

Stereospecific Ring-Opening Metathesis Polymerization of Norbornadienes Employing Tungsten Oxo Alkylidene Initiators

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S Supporting Information

ABSTRACT: We report here the polymerization of several 7-isopropylidene-2,3-disubstituted norbornadienes, 7-oxa-2,3-dicarboalkoxynorbornadienes, and 11-oxa-benzonorbornadienes with a single tungsten oxo alkylidene catalyst, $W(O)(CH-t-Bu)(OHMT)(Me_2Pyr)$ (OHMT = 2,6-dimesitylphenoxide; Me_2Pyr = 2,5-dimethylpyrrolide) to give *cis*, stereoregular polymers. The tacticities of the menthyl ester derivatives of two polymers were determined for two types. For poly(7-isopropylidene-2,3-dicarbomethoxynorbornadiene) the structure was shown to be *cis, isotactic*, while for poly(7-oxa-2,3-dicarbomethoxynorbornadiene) the structure was shown to be *cis, syndiotactic*. A bis-trifluoromethyl-7-isopropylidene norbornadiene was *not* polymerized stereoregularly with $W(O)(CHCMe_2Ph)(Me_2Pyr)(OHMT)$ alone, but a *cis*, stereoregular polymer *was* formed in the presence of 1 equiv of $B(C_6F_5)_3$.

The preparation of highly tactic polymers through ring-opening metathesis polymerization¹ (ROMP) is a key to the advancement of many applications involving ROMP with well-defined catalysts,² in part because the properties of stereoregular polymers (melting point, crystallinity, solubilities, etc.) usually are more sharply defined for tactic polymers relative to atactic polymers.³ Molybdenum-based imido alkylidene ROMP initiators that contain a biphenolate ligand were the first well-defined initiators to be shown to yield stereoregular *cis, isotactic* polymers through enantiomorphic site control.⁴ More recently, monoaryloxide pyrrolide (MAP) complexes with the general formula $M(NR)(CHR')(pyrrolide)(OR'')$ ($M = Mo$ or W) have been shown to yield *cis, syndiotactic* poly(DCMNBD) (DCMNBD = 2,3-dicarbomethoxynorbornadiene) as a consequence (it is proposed) of inversion of the configuration at the metal with each monomer insertion (stereogenic metal control);⁵ inversion of the configuration at the metal forces the monomer to approach first one side of the $M=C$ bond and then the other. The most recent variation of MAP complexes are tungsten oxo alkylidene complexes, $W(O)(CHR)(Me_2Pyr)(OAr)$ ($R = CMe_2Ph$ or $t-Bu$; $Me_2Pyr = 2,5$ -dimethylpyrrolide; $OAr =$ an aryloxide), or monoadducts thereof that contain a labile phosphine or acetonitrile.⁶ Tungsten oxo MAP complexes have been shown to be efficient initiators for formation of *cis, syndiotactic*-poly(DCMNBD).⁷ A potentially important feature of polymerization of DCMNBD employing tungsten oxo initiators is that the rate of polymerization is accelerated

dramatically upon addition of $B(C_6F_5)_3$ as a consequence of its binding reversibly to the oxo ligand and thereby enhancing the electrophilicity of the metal.^{6,7}

We now find that tungsten oxo alkylidene MAP complexes can be employed for the synthesis of *cis* and highly tactic polymers from monomers other than DCMNBD. These monomers (Figure 1) either have not been polymerized before, or if they have, the polymer that is formed is not stereoregular.

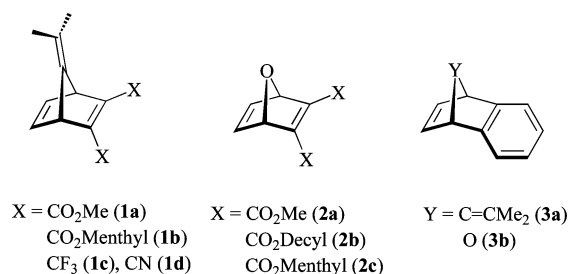


Figure 1. Norbornadienes explored in this study.

We were drawn to 7-isopropylidenenorbornadienes because polymers made from them through ROMP have potential as intermediates in the synthesis of highly conjugated polymers and because polymerization of 7-isopropylidenenorbornadienes in a stereospecific manner with selected Mo or W initiators has been challenging.^{8–10} We chose first to examine the polymerization of 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene (**1a**), the 7-isopropylidene analogue of DCMNBD. A previous attempt to polymerize **1a** with $Mo(NAr)(CH-t-Bu)(O-t-Bu)_2$ ($Ar = 2,6-i-Pr_2C_6H_3$) failed, even at 45–55 °C.¹⁰ A monoinsertion product could be isolated and structurally characterized, but it would not react further with **1a**.

Monomer **1a** (100 equiv, 0.1 M in $CDCl_3$) is polymerized smoothly by $W(O)(CH-t-Bu)(Me_2Pyr)(OHMT)(PMe_2Ph)$ (**A**; OHMT = *O*-2,6-Mes₂C₆H₃) to give *cis* and highly tactic poly(**1a**)_A in essentially 100% yield. In the IR spectrum a relatively intense absorption near 980 cm^{-1} for the CH vibrational mode that is characteristic of *trans* double bonds between units is absent. Therefore, poly(**1a**)_A contains *cis* C=C linkages. The ¹H NMR spectrum of poly(**1a**)_A contains characteristic second-order olefinic (at 5.23 ppm) and methine (at 4.63 ppm) proton resonances, each of which simplifies upon decoupling the other (Figure 2). The ¹³C NMR spectrum also

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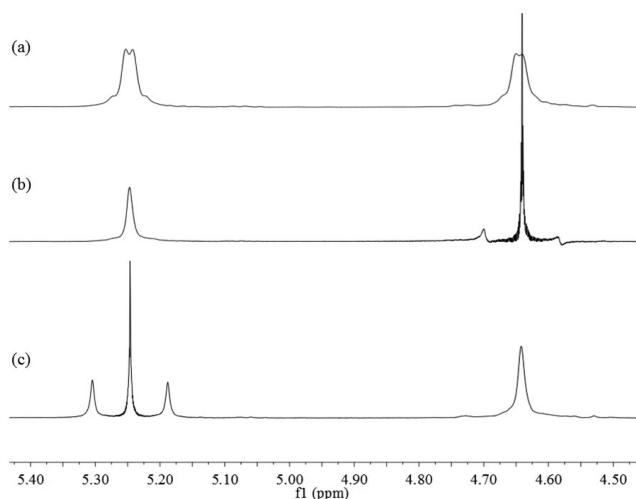


Figure 2. (a) ^1H NMR (500 MHz) spectrum of the olefinic region of poly(**1a**)_A with (b) the methine proton selectively decoupled, and with (c) the olefinic proton selectively decoupled, in CDCl_3 at 22 °C.

contains only the number of sharp resonances expected for a single structure (see Supporting Information (SI)). The relatively simple and sharp proton and ^{13}C NMR resonances are both consistent with poly(**1a**)_A having a single tacticity (>99%). The polymerization of 50 equiv of **1a** with $\text{W}(\text{O})\text{-(CHCMe}_2\text{Ph)(Me}_2\text{Pyr)(OHMT)}$ ⁷ (**B**) resulted in a polymer whose proton and ^{13}C NMR spectra are identical to the spectra obtained for poly(**1a**)_A. Initiator **A** is known to lose the relatively labile phosphine to give **B**, so the propagating species in each case is the four-coordinate 14e species.

To prove the tacticity of a stereoregular polymer it is necessary that a chiral group be present. For example, the tacticity of 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene could be proven^{4,11} if two separate olefinic proton resonances are found in the ^1H NMR spectrum of the polymer. If the two olefinic protons are coupled strongly with $J_{\text{HH}} \approx 11$ Hz, the structure is *cis, isotactic* (Figure 3; $\text{Y} = \text{C}=\text{CMe}_2$). If the two olefinic protons are not coupled strongly, then the structure is *cis, syndiotactic* (Figure 3; $\text{Y} = \text{C}=\text{CMe}_2$).

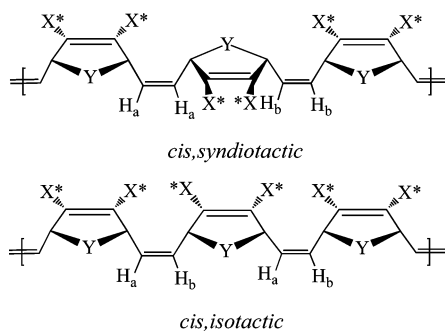


Figure 3. Olefinic protons H_a and H_b in *cis, syndiotactic* and *cis, isotactic* polymers, where $\text{X}^* = \text{carbomethoxy}$.

Neither **A** nor **B** initiates the homopolymerization of **1b** at room temperature in several hours. However, in the presence of 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ polymerization of **1b** by **B** is complete in chloroform in ~ 3 h under the standard set of conditions (see SI) to give an all *cis*, highly tactic polymer, according to IR and ^{13}C NMR spectra. The ^1H NMR spectrum in the olefinic proton region contains overlapping resonances for two methinyl OCH

protons, two polymer methine protons, and two polymer olefinic protons (see SI). In $\text{toluene-}d_8$ at 80 °C the olefinic protons are separated from each other and from the four other proton resonances (Figure 4). The pseudo triplet structure of each (at

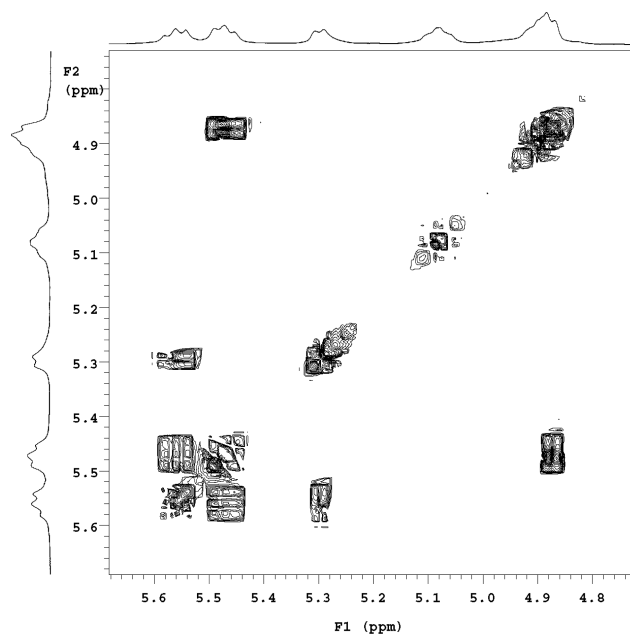


Figure 4. $^1\text{H}/^1\text{H}$ COSY NMR spectrum of the 4.8–5.6 ppm region for poly(**1b**)_B in $\text{toluene-}d_8$ at 80 °C.

~ 5.48 and ~ 5.56 ppm) suggests that H_a and H_b are coupled. This conclusion is confirmed through a $^1\text{H}/^1\text{H}$ COSY NMR spectrum, which shows strong cross peaks between H_a and H_b (lower left in Figure 4). Therefore, the structure of poly(**1b**)_B is *cis, isotactic* (Figure 3) when prepared in the presence of 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$, not *cis, syndiotactic*, as we initially proposed would be the case on the basis of the tendency of MAP catalysts to yield *cis, syndiotactic* polymers from a small collection of monomers through what we have called stereogenic metal control.² We ascribe the acceleration of the polymerization to binding of boron to the oxo ligand and a resulting increase in the electrophilicity of W .⁶

An important question is whether the structure of poly(**1b**) is the same when prepared in the absence of $\text{B}(\text{C}_6\text{F}_5)_3$. Fortunately, **1b** is polymerized completely by **B** at 55 °C in 16 h. According to the ^1H NMR spectra the structure of the resulting polymer is identical to the polymer made from **B** in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$. Therefore, the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ does not alter the structure of the polymer that is formed.

To discover other examples of the stereospecific ROMP of monomers by **A**, **B**, or **B** in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$, we chose to investigate the 7-oxanorbornadiene monomers (Figure 1), 2,3-dicarbomethoxy-7-oxanorbornadiene (**2a**), 2,3-dicarbodecyloxy-7-oxanorbornadiene (**2b**), and 2,3-dicarbomethoxy-7-oxanorbornadiene (**2c**). Monomer **2a** has been polymerized previously using $\text{Mo}(\text{NAr})(\text{CHR})(\text{O-}t\text{-Bu})_2$ ($\text{R} = t\text{-Bu}$ or CMe_2Ph) as the initiator to give poly(**2a**) that contains both *cis* and *trans* $\text{C}=\text{C}$ bonds.¹¹

The polymerizations of 50 equiv of **2a** and **2b** by **A** proceeded relatively rapidly and smoothly to give CDCl_3 -soluble polymers within 5 min at 22 °C. Addition of **A** to the monomer solutions caused an initial color change to red-orange which faded to orange as polymerization proceeded. After poly(**2a**)_A was

precipitated from methanol, the resulting white polymer was insoluble in common organic solvents at 22 °C. However, ^1H and ^{13}C NMR spectra of poly(**2a**)_A could be obtained in CD_2Cl_4 at 80 °C. From IR spectroscopy it was determined that isolated poly(**2a**)_A and poly(**2b**)_A are *cis*. In addition, the ^1H and ^{13}C NMR spectra reveal that each of the polymers has a highly regular structure (see SI).

Polymerization of **2c** with **A** was complete within 10 min at 22 °C to give a CDCl_3 -soluble, white polymer. From IR spectroscopy it is clear that poly(**2c**)_A has all *cis*-olefinic linkages. In the ^1H NMR spectrum of isolated poly(**2c**)_A, there are two methine resonances at 5.85 ppm and two resonances for H_a and H_b at 5.50 ppm (Figure 5 and SI). (The olefinic protons were identified

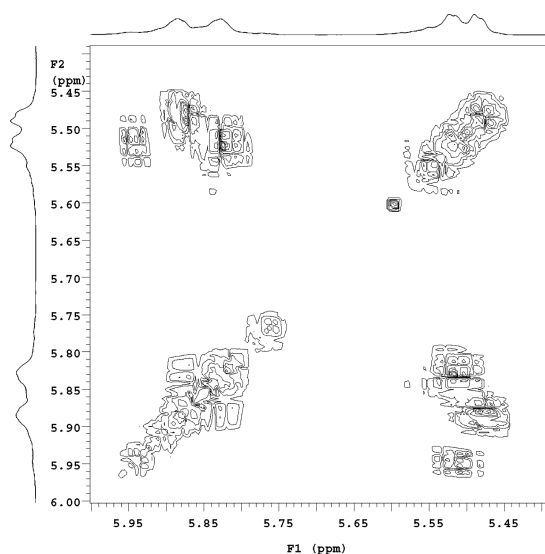


Figure 5. gCOSY of the methine (~5.85 ppm) and olefinic proton (~5.50 ppm) region for poly(**2c**)_A in CDCl_3 at 22 °C.

through an HSQC experiment; see SI.) Upon decoupling a given methine proton, one olefinic resonance sharpens in a manner analogous to that shown in Figure 2. The absence of olefinic cross-peaks between H_a and H_b resonances in the gCOSY ^1H NMR spectrum (500 MHz) of poly(**2c**)_A confirmed that H_a and H_b (with resonances at 5.48 and 5.52 ppm) are *not* coupled (Figure 5) and that poly(**2c**)_A therefore has a *cis,syndiotactic* structure. The weak cross peaks between the two types of methine protons (with resonances at 5.83 and 5.88 ppm) on one furan ring in poly(**2c**)_A are ascribed to a small (~4 Hz) four-bond coupling between them.

2,3-Bis(trifluoromethyl)-7-isopropylidenenorbornadiene (**1c**) was previously polymerized by Feast and Millichamp¹² using a classical catalyst ($\text{MoCl}_5/\text{SnMe}_4$) in 30 min at 70 °C in chlorobenzene. The *cis* content was proposed to be “high”, but the degree of tacticity of the polymer was not stated. Monomer **1c** is polymerized by **A** in 16 h at 22 °C or 1 h at 45 °C to yield a THF-soluble polymer whose ^1H NMR spectrum in the olefinic and methine proton region is unexpectedly complex (Figure 6a). The same is true for poly(**1c**)_C prepared employing $\text{W}(\text{O})-(\text{CHCMe}_2\text{Ph})(\text{Me}_2\text{Pyr})(\text{ODFT})(\text{PPh}_2\text{Me})^7$ (**C**; ODFT = *O*-2,6-(C_6F_5)₂ C_6H_3) as the initiator. IR spectroscopy confirmed that poly(**1c**)_A contains no *trans* linkages, so *cis/trans* isomerism is not the cause of the relatively complex set of olefinic resonances around 5.4 ppm in Figure 6a. In contrast, **1c** (50 or 250 equiv) is polymerized smoothly by **A** in 3 h at 22 °C in the

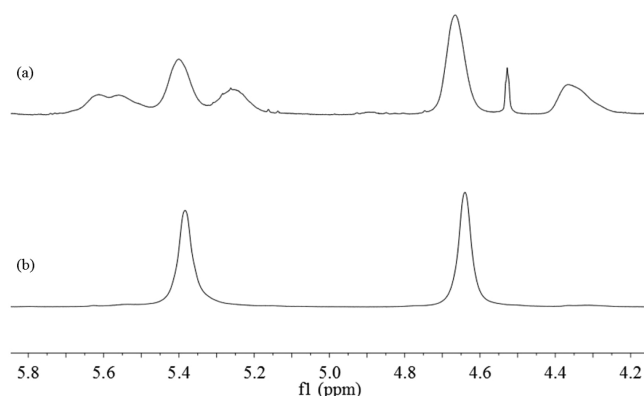


Figure 6. ^1H NMR (500 MHz) spectra in $\text{THF}-d_8$ at 22 °C of the olefinic region for poly(**1c**) formed (a) from initiator **A**, and (b) from initiator **A** in the presence of 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$.

presence of two equivalents of $\text{B}(\text{C}_6\text{F}_5)_3$ to give a *cis*, highly tactic polymer in high yield, whose ^1H and ^{13}C NMR spectra are comparatively simple (see SI). The 4.2–5.8 ppm region of the ^1H NMR spectrum (Figure 6b) reveals only relatively sharp olefinic (at ~5.4 ppm) and methine (at ~4.6 ppm) resonances. We propose that the poly(**1c**)_A formed with **A** in the *absence* of $\text{B}(\text{C}_6\text{F}_5)_3$ contains isotactic (*r*) and syndiotactic (*m*) dyads, but also longer range variations in tetrads (i.e., *mrm*, *mrr/rmm*, *mmr/rmm*, and *rmr*) that introduce other olefinic proton resonances. We entertained the possibility that the polymer had undergone various 1,3-proton shifts of the triply allylic methine proton during polymerization,¹³ but at this stage we reject that possibility in favor of the simpler explanation. We propose that coordination of $\text{B}(\text{C}_6\text{F}_5)_3$ to the oxo ligand^{6,7} leads to a faster formation of either a *rrr* (*syndiotactic*) or a *mmm* (*isotactic*) structure.

2,3-Dicyano-7-isopropylidenenorbornadiene (**1d**) can be polymerized in 16 h at 22 °C or 1 h at 45 °C to give a relatively insoluble polymer whose ^1H NMR spectrum in the olefinic region is similar to that shown in Figure 6a for poly(**1c**)_A (see SI). However, an attempted polymerization of **1d** in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$ did *not* yield a polymer with a simplified spectrum. We propose that poly(**1d**)_A is also a mixture of *rrr* tetrads, *mmm* tetrads, and variations, but $\text{B}(\text{C}_6\text{F}_5)_3$ must bind essentially exclusively to the cyano groups in the monomer or polymer instead of to the oxo group, so the structure in this case does not simplify when the polymerization is run in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$. In spite of the fact that poly(**1d**)_A is not stereoregular, **1d** simply could not be polymerized by other Mo, W, and Ru initiators that were examined (see SI).

11-Isopropylidenebenzonorbornadiene (**3a**) has been polymerized (48 h at room temperature) previously using $\text{Mo}(\text{NAr})(\text{CH}-t\text{-Bu})(\text{OR})_2$ ($\text{R} = t\text{-Bu}$ or $\text{CMe}(\text{CF}_3)_2$) initiators.^{8c} The resulting poly(**3a**) was found to contain 80% *trans*-olefinic bonds. Monomer **3a** can be polymerized by **A** in ~5 min to give a highly regular, CDCl_3 -soluble polymer. IR spectroscopy confirmed that poly(**3a**)_A is *cis*, while the relatively sharp resonances in the proton and ^{13}C NMR spectra are what would be expected for a tactic structure (see SI), but in view of poly(**1b**)_B having a *cis,isotactic* structure, we are reluctant to assign a tacticity to poly(**3a**)_A.

11-Oxabenzonorbornadiene (**3b**) (50 equiv) can be polymerized by **A** to yield a polymer that precipitates out of CDCl_3 within 30 s and is insoluble in common organic solvents at 22 °C. However, the proton and ^{13}C NMR spectra of poly(**3b**)_A could

be obtained in 1,1,2,2-tetrachloroethane- d_2 at 120 °C (see SI). The resonances in both the ^1H and ^{13}C NMR spectra are highly resolved single resonances, indicative of a highly regular structure. From IR spectroscopy it was again confirmed that poly(**3b**)_A is *cis*, but again we are reluctant to assign a tacticity.

The polymerization of all monomers presented in this work (except the dimethylolates) were investigated using a variety of Mo and W imido alkylidene and Ru alkylidene initiators (see SI). In some cases the monomer is polymerized, but the resulting polymer is not stereoregular. Monomers **1a**, **1b**, and **1c** were not polymerized by the Ru initiators **G2** or **G3**.

We conclude that **A** or **B** (alone or in the presence of $\text{B}(\text{C}_6\text{F}_5)_3$) will initiate the stereospecific polymerization of several 7-isopropylidenenorbornadienes and 7-oxanorbornadienes. We also conclude that *cis,syndiotactic* and *cis,isolactic* structures can both be formed employing the tungsten oxo MAP initiators, the latter probably *without* inversion of configuration at W.

One piece of evidence in the literature suggests that *cis,isolactic* and *cis,syndiotactic* structures can be formed with *different* MAP initiators; although $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHR})(\text{Me}_2\text{Pyr})(\text{OHMT})$ ($\text{R} = \text{CMe}_2\text{Ph}$) yields >98% *cis,syndiotactic*-poly(DCMNBD), $\text{Mo}(\text{NC}_6\text{F}_5)(\text{CHR})(\text{Me}_2\text{Pyr})(\text{ODFT})$ ($\text{ODFT} = \text{decafluoro-terphenoxide} = \text{O-2,6-(C}_6\text{F}_5)_2\text{C}_6\text{H}_3$) yields 95% *cis*, 91% *isolactic*-poly(DCMNBD).¹⁴

We propose that a key issue that determines whether an isotactic or syndiotactic structure is formed with a MAP catalyst is the slow rate at which a five-coordinate metallacyclobutane intermediate rearranges its configuration at the metal (aryloxide/pyrrolide exchange) through a Berry-type process¹⁵ relative to the rate at which the metallacyclobutane ring opens to give a propagating species without rearrangement at the metal. In the case of monomers that create some steric challenges, as with **1b**, both the rate of rearrangement of a five-coordinate metallacyclobutane complex and the rate of opening the metallacyclobutane to give the next alkylidene could be altered dramatically, perhaps in opposite directions. Some form of chain end control always remains a possibility in any given circumstance, but the simplicity of the above proposal is attractive. The facts that each structure can be formed with a high degree of precision and specificity employing one MAP initiator and different monomers, and that $\text{B}(\text{C}_6\text{F}_5)_3$ can speed up formation of *one* of these two stereoregular structures, are surprising, but fascinating, developments.

Finally, it should be noted that a MAP catalyst is known to catalyze formation of *trans,isolactic*-poly((+)-2,3-dicarboxymethoxynorbornene).^{5d} The mechanism of formation of the *trans,isolactic* polymer is proposed to involve formation of a *trans*-metallacyclobutane ring that flips over rapidly in a Berry-type process (without exchanging the aryloxide and pyrrolide) before it opens to give the propagating alkylidene.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental details for the syntheses and characterization of new monomers and all polymers, along with a description of NMR studies that prove two tacticities. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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