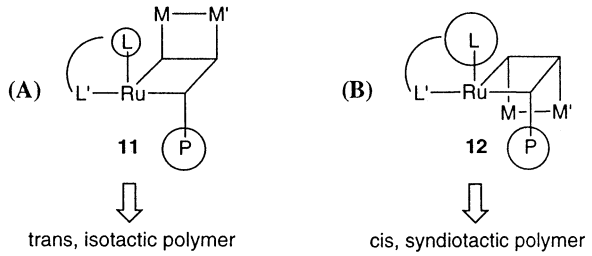


Figure 8. Schematic representations of metallacyclobutane intermediates **11** and **12** showing the influence of the ligand size on the polymerization stereoselectivity (L−L′ = M−M′ = **9**; P = polymer chain).

the carbene moiety to form the key metallacyclobutane intermediate central to olefin metathesis.[40] It can be assumed with a great degree of certainty that the monomer will react through the exo face of its unsubstituted double bond. The fact that the exo face of norbornenes and norbornadienes is highly reactive toward electrophiles while the endo face remains inert is indeed supported by various experimental results and theoretical calculations.[38,41] Yet, there are still two possible modes of approach for monomer **9** in the propagation step. The first one (path A in Scheme 2) leads to a metallacyclobutane intermediate, **11**, where the monomer substituents are disposed trans to the growing polymer chain. The opening of this intermediate does not alter the absolute configuration of the ruthenium center and results in the joint formation of a trans exocyclic double bond and a meso dyad. Thus, it can be invoked to explain the formation of *all-trans*-poly(**1**) and should constitute the preferred reaction path with more sterically demanding monomers like **2** or **3**, giving high-trans, highly isotactic polymers. The second possible interaction between the exo face of monomer **9** and intermediate **10** corresponds to path B in Scheme 2. It gives rise to adduct **12** in which the monomer substituents are disposed on the same side of the metallacycle than the growing polymer chain, i.e., in a cis relationship. Upon opening of the four-membered ring, a new metal-carbene complex in which the chirality of the metal center is opposite to that of the reacting complex is formed. This leads to a cis junction between two repeating units with reverse configurations, i.e., a cis-syndiotactic arrangement.

Comparison of intermediates **11** and **12** in terms of steric requirements indicates that repulsions between the monomer substituents and the polymer chain are much more important in the latter structure, thereby explaining the predominant trans-isotacticity observed in the $[RuCl_2(p\text{-cymene})]_2$ + TMSD catalyzed ROMP of norbornene and norbornadiene diesters. Only when bulky alkyl groups are introduced on the ester side chains should the steric hindrance between the chelating and the incoming monomer result in an antagonist effect that would favor the cis geometry to some extent. This is schematically represented in Figure 8 that also serves as a graphical conclusion to this study. Monomers **1** and **7** bearing methyl ester functions give all-trans highly isotactic polymers and are believed to react through path A exclusively. Monomers **2** or **3** and the isopropyl or *tert*-butyl derivatives examined previously[15] afford macromolecular chains with increasing proportions of cis-syndiotactic double bonds. In these cases, the larger alkyl groups allow the formation of intermediate **12** instead of **11** and lead to an increasing contribution of path B to the ROMP mechanism.

Experimental Section

Materials and Methods. All the solvents were freshly distilled from standard drying agents and kept under argon. The ruthenium complex $[RuCl_2(p\text{-cymene})]_2$[42] was purchased from Strem. (*S*)-(−)-2-Methyl-1-butanol and (*R*)-(−)-2-butanol were used as received from Acros. Trimethylsilyldiazomethane[43] (TMSD, from Aldrich) came as a 2 M solution in hexanes and was further diluted with dry THF. NMR spectra were recorded on a Bruker AM400 spectrometer. ^1H and ^{13}C chemical shifts are listed in parts per million downfield from TMS. FT-IR spectra were recorded on a Perkin-Elmer 16 PC spectrometer. Optical rotations were measured with an Optical Activity AA-10 automatic polarimeter (cell length 1 dm). Mass spectral analyses were performed on a Q-TOF Ultima Global Micromass spectrometer at the Laboratory of Mass Spectroscopy of the University of Liège.

Synthesis of Monomers. The following monomers were prepared according to the literature: 2,3-dicarbomethoxynorbornadiene (**1**),[44] *exo,exo*-2,3-dicarbomethoxy-5-norbornene (**4**),[21,45,46] *endo,endo*-2,3-dicarbomethoxy-5-norbornene (**5**),[45−47] and *endo,exo*-2,3-dicarbomethoxy-5-norbornene (**6**).[46,48,49]

2,3-Bis((1-methylpropoxy)carbonyl)norbornadiene (2). A solution of (*R*)-(−)-2-butanol (1.85 g, 25 mmol) and pyridine (1.98 g, 25 mmol) in Et_2O (40 mL) was cooled to −10 °C in an ice/salt bath before 2,5-norbornadiene-2,3-dicarboxylic acid dichloride[50] (2.17 g, 10 mmol) in Et_2O (10 mL) was added dropwise over a 1 h period. The resulting suspension was further stirred for 1 h at −10 °C and 2 h from −10 °C to room temperature. The precipitated pyridinium chloride was filtered off and rinsed with Et_2O (150 mL). The etheral filtrate was washed with 1 M aqueous HCl (100 mL), saturated aqueous $NaHCO_3$ (100 mL), and saturated brine (100 mL). It was dried over $MgSO_4$, and the solvent was evaporated. The residue was purified by column chromatography on silica gel with $CHCl_3$ as eluent to afford **2** as a pale yellow oil (1.55 g, 55% yield). ^1H NMR ($CDCl_3$): δ 6.84 (d, 2H, CH=CH, J = 2 Hz), 4.86 (m, 2H, OCH), 3.83 (m, 2H, =CH−C*H*), 2.21 and 2.00 (dd, 2H, CH−CH_2−CH, J = 6.6 and 86.2 Hz), 1.52 (m, 4H, CH−CH_2−CH_3) 1.20 (d, 6H, CH−CH_3, J = 6.8 Hz), 0.85 (t, 6H, CH_2−CH_3, J = 7.6 Hz). ^{13}C NMR ($CDCl_3$): δ 165.1 and 165.0 (C=O), 152.2 and 151.9 (=*C*−CO), 142.6 and 142.5 (=CH), 73.2 (OCH), 72.7 (CH−*C*H_2−CH), 53.6 and 53.5 (=CH−*C*H), 28.8 (*C*H_2−CH_3), 19.5 (CH−*C*H_3), 9.8 (CH_2−*C*H_3). IR (neat, cm^{-1}): 2975 (m), 2941 (w), 2879 (w), 1705 (m), 1628 (w), 1559 (w), 1456 (w), 1380 (w), 1319 (w), 1292 (m), 1261 (m), 1236 (m), 1158 (w), 1097 (m), 1048 (w). $[\alpha]^{20}_D = -29.4$ (c = 5.175, $CHCl_3$). HR−MS analysis (ESI +) m/z: calculated for $C_{17}H_{25}O_4$ [$(M + 1)^+$], 293.1753; found, 293.1755.

2,3-Bis((2-methylbutoxy)carbonyl)norbornadiene (3). (*S*)-(−)-2-Methyl-1-butanol (2.20 g, 25 mmol) was reacted with 2,5-norbornadiene-2,3-dicarboxylic acid dichloride[50] (2.17 g, 10 mmol) and pyridine (1.98 g, 25 mmol) as described above to afford **3** as a pale yellow oil (1.82 g, 56% yield). ^1H NMR ($CDCl_3$): δ 6.84 (d, 2H, CH=CH, J = 2 Hz), 3.97 and 3.88 (dm, 4H, OCH_2), 3.85 (s, 2H, =CH−C*H*), 2.21 and 2.01 (dd, 2H, CH−CH_2−CH, J = 6.4 and 81.2 Hz), 1.65 (m, 2H), 1.37 (m, 2H), 1.13 (m, 2H), 0.85 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$): δ 165.3 (C=O), 152.2 (=*C*−CO), 142.5 (=CH), 72.8 (CH−CH_2−CH), 69.7 (OCH_2), 53.6 (=CH−*C*H−), 34.2 (CH), 26.1 (*C*H_2−CH_3), 16.5 (CH_3), 11.3 (CH_3). IR (neat, cm^{-1}): 2964 (m), 2877 (w), 1709 (m), 1627 (w), 1464 (w), 1380 (w), 1319 (w), 1292 (m), 1250 (m), 1234 (m), 1151 (m), 1099 (m), 1052 (m), 1017 (w). $[\alpha]^{20}_D = +6.8$ (c = 4.425, $CHCl_3$). HR−MS analysis (ESI +) m/z: calculated for $C_{19}H_{29}O_4$ [$(M + 1)^+$], 321.2066; found, 321.2065.

General Polymerization Procedure. $[RuCl_2(p\text{-cymene})]_2$ (0.0153 g, 2.5 × 10^{-5} mol) was placed in a 25 mL round-bottomed reaction flask containing a magnet bar and capped by a three-way stopcock. Air was expelled by three vacuum−argon cycles before dry THF (4 mL) and a norbornene or norbornadiene diester monomer (5 × 10^{-3} mol) were added with dried syringes under argon. The mixture was stirred in an oil bath at 60 °C. After a few minutes, a 0.1 M solution of TMSD in hexanes/THF (1 mL, 10^{-4} mol) was added dropwise

with a syringe pusher over a 30 min period. The resulting mixture was kept at 60 °C for an additional 5.5 h. It was then cooled to room temperature and added dropwise to 500 mL of vigorously stirred methanol. The precipitated polymer was filtered, dissolved in $CHCl_3$ (5−10 mL), and purified by passing through a short plug of alumina. The solvent was removed on a rotary evaporator and the residue was dried overnight under high vacuum.

ROM Polymer of 2,3-Bis((1-methylpropoxy)carbonyl)-norbornadiene (2). ^{1}H NMR ($CDCl_3$): δ 5.51 and 5.39 (br, 2H, cis and trans =CH), 4.83 (m, 2H, OCH), 3.48 (br, 2H, =CHC*H*), 2.32 (m, 2H, CH−CH_2−CH), 1.58−1.46 (br m, 4H, CH−CH_2−CH_3 + 1H, CH−CH_2−CH), 1.15 (m, 6H, CH−CH_3), 0.83 (m, 6H, CH_2−CH_3). ^{13}C NMR ($CDCl_3$):[16] δ 165.0, 164.8, 164.7, 164.4 (C=O), 142.2, 141.8 ($C_{5,6}$), 132.4, 132.3, 131.8 ($C_{2,3}$), 73.1 (OCH), 49.5, 49.3, 48.7, 48.5 ($C_{1,4}$), 37.6 (C_7), 28.8 (*C*H_2−CH_3), 19.5, 19.3 (CH−*C*H_3), 9.9, 9.8 (CH_2−*C*H_3).

ROM Polymer of 2,3-Bis((2-methylbutoxy)carbonyl)-norbornadiene (3). ^{1}H NMR ($CDCl_3$): δ 5.45 and 5.40 (br, 2H, cis and trans =CH), 3.94 and 3.84 (dm, 4H, OCH_2), 3.50 (br, 2H, =CH−C*H*), 2.33 and 1.35 (dm, 2H, CH−CH_2−CH), 1.62 (m, 2H), 1.41 (m, 2H), 1.10 (m, 2H), 0.81 (m, 12H, CH_3). ^{13}C NMR ($CDCl_3$):[16] δ 165.2 (C=O), 142.1 ($C_{5,6}$), 132.4, 132.1 ($C_{2,3}$), 69.8 (OCH_2), 49.4, 49.1 ($C_{1,4}$), 37.9 (C_7), 34.2 (CH), 26.1 (*C*H_2−CH_3), 16.7, 16.6, 16.5 (CH_3), 11.3 (CH_3).

ROM Polymer of *exo,exo*-2,3-Dicarbomethoxy-5-norbornene (4). ^{1}H NMR ($CDCl_3$): δ 5.41 (s, 2H, trans =CH), 3.63 (s, 6H, OCH_3), 2.95 (br, 2H, =CH−C*H*), 2.82 (m, 2H, =C*H*−CO), 2.05 and 1.29 (dm, 2H, CH−CH_2−CH). ^{13}C NMR ($CDCl_3$):[16] δ 173.3 (C=O), 132.2 ($C_{2,3}$), 52.6 ($C_{5,6}$), 51.9 (OCH_3), 45.4 and 45.3 ($C_{1,4}$), 39.3 (C_7).

Hydrogenation of Polymers. *m*-Xylene (10 mL) was added to 100 mg of *all-trans*-poly(**1**) or *all-trans*-poly(**4**) placed in a two-neck 25 mL round-bottomed reaction flask containing a magnet bar and capped by a three-way stopcock. The mixture was degassed by bubbling argon and heated at 120 °C until the polymer was completely dissolved. This took only a few minutes for *all-trans*-poly(**1**). In the case of *all-trans*-poly(**4**), it was necessary to add 10 mL more of *m*-xylene and to keep heating for 2 h. *p*-Toluenesulfonyl hydrazide (2 g) was then added through the sidearm and the resulting yellow solution was stirred for 2 h at 120 °C under argon. After the reactiom mixture was allowed to cool to room temperature, it was poured into 250 mL of vigorously stirred methanol. The precipitated polymer was filtered with suction, washed twice with small portions of methanol, and dried overnight under high vacuum.

The reduced polymer poly(**7**) was obtained in 73% and 31% yield from *all-trans*-poly(**1**) and *all-trans*-poly(**4**), respectively. Both samples gave similar spectra. ^{1}H NMR ($CDCl_3$): δ 3.67 (s, 6H, OCH_3), 2.72 (s, 2H, CH−CO), 2.28 (s, 2H, $(CH_2)_2$C*H*-CH_2), 2.20 (m, 1H, CH−CH_2−CH), 1.61 (s, 2H, CH_2−CH), 1.20 (s, 2H, CH_2−CH), 0.86 (br s, 1H, CH−CH_2−CH). ^{13}C NMR ($CDCl_3$):[16] δ 174.1 (C=O), 52.7 ($C_{5,6}$), 51.9 (OCH_3), 42.6 and 42.3 ($C_{1,4}$), 39.0, 38.9, and 38.7 (C_7), 34.0, 33.9, and 33.6 ($C_{2,3}$).

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