Comparative Reactivity of *Exo*- and *Endo*-Isomers in the Ru-Initiated Ring-Opening Metathesis Polymerization of Doubly Functionalized Norbornenes with Both Cyano and Ester Groups

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ROMP is a widespread tool to synthesize well-defined and highly functionalized polymers.[1] In particular, ruthenium initiators have been employed most often for the synthesis of polymers from a variety of cyclic olefins such as norbornenes and norbornadienes.[2] They tolerate a wide range of polar functionalities such as cyano[3] or ester[4] groups in norbornene derivatives. Additionally, some reports have been shown to produce polymers with well-defined microstructures in a living manner.[5]

Recently, on the other hand, a detailed mechanistic investigation of the ROMP of *endo*- and *exo*-dicyclopentadiene has shown that the rate difference (>19 times) between *exo*/*endo*-isomers is primarily due to steric interactions between the growing polymer chains and the incoming monomer.[6] Although there have been reports on the reactivity in ROMP using the *exo*/*endo*-isomers of norbornene derivatives bearing the polar groups,[7] in most cases these polar functional groups are the ester functionalities and a cyano group lie far from a norbornene skeleton, which may retard the appropriate evaluation of substituent effect by a cyano group toward the polymerization.

It would be of great interest to evaluate reactivity for each of the isomerically pure *exo*- and *endo*-norbornene derivatives bearing both cyano and ester groups toward polymerization behavior. However, to the best of our knowledge, there are no reports in the literature on the ruthenium-initiated ROMP of such norbornenes including comparison of the reactivity between *exo*- and *endo*-monomers due to the rather limited synthetic methods for the simultaneous introduction of different two functional groups into the norbornene skeleton and isolation as pure isomeric *exo*- and *endo*-forms.

Recently, we reported the palladium-catalyzed cyanoesterification of norbornadiene by ethyl cyanoformate, in which the cyano and ester groups can be introduced simultaneously and directly to a norbornene molecule, affording doubly functionalized *exo*-ethyl 3-cyanobicyclo[2.2.1]hept-5-ene-2-carboxylate (**A**) with excellent chemo- and stereoselectivities.[8] In addition, we prepared isomerically pure *endo*-form B by Diels−Alder reaction of freshly cracked cyclopentadiene and ethyl (*Z*)-3-cyano-2-propenoate followed by a careful separation by column chromatography on silica gel (Scheme 1). We herein describe ROMP of *exo*-isomer **A**, *endo*-isomer **B**, and the parent norbornene using the second-generation Grubbs' catalyst, (H_2-IMes)(PCy_3)Cl_2Ru=CHPh (**1**) (H_2IMes = *N*,*N*-bis(mesityl)-4,5-dihydroimidazol-2-ylidene).

Scheme 1. Synthesis of Isomerically Pure *Exo*- (A) and *Endo*- (B) Monomers

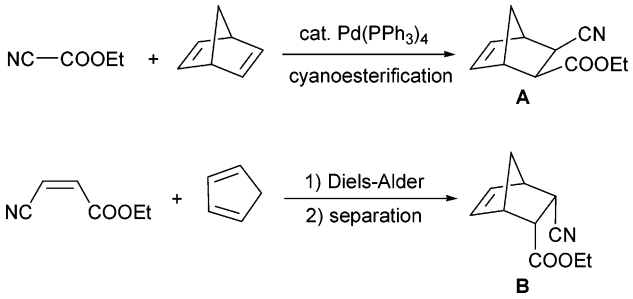
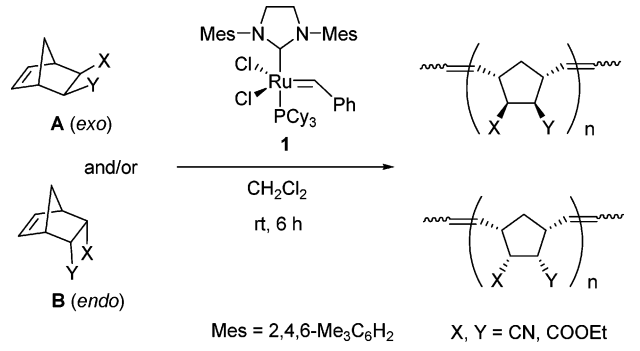


Table 1. ROMP of Monomers A and/or B Initiated by Ruthenium Carbene Complex 1[a]



entry	[M]/[I] (mole ratio)	[**A**]/[**B**]	yield (%)[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n[c]	*cis* content (%)[d]	T_g (°C)[e]	T_d^5 (°C)[f]
1	2000	100/0	86	36.1	1.86	56	111	371
2	333		87	21.8	1.87	56	110	374
3	100		90	10.3	1.86	56	112	371
4	50		85	7.8	1.76	55	112	368
5	20		87	5.1	1.71	56	110	362
6	100	75/25	92	6.5	2.06	nd[g]	117	365
7	100	50/50	94	6.1	1.79	nd[g]	136	361
8	100	25/75	97	5.1	1.34	nd[g]	141	353
9	100	0/100	99	2.0	1.24	nd[g]	151	354

[a] The reactions were carried out under the following conditions: CH_2Cl_2 (1 mL) at room temperature for 6 h. [b] Isolated yield after reprecipitation. [c] Determined by GPC with polystyrene standards. [d] Determined by ^{1}H NMR. [e] Measured in a nitrogen atmosphere with a heating rate of 10 °C/min. [f] Temperature at 5% weight loss. [g] Not determined due to the overlapped signals in the olefinic region.

The ROMP of *exo*-monomer **A** using the first-generation Grubbs' initiator, (PCy_3)$_2Cl_2$Ru=CHPh, was attempted but suffers from the drawbacks of poor initiation, lower activity, and incompatibility with a cyano group.[9] With the introduction of initiator **1** with higher functional-group tolerance, ROMP of *exo*-isomer **A** became accessible.

Under the experimental protocol adopted with different ratio of [M]/[I], the yields, GPC, cis contents around the double bonds in the polymer backbone, DSC, and TGA of obtained polymers derived from *exo*-monomer **A** are summarized in entries 1−5 of Table 1.[10] All the obtained poly-**A** exhibited monomodal molecular weight distributions with a much broader molecular weight distribution of 1.71−1.87 and much higher number-average molecular weights particularly for the formed polymers in smaller [M]/[I] ratios (51 000−361 000) than expected for a living polymerization (theoretical M_n: 3820−382 000). The correlation between theoretical and observed M_n values was rather poor.[11] These results imply that, with *exo*-monomer **A** propagation is significantly faster than initiation resulting in a poor initiation efficiency, as concluded from the ^{1}H NMR

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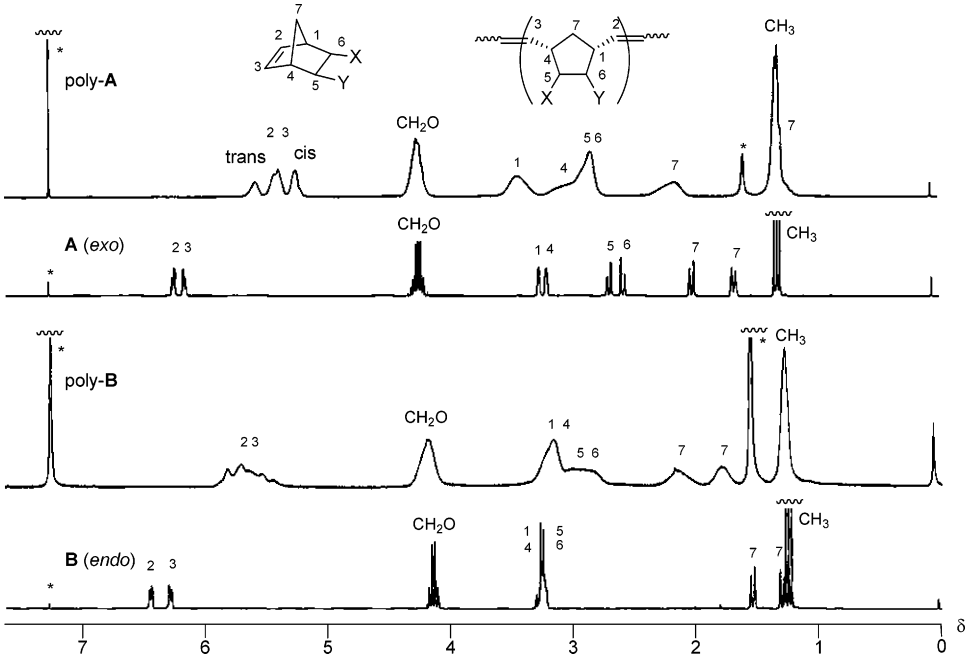

Figure 1. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of poly-**A**, monomer **A**, poly-**B**, and monomer **B**. The signal with an asterisk is due to the solvent and the contaminated water.

monitoring of the consumption of monomers (vide infra). Additionally, the broadening molecular weight distribution of polymers may be due to its propensity to perform intramolecular backbiting reactions[12] between the more reactive propagating chain end and double bonds in the polymer backbone; however, this is probably a minor effect because these polymer chains are highly sterically shielded.

All polymers obtained were soluble in chloroform, dichloromethane, and tetrahydrofuran and insoluble in methanol and pentane. The IR spectra of all the polymers obtained were very similar; signals characteristic of the cyano group and ester carbonyl group at 2304 and 1734 cm^{-1}, respectively, were prominent features of the spectra. The stereochemistry around the double bond in the polymer chain was determined by integration of the appropriate signals in the ^{1}H NMR spectra (Figure 1); the peak at δ 5.40 was used to quantify the *trans* double bond amount, while the signal at δ 5.25 is indicative for a *cis* geometry.[13] On the basis of these observations, the synthesized polymers derived from *exo*-monomer **A** have around 56% *cis* vinylene contents between two rings in the polymer backbone, indicating that the double bonds are roughly equal amounts of *cis* and *trans*.

Although the role of the substituents on the ruthenacyclobutane and the ligand substituent interactions on the stereochemistry is unknown, *cis* preference against the thermally stable *trans* configuration is presumably due to the steric congestion between the polymer backbone or the coordinating norbornene monomers and the bulky *N*-heterocyclic carbene ligands in the ruthenacyclobutane intermediate during polymerization. Additionally, because the employed monomer **A** herein is an isomerically pure *exo*-form, but the mixture of enantiomers (*R*/*S*), head-to-tail isomerism would be uncontrollable. In conjunction with the mixture of *cis* and *trans* configuration around the double bonds determined by the ^{1}H NMR of the olefinic region, the complexity of the signals in the $^{13}C\{^1H\}$ NMR spectrum of the bridgehead carbons for poly-**A** can be assigned to an atactic and/or regioirregular structure.

The polymers synthesized from monomer **A** displayed similar glass transition temperatures about 110 °C, and no evidence of crystalline melting point was detected. A 5% weight loss was observed for all polymers at about 370 °C. The small differences observed may be a consequence of different molecular weight and/or tacticity but do not justify detailed analysis.

Mixtures of monomers **A** and **B** in different ratios were also polymerized (entries 6−8, Table 1). The multiplicity and broadening of the backbone resonances are again consistent with a multiplicity of overlapping environments associated with low regularities of microstructures. The values of molecular weights and molecular weight distributions decreased as the fraction of *endo*-monomer **B** increased. When the isomerically pure *endo*-monomer **B** was polymerized, observed M_n of 20 000 has an excellent fit with the calculated value (entry 9, Table 1). The narrower molecular weight distribution (1.24) for **B** indicates the living nature.

In the widely accepted mechanism of norbornene ROMP the initiator approaches the monomer from the *exo*-face of the double bond;[14] the *exo*/*endo* disposition of the substituents on the other side of the ring can have little or no steric effect, but there may be an electronic effect between *endo*-substituents which could increase or decrease the π donor capacity of the double bond. However, the $^{13}C\{^1H\}$ NMR spectra of monomers revealed *endo*-monomer **B** seems to be slightly electron-rich relative to monomer **A** (δ 135.9 and 138.4 for **A** vs δ 133.8 and 137.7 for **B**).

The exact nature of the propagating species in ROMP is unknown, but we assume that the living characterization is ascribed to the relatively slow propagation of **B** because an *endo*-monomer is capable of coordinating to the Ru center as a bi- or tridentate ligand suppressing its polymerization. In a sharp contrast, in the case of *exo*-monomer **A**, because two functional groups are far from the metal center, the smooth propagation proceeds by the less hindered end of the catalyst to produce the larger molecular weighs and molecular weight distribution than that for *endo*-monomer **B**. Comparing the molecular weights between *exo*- and *endo*-monomers (entry 3 vs 9), the initiation efficiency for **A** is 5 times poorer than that for **B**.

The *cis* contents for poly-**B** could not be determined due to the complicated overlapped signals in the olefinic region, shown in Figure 1.

The glass transition temperatures (T_gs) of the polymers obtained from **B** (151 °C) are significantly higher than those observed for polymers derived from *exo*-monomer **A** (113 °C)

under the same reaction conditions. This is a similar trend to higher T_g with increasing the amounts of *endo*-monomers observed for other systems.[3a,15] Thus, random copolymerization of **A** with **B** is effective to adjust the desired T_g for different purpose, although the yield of the obtained polymers slightly decreased when more *exo*-monomer was involved. In a sharp contrast, the 5% weight loss for these polymers occurs at about 354 °C, indicating a slightly poorer thermal stability than the polymers from the *exo*-monomers (371 °C).

To gain insights into the mechanistic implication for the polymerization, reactions of monomers **A** and **B** initiated by **1** were monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. After the addition of 50 equiv of *exo*-norbornene **A** to **1** in CD_2Cl_2 at room temperature, the singlet resonance at δ 19.1 due to the initiator alkylidene hydrogen remains unchanged during polymerization for 6 h. Meanwhile, in the ^{31}P{^{1}H} NMR the signal at δ 30.47 assigned to the PCy_3 ligand coordinated to the Ru center also remains unchanged, and no free PCy_3 ligand (δ 11.50) was observed during polymerization. This observation indicates that initiation is much slower than propagation, which renders the determination of the initiation rates for each monomer difficult.

Monitoring the consumption of monomers by ^{1}H NMR spectroscopy allowed the determination of the apparent propagation rate constants, k_p.[16] In CD_2Cl_2, with $[I]_0 = 0.00416$ mol L^{-1}, $[M]_0 = 0.208$ mol L^{-1}, $[M]_0/[I]_0 = 50$, the values of k_p were 1.14×10^{-3} s^{-1} for *exo*-monomer **A** and 0.817×10^{-3} s^{-1} for *endo*-monomer **B**. Thus, the k_p values apparently seem to be slightly dependent upon the stereochemistry of the monomers, with the *exo*-isomer propagating 1.4 times faster than the *endo*-isomer. When the 50/50 mixture of monomers **A** and **B** was employed under the identical conditions shown above, the difference of k_p values appeared more remarkably, where $k_p = 1.71 \times 10^{-3}$ s^{-1} for *exo*-monomer **A** and 0.739×10^{-3} s^{-1} for *endo*-monomer **B**. These results should be considered including a difference of the actual initiation efficiency described above. Thus, the net reactivity between **A** and **B** would be different over 10 times. In sharp contrast to the substituted norbornenes, the propagation rate of norbornene was too fast to determine (at least larger than 0.15 s^{-1}) under the identical reaction conditions. These results suggest that propagation rates are certainly affected by the stereochemistry of monomers; however, the effect is apparently small compared to the reported values between norbornenes bearing only the ester groups. Compared to the parent norbornene, cyano and ester functional groups seem to have an interaction with the Ru center, suppressing the polymerization. Obviously, the results obtained herein should be attributed to the presence of a cyano group that have coordination affinity to the metal centers as well as an ester group in the monomers.

Synthesis of a series of block copolymers was attempted using *exo*- and *endo*-isomers as comonomers. However, the ill-defined initiator **1** is unsuited to the preparation of block copolymers.

In conclusion, ROMP of *exo*- and *endo*-doubly functionalized polar norbornenes bearing both cyano and ester groups have been successfully established. The thermal stability of these polymers is also dependent upon monomer stereochemistry. Although the initiation rate constants could not be determined due to the unchanged signals of alkylidene species in the ^{1}H and ^{31}P{^{1}H} spectra, higher molecular weights than expected and a broadening of the molecular weight distribution for polymers prepared from exo-monomer **A** imply that with the initiator **1** propagation is significantly faster than initiation, resulting in the poorer initiation efficiency than endo-monomer **B**. More detailed studies on the microstructure analysis of the polymers using synthesizing enantiomerically pure monomers and other Ru catalysts and elucidation of block copolymerization in a living manner are currently under investigation.

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Supporting Information Available: Detailed experimental procedures for polymerization and kinetic experiments, characterization of all monomers and polymers, and ^{13}C{^{1}H} NMR spectrum of poly-**A**. This material is available free of charge via Internet at http://pubs.acs.org.

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