On the Stereoselectivity of Ring-Opening Metathesis Polymerization (ROMP) of N-Arylpyrrolidine-Fused Cyclobutenes with Molybdenum— and Ruthenium—Alkylidene Catalyst

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ABSTRACT: Ring-opening metathesis polymerization (ROMP) of cyclobutenes fused with N-arylpyrrolidine with Schrock–Hoveyda catalyst containing a racemic biphenolate ligand \([\text{Mo}(\text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{biphenolate})]\) gives polycyclobutenes with homogeneous tacticity and predominantly double bonds in Z-conformation. Reactions of the same substrates with the first-generation Grubbs catalyst \([(\text{Cy}_3\text{P})_2\text{Cl}_2\text{Ru} \equiv \text{CHPh}]\) or Schrock molybdenum carbene with monodendate alkoxy ligands \([\text{Mo}(\text{N-2,6-}i\text{-Pr}_2\text{C}_6\text{H}_3)(\text{CHCMe}_2\text{Ph})(\text{OCMe(CF}_3)_2])\) yield the corresponding polycyclobutene containing a mixture of Z- and E-double bonds. Upon diimide reduction, all these polycyclobutenes give the same tactic hydrogenated polymers, indicating that the stereochemistry at the asymmetric carbons remains the same in all these reactions. The stereoselectivities of ROMP with cyclobutenes and with norbornenes are compared, and the plausible mechanisms are proposed.

INTRODUCTION

Metal—carbene-catalyzed ring-opening metathesis polymerization (ROMP)\(^1\) of strained cycloalkenes has been extensively used in synthesizing different kinds of polymers for 193 nm photoresists,\(^2\) nonlinear optical properties,\(^3\) brush polymers for optoelectronic applications,\(^4\) assembly of double-stranded ladderphanes,\(^5\) and membrane transporting carriers.\(^6\) Bicyclo[2.2.1]heptene systems have been extensively studied, and the reaction can proceed stereoselectively depending on the nature of the substrates and catalysts. Thus, syndiotactic-
\(cis,\)\(^7\) isotactic-
\(trans,\)\(^8\) and isotactic-
\(cis\)-polynorbornenes\(^9\) are readily obtained. Relatively speaking, ROMPs of cyclobutene derivatives have received much less attention, and the reactions in general are nonselective, polymers with a mixture of Z- and E-double bonds being obtained,\(^10\) unless specially designed substrates are employed.\(^11\) We have previously shown that, upon treatment with the first-generation Grubbs catalyst \(1a,\)\(^12\) ROMPs of norbornenes fused with N-aryl-endc-pyrrolidine give the corresponding polynorbornenes having isotactic stereochemistry with trans double bonds.\(^5,8\) It is believed that the endo-fused substituents in 2 provide a bulky environment so that the stereoselectivity of the reaction may be directed. More recently, treatment of 2 with a Schrock–Hoveyda molybdenum–carbene catalyst\(^13\) containing a bidentate ligand 3a yields polynorbornenes in \(cis,\) isotactic selectivity.\(^9a\) The span for each of the monomeric species in polynorbornenes is about 5.5 Å, and interactions between adjacent pendants in polynorbornenes or linkers in ladderphanes have been shown to be prominent.\(^5,8\) The spacing occupied by each of the monomeric units in polycyclobutenes would be expected to be somewhat shorter because the bridging methylene groups are missing in polycyclobutenes. The distance separating adjacent pendants in polycyclobutene would therefore be shorter than that in polynorbornenes. Accordingly, interactions between pendants in polycyclobutenes would be different from those in polynorbornenes. In this paper, we describe a systematic investigation on the ROMPs of 4 in the presence of molybdenum— and ruthenium—alkylidene catalysts.
RESULTS AND DISCUSSION

Synthesis of Monomers. The syntheses of monomers 4a and 4b are outlined in Scheme 1, and the details are described in the Experimental Section. Monomer 11 having zinc porphyrin pendant was also synthesized for the conformational elucidation of the pendants in polycyclobutenes 12a described below.

Scheme 1. Synthesis of Cyclobutene 4 and 11

| Reaction conditions: (a) (i) 4-bromoaniline; (ii) NaOAc, Ac2O, 52%; (b) Zn dust, Ac2O, 80%; (c) LiALH4, 92%; (d) (i) n-ButLi, −78 °C, (ii) CO2, (iii) HCl, 81%; (e) (i) COCl2, (ii) EtOH, Et3N, 86%; (f) COCl2, (ii) 10, Et3N, 82%; (g) Zn(OAc)2, 94%. |

Z-Isotactic Polycyclobutenes. Treatment of 4a with 3 mol % of 3b afforded the corresponding polycyclobutene 12a in 92% yield ($M_n = 7600$, $PDI = 1.24$). The $^{13}$C NMR spectrum of 12a shows only one set carbon signals indicating that 12a would be a regularly tactic polymer with a single type double-bond configuration (Figure 1a). The allylic carbons in 12a appear as a single peak at $\delta$ 40.5 ppm, reflecting that the double bond may adopt the Z-configuration (see below). In addition, the olefinic carbon appears as a single peak at $\delta$ 129.7. Diimide reduction of 12a gave 13a in 72% yield ($M_n = 6500$, $PDI = 1.29$). The disappearance of the peak at $\delta$ 129.7 and the appearance of a new peak at $\delta$ 26.3 for the ethylene bridge suggest the complete conversion. Again, that the 13C NMR spectrum for 13a shows a single set of stereoisomer further supports that 12a would have homogeneous tacticity (Figure 1b).

It is known that polynorbornenes with similar fused N-arylpyrrolidine moieties, obtained from the reaction of 2 with 1a or 3a, have all pendants in the syn conformation and adopt isotactic stereochemistry no matter whether the configuration of double bonds is cis or trans. Double-stranded ladderphanes can thus be obtained from the corresponding bisnorbornene derivatives. It is therefore envisioned that a similar conformational aspect might be held for 12a.

In order to establish the syn conformation for 12a, polymer 14a ($M_n = 19 000$, $PDI = 1.17$) was obtained in 95% yield from a similar reaction of 11 with 5 mol % of 3b. The chemical shifts of porphyrin protons in 14a appear at much higher field than those in 11 (Figures S6 and S10) and even somewhat higher than those of 15. $^{15}$ In addition, similar to the absorption spectrum of 15, the Soret band of 14a also splits into two (Figure S14). These results suggest that the porphyrin pendants in 14a would be in close proximity and imply that all pendants in 14a should be in the syn configuration.

In order to establish the similarity in stereochemistry for 14a and 12a, ethanolysis of 14b ($M_n = 12 600$, $PDI = 1.06$) with NaOEt afforded 92% yield of 12b ($M_n = 2700$, $PDI = 1.08$). The $^{13}$C NMR spectrum of 12b was essentially identical to that of 12a, and the relative intensity for peaks at $\delta$ 40 vs 45 ppm was 96/4 (Figure S7). These results indicate that the presence of the porphyrin moiety in the pendant would essentially give the similar stereoselectivity as the ROMP of 4a with 3b. Given the simplicity of the $^{13}$C NMR spectrum for 12a and syn conformation for pendants, it seems likely that 12a might adopt Z-isotactic stereochemistry.

The high stereoselectivity of this transformation suggests that the reaction may proceed via a similar mechanism as that described for the formation of 16 from 2 (R = Et) using a similar molybdenum catalyst 3a having a bidendate bulky ligand.

E,Z-Polycyclobutenes. In order to test the role of the bidendate ligand in 3 on the stereoselectivity of polycyclobutene, molybdenum—carbene with two alkoxy monodendate ligands 17 (3 mol %) was used as the catalyst for the reaction.

Scheme 1.

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of 4a. The corresponding polycyclobutene 18a ($M_n = 13\,100$, $PDI = 1.17$) was isolated in 93% yield. The $^{13}$C NMR spectrum of 18a shows, in addition to the peak at $\delta 40.6$ ppm (a peak attributed to allylic carbon next to a Z-double bond), a signal at $\delta 45.4$ ppm assigned as the same carbon adjacent to an E-double bond, and the Z to E ratio is 82 to 18. It is noteworthy that polymerization of norbornene analogues such as (1R,2S,5R)-bis(menthyldicarboxy)norbornene and (R)-bis-(pentalactolyldicarboalkoxy)norbornene by 17 gave polynorbornenes up to 99% cis double bonds and isotactic stereochemistry.19

Treatment of 4a with 3 mol % of 1a gave 18b in 90% yield ($M_n = 7100$, $PDI = 1.10$). The $^{13}$C NMR spectrum of 18b was similar to that of 18a. Two signals due to olefinic carbons at $\delta 129.5$ and 130.2 are observed and assigned to Z and E double bonds of 18b, respectively. The Z to E ratio for 18b is 64 to 36. In a similar manner, 18c was obtained in 90% yield ($Z/E = 61/39$) from the reaction of 4a with second-generation Grubbs catalyst 1b (2 mol %). The results are also tabulated in Table 1.

Diimide reduction of both 18a and 18b gave the corresponding hydrogenated polymer 13b ($M_n = 11\,500$, $PDI = 1.19$) and 13c ($M_n = 6500$, $PDI = 1.16$) in 80% and 78% yield, respectively. It is noteworthy that both 13b and 13c show identical $^{13}$C NMR spectra as that of 13a obtained from the reduction of 12a under the same conditions. These results suggest that the relative stereochemistry at the asymmetric carbon atoms C3 and C4 on pyrrolidine rings is same in 12a and 18.

Plausible Mechanism for the Stereoselectivity of ROMP Catalyzed by Metal–Carbene Catalyst. As discussed in the previous sections, the stereoselectivity of

<table>
<thead>
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<th>run</th>
<th>polymer</th>
<th>catalyst (mol %)</th>
<th>$M_n$ ($M_n^*$)</th>
<th>$PDI$</th>
<th>$E/Z$</th>
<th>yield (%)</th>
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<td>1</td>
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<td>7600 (8100)</td>
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<tr>
<td>2</td>
<td>14a</td>
<td>3b (5)</td>
<td>19000 (22500)</td>
<td>1.17</td>
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<td>95</td>
</tr>
<tr>
<td>3</td>
<td>18a</td>
<td>17 (3)</td>
<td>13100 (8100)</td>
<td>1.17</td>
<td>18:82</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>18b</td>
<td>1a (3)</td>
<td>7100 (8100)</td>
<td>1.10</td>
<td>36:64</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>18c</td>
<td>1b (2)</td>
<td>19600 (12200)</td>
<td>1.36</td>
<td>39:61</td>
<td>90</td>
</tr>
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</table>

$M_n^*$ is the theoretical molecular weight based on the mol % of the catalyst used.

ROMP of strained cycloalkenes is related to the nature of the strained ring system and the catalyst. Norbornene derivatives 2 give either Z- or E-isotactic polynorbornenes depending on whether molybdenum 3a or ruthenium 1a catalyst is used. However, reactions with cyclobutene derivatives are highly selective when 3b is used, whereas the reaction is nonselective when 1a is employed. Such discrepancy would be closely related to the mechanism of the reactions and different structural features between cyclobutenes 4 and norbornenes 2.

The ligands in molybdenum catalyst 3b are bulky and robust. It is known that the stereoselectivity of ROMP based on molybdenum catalysts would be closely related to the conformation of the carbene moiety. In general, the syn conformer 19a would be preferred to the anti conformer 19b, in particular when bidendate ligand is employed, and the rate of conversion from 19a to 19b is slow. It has been suggested that polynorbornenes with Z-double bonds would preferentially be formed from the catalyst with syn conformation 19a via olefin attack on the CNO face of the initiator. Although polynorbornenes containing a significant
amount of E-double bonds have been found by using related molybdenum catalysts, the reaction appears to be substrate dependent.22 Because of lack of the methylene bridge and different orientation of bridgehead hydrogens, the steric environment of the exo site of cyclobutene monomer 4a is very different from that of norbornene derivative 2. Thus, reaction of 4a with 3b may proceed via metallo-cyclobutanes 20a or 20b. For the syn rotamer 19a, the exo face of the incoming cyclobutene would selectively react to form metallo-cyclobutane intermediate 20a, which would lead to the formation of the isotactic polycyclobutene with all double bonds in the Z configuration. Alternatively, the anti rotamer 19b may also interact with the exo face of the cyclobutene to afford 20b, which would give the corresponding polycyclobutene with Z-isotactic selectivity. Since the bidendate ligand in 3 has C2 rotation axis, the two CNO faces in 19 are diastereotopic. It seems likely that the reaction may preferentially take place from one of these two faces leading to polycyclobutenes with homogeneous tacticity.

As to the ruthenium-catalyzed reactions, rotation of the carbene ligand from the inactive orientation to the active one may play a key role in these metathesis reactions.23 It is therefore envisaged that the stereochemistry of the active ruthenium–carbene intermediate may determine the stereoselectivity of the ROMP of strained cycloalkenes. Thus, the plausible mechanism for the reaction of 2 with 1a is outlined in Scheme 2. The first generated ruthenium–carbene intermediate 21, which would be an inactive species, may rearrange into active metal–carbene intermediate 22. There would be two possible diastereomers 22a and 22b, where the carbene C–H bond is in either outward or inward orientation, respectively. Complexation with another molecule of 2 would take place from the bottom side of either 22a or 22b to give metallo-cyclobutane 23a or 23b, which would lead to E- or Z-olefin, respectively. It is worth noting that the steric hindrance for 23b would be much more severe than that for 23a. The reaction would thus give selectively E-isotactic polynorbornene.

As mentioned, the steric environment of the exo site of cyclobutene monomer 4a is very different from that of norbornene derivative 2. Accordingly, the difference in steric hindrance between two transition states 24a and 24b would be much less than that between 23a and 23b. It is therefore not surprising to see that a mixture of E- and Z-olefins is obtained from the ROMP of 4a with 1a.

**CONCLUSION**

In summary, we have demonstrated ROMP of cyclobutenes fused with N-arylpyrrolidine moieties with Schrock–Hoveyda catalyst 3 giving the corresponding polycyclobutene in Z-
isotactic stereoregion formation. When the molybdenum carbene catalyst with monodentate alkoxy ligand 17 is employed, poly(cyclobutene) thus obtained contains a mixture of E- and Z-double bonds, but the stereoregion at the asymmetric centers in the polymeric backbones remains the same in all these cases. When either the first- or second-generation Grubbs catalyst is used, the reactions of 4 also give nonselectively poly(cyclobutene) with a mixture of E- and Z-double bonds; the corresponding plausible mechanisms to rationalize these stereochemical discrepancies are proposed.
The mixture was added dropwise to vigorously stirring Et₂O (100 mL). 1H NMR (CDCl₃, 400 MHz) δ 0.90–1.80 (br, 2 H), 2.00–2.50 (br, 2 H), 2.70–3.20 (br, 2 H), 3.20–3.70 (br, 2 H), 4.10–4.42 (br, 2 H). 13C NMR (CDCl₃, 100 MHz) δ 14.4, 26.5, 41.3, 51.5, 60.1, 60.2, 110.1, 116.7, 131.2, 150.6, 166.9. GPC Mₚ = 11 700, PDI = 1.32.

**Polymer 13b.** In a manner similar to that described above for 13a, reaction of 18a (25 mg, 0.1 mmol) and p-toluene sulfonil hydrazide (0.5 g, 5 mmol) yielded 13b as a white solid (20 mg, 80%). 1H NMR (CDCl₃, 400 MHz) δ 0.90–1.80 (br, 2 H), 2.00–2.50 (br, 2 H), 2.70–3.20 (br, 2 H), 3.20–3.70 (br, 2 H), 4.10–4.42 (br, 2 H). 13C NMR (CDCl₃, 100 MHz) δ 14.4, 26.5, 41.3, 51.5, 60.0, 110.4, 116.9, 131.2, 150.6, 166.9. GPC Mₚ = 11 700, PDI = 1.15.

**Polymer 14a.** Under a N₂ atmosphere, a solution of 11 (50 mg, 0.04 mmol) in CH₂Cl₂ (5 mL) was stirred for 20 min at rt, after which benzaldehyde (0.2 mL) was added, and the mixture was stirred for an additional 2 h. The mixture was then treated with vigorously stirring Et₂O (100 mL), affording a fine solid. The solid was collected, washed MeOH, and dried in vacuo to afford 14a as purple solid (47 mg, 95%). 1H NMR (CDCl₃, 400 MHz) δ 0.80–1.50 (br, 57 H), 1.50–4.70 (br, 18 H), 5.20–6.00 (br, 2 H), 6.12–7.20 (br, 6 H), 7.30–8.80 (br, 12 H). 13C NMR (CDCl₃, 125 MHz) δ 14.0, 22.6, 29.3, 29.5, 29.8, 29.9, 31.0, 31.8, 32.0, 33.1, 35.6, 38.4, 40.8, 51.1, 54.2, 111.2, 116.3, 117.4, 117.9, 118.7, 119.6, 126.9, 128.2, 130.1, 132.4, 135.4, 139.5, 147.4, 150.3, 165.4. GPC Mₚ = 19 000, PDI = 1.17.

In a separate run, 11 was treated with 3b (10 mol %) and afforded 14b as a white powder (10 mg, 92%, GPC Mₚ = 8 700, PDI = 1.74). 1H NMR (CDCl₃, 400 MHz) δ 0.70–1.80 (br, 2 H). 13C NMR (CDCl₃, 100 MHz) δ 14.4, 26.5, 41.3, 51.5, 60.1, 60.2, 110.4, 116.9, 131.2, 150.6, 166.9. GPC Mₚ = 12 500, PDI = 1.34.

**Polymer 18b.** Under a N₂ atmosphere, a solution of 4a (50 mg, 0.2 mmol) in CH₂Cl₂ (3 mL) was treated with a solution of first-generation Grubbs catalyst 1a (5.0 mg, 6.2 × 10⁻⁵ mmol) in CH₂Cl₂ (0.5 mL). The reaction mixture was stirred for 0.5 h at rt, after which ethyl vinyl ether (0.2 mL) was added, and the mixture was stirred for 20 min. The reaction mixture was concentrated, and the residual solution was added to Et₂O (30 mL). Precipitate was collected, rinsed with Et₂O, and dried in vacuo to afford polymer 18b as a white powder (45 mg, 90%). 1H NMR (CDCl₃, 400 MHz) δ 1.10–1.50 (br, 3 H), 2.60–3.70 (br, 6 H), 4.10–4.50 (br, 2 H), 5.10–5.70 (br, 2 H), 6.20–6.60 (br, 2 H), 7.70–8.10 (br, 2 H). 13C NMR (CDCl₃, 100 MHz) δ 14.5, 40.7, 45.6, 52.7, 60.1, 110.4, 117.4, 129.5, 130.2, 131.1, 149.9, 166.5. GPC Mₚ = 7100, PDI = 1.10.

**Estimation of E/Z Ratio in 18.** Quantitative estimation of E/Z double bonds ratio was according to the integration of 13C NMR spectra recorded on a Bruker AVIII 800 MHz NMR machine at an operating frequency of 210.23 MHz for carbon with inverse gate proton decoupling during acquisition. About 1750 scans were collected for the spectrum using 30° pulse, a relaxation delay of 7 s, and using inverse gate decoupled pulse sequence to ensure the quantitative information. Exponential multiplication of LB = 5 was applied prior to the Fourier transformation. The spectra are shown in Figure S12.

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(9) When the catalyst contains bulky imido ligand such as those having 2,6-disopropylphenyl substituent in 3a and 3b, polynorbornene thus obtained may contain a significant amount of E-doubled bonds. (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. J. Am. Chem. Soc. 1993, 115, 4413–4414.


(c) See also ref 9a.