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Polymerization

Alternating Copolymerizations Using a Grubbs-Type Initiator with an Unsymmetrical, Chiral N-Heterocyclic Carbene Ligand**

Kati Vehlow, Dongren Wang, Michael R. Buchmeiser, and Siegfried Blechert**

Reports on alternating copolymers prepared by metathesis copolymerization of two different monomers are relatively rare.[1–7] In 2005, Chen et al. reported on the mechanism-based design of a ROMP (ring-opening metathesis polymerization) catalyst for sequence-selective copolymerization.[8,9] Here, we report on an alternative system for the synthesis of alternating copolymers based on Grubbs-type initiators containing an unsymmetrical, chiral N-heterocyclic carbene (NHC) ligand.

As part of our on ongoing research on ruthenium metathesis catalysts with saturated unsymmetrical NHC ligands[10,11] initiator **1** was prepared from $[RuCl_2(PCy_3)_2(CHPh)]$ and 1-mesityl-3-((1′R)-1-phenylethyl)-4,5-dihydroimidazolium tetrafluoroborate in 90% yield. This initiator was used for the copolymerization of norbornene (NBE) and cyclooctene (COE) using a stoichiometry of **1**/NBE/COE of 1:2000:100000. Reactions kinetics recorded for this copolymerization in CH_2Cl_2 revealed that NBE was consumed in less than 15 min. Terminating the copolymerization after 60 min in fact provided an almost perfectly alternating copolymer of NBE and COE. Unfortunately, the polymer was only partially soluble in standard solvents such as $CHCl_3$. However, the soluble fraction showed a unimodal molecular weight distribution (PDI = 2.19), and $M_n = 40400\ \mathrm{g\,mol^{-1}}$ was found. Longer reaction times led to the formation of substantial amounts of a poly(COE) homopolymer block attached to the alternating copolymer. This homopolymer block is easily identified by NMR spectroscopy.

The ^{13}C NMR spectrum of the alternating copolymer (97% alternating units, $\delta = 128$–136 ppm) is shown in Figure 1. Hardly any signals for poly(NBE) or poly(COE) can be detected.[2,12] The signals for the alternating copolymer are observed around $\delta = 135.0$ and 128.5 ppm. The first set of signals around $\delta = 135.0$ ppm is assigned to the *C*=C−CH$_2$ carbon atoms and consists of eight different signals at $\delta =$ 135.28, 135.26, 135.14, 135.00, 134.98, 134.95, 134.83, and 134.80 ppm, which we attribute, without specific assignment, to the *ccc*, *tcc*, *ctc*, *cct*, *ttc*, *tct*, *ctt*, and *ttt* triads. The fact that all eight signals display roughly the same intensity is indicative for a *cis* content of about 50% and is in accordance with the ^{1}H NMR spectrum, which shows signals of the *cis* and *trans* double bonds in a 1:1 ratio at $\delta = 5.36$ and 5.28 ppm, respectively. Such a high *cis* content is rather unusual for polymers prepared by Grubbs-type initiators; most display a *cis*/*trans* ratio of roughly 25:75. The less well-resolved signals around 128.5 ppm are assigned to the C=*C*−CH$_2$ carbon atoms and correspond to the same triads. DSC measurements of the alternating copolymer revealed a single glass transition at $T_g = -50.9\,°C$ ($\Delta c_p = 0.32\ \mathrm{J\,g^{-1}}$)), which is in between the glass transition temperatures of poly(COE) (−78 °C, 50% *trans*)[13] and various poly(NBE)s (40–64 °C).[14]

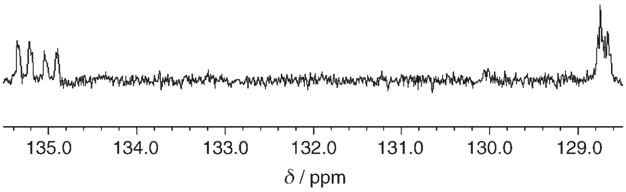

Figure 1. ^{13}C NMR spectrum of poly(NBE-*alt*-COE)$_n$ prepared with initiator **1**.

We next turned our attention to the initiation efficiency of **1**. Second-generation Grubbs-type initiators having one NHC and one phosphine ligand are known to display rather poor initiation efficiencies as a result of unfavorable ratios of the rate constants of initiation and polymerization (k_i and k_p, respectively).[15,16] ^{1}H NMR experiments carried out with **1** and either of the two monomers, that is, NBE or COE, in a 1:5 ratio in fact revealed poor initiation efficiencies of less than 1 and 3.8%, respectively. We therefore prepared the monopyridine adduct of **1**, $[RuCl_2(Py)$(1-mesityl-3-((1′R)-1-phenylethyl)-4,5-dihydroimidazolin-2-ylidene)(CHPh)] (**2**), in analogy to the known complex $[RuCl_2(Py)_2(IMesH_2)(CHPh)]$ ($IMesH_2$ = 1,3-dimesitylimidazolidin-2-ylidene), by reaction of **1** with excess pyridine (Scheme 1). Owing to the high solubility of **2** in conventional organic solvents, purification by recrystallization was not possible. Instead, a Cu^{I}-loaded polymer-bound triphenylphosphine was used to remove the released PCy_3 and isolate **2** in a pure form. The fact that only *one* pyridine ligand is capable of coordination to the catalyst is indicative for the significant steric demand of the NHC ligand [17] and is relevant to mechanistic considerations (vide infra).

To our great delight, catalyst **2** displayed significantly improved initiation efficiencies for NBE and COE—values of

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[*] Dr. K. Vehlow, Prof. Dr. S. Blechert
Institut für Chemie, Technische Universität Berlin
Strasse des 17. Juni 135, 10623 Berlin (Germany)
Fax: (+49) 30-314-29745
E-mail: blechert@chem.tu-berlin.de

Dr. D. Wang, Prof. Dr. M. R. Buchmeiser
Leibniz-Institut für Oberflächenmodifizierung e.V. (IOM)
Permoserstrasse 15, 04318 Leipzig (Germany)
Fax: (+49) 341-235-2584
E-mail: michael.buchmeiser@iom-leipzig.de

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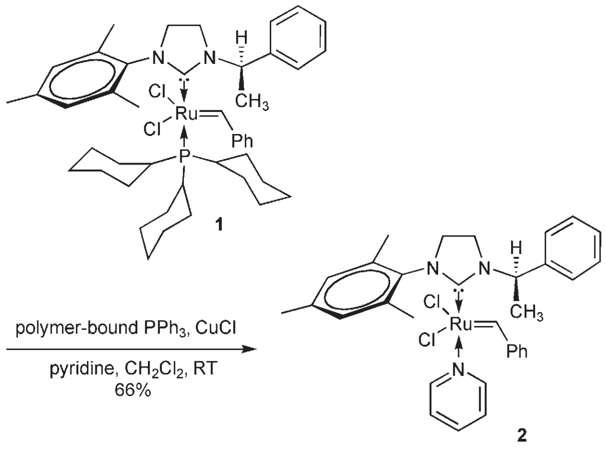


Scheme 1. Synthesis of the monopyridine adduct **2**.

Table 1: Summary of copolymers obtained.

M^1	M^2	Ratio	Initiator	Alternating dyads (M^1-M^2)
COE	NBE	50:1	**1**	97
COE	NBE	50:1	**2**	97
NBE	CPE	1:7	**2**	90
3	NBE	5:1	**2**	74
4	NBE	1:1	**1**	72
5	NBE	1:1	**1**	60
6	NBE	1:1	**1**	49
5	COE	1:1	**1**	48
6	COE	1:1	**1**	9

Monomers tested: **3**: *endo*,*endo*-*N*,*N*-(norborn-5-ene-2,3-dicarbimido)-L-valine ethyl ester, **4**: octa-1,4-dieneoxide, **5**: *endo*,*endo*-*N*-methyl-7-oxanorborn-5-ene-2,3-dicarboximide, **6**: *exo*,*exo*-*N*-methylnorborn-5-ene-2,3-dicarboximide.

21.3 and 88.4%. In the ^{1}H NMR spectrum of the resulting poly(NBE), doublets at $\delta = 18.37$ and 18.32 ppm (d, $^3J = 8.3$ Hz) could clearly be attributed to the insertion products. The same was found for the analogous poly(COE), where the corresponding signals were found at $\delta = 18.79$ (t, $^3J = 5.0$ Hz). Since both the initiation rates and the rates of polymerization changed for the two monomers, the **2**/NBE/COE ratio necessary to realize a perfectly alternating copolymer remained at 1:2000:100000. The polymer we obtained when copolymerization was terminated after less than 1 min gave an ^{13}C NMR spectrum identical to that shown in Figure 1; however, the polymer was completely soluble in CHCl$_3$. GPC investigations revealed a unimodal molecular weight distribution with a PDI of 1.59 and $M_n = 142\,400$ g mol^{-1}, far lower than the theoretical value of $M_n = 388\,000$. This, along with the alternating structure of the polymer and the fact that all 2000 equivalents of NBE (and COE) had been consumed, suggests that significant chain transfer occurs. Hydrogenation of the perfectly alternating copolymer yielded poly(cyclopentene-*alt*-(ethylene)$_5$)$_n$, which may alternatively form from cyclopentene (1,3-insertion) and five consecutive ethylene insertions in a Ziegler-type polymerization and may well serve as a model compound for such copolymerizations.

Next, we considered whether the concept of alternating copolymerization is restricted to the monomers NBE and COE. One might argue that the highly reactive, yet sterically somewhat demanding NBE and the less reactive, yet more flexible COE form something such as a "perfect couple". We therefore investigated the copolymerization of various functional monomers, with NBE and COE. A summary is given in Table 1. To our great pleasure, the copolymerization of NBE with cyclopentene (CPE) by the action of **2** could be accomplished, too. An NBE:CPE ratio of only 1:7 resulted in the formation of a copolymer containing roughly 90% alternating units, the highest value found so far (Figure 2, Table 1).[4] This is of particular interest, since CPE usually displays a rather limited propensity to undergo ROMP,[18] and homopolymerization of CPE is often counterbalanced by "backbiting", yielding cyclic, low-molecular-weight polymers.[19] DSC measurements again revealed only a single glass transition at $T_g = -37.7\,°C$ ($\Delta c_p = 0.31$ J g^{-1}). Hydrogenation yielded a fully saturated, hydrocarbon-based polymer whose backbone formally consists of CPE units (1,3-insertion) followed by an odd number (7) of methylene units. This type of polymer may not be realized by any other polymerization method.

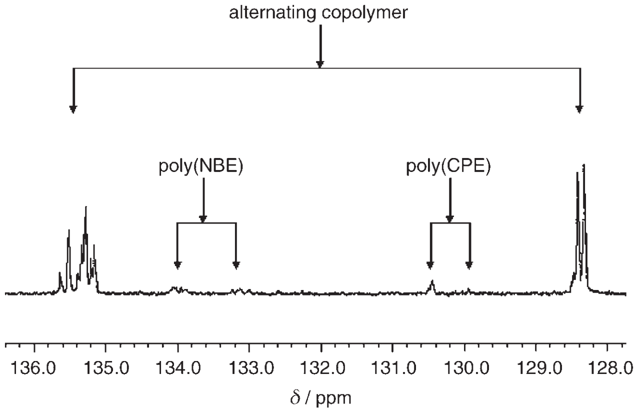
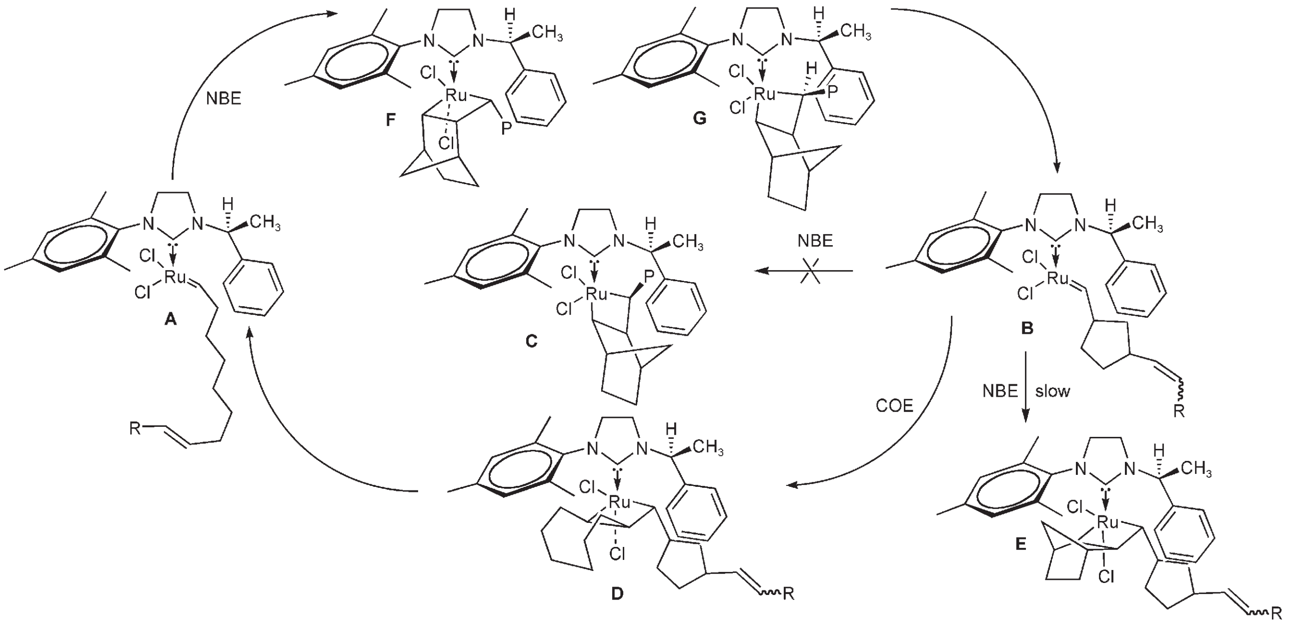


Figure 2. ^{13}C NMR spectrum of poly(NBE-*alt*-CPE)$_n$ (90% alternating) prepared with initiator **2**.

In further studies we examined the mechanism of the alternating copolymerization. A simple explanation for the alternating copolymerization of NBE and COE with either **1** or **2** as the initiator would cite the different reactivities of the two monomers and the large excess of COE, which would shift the insertion statistics in favor of insertion of COE. However, this would rather result in a gradient block copolymer than an alternating one. A brief glance at the kinetic parameters clearly shows that this description is not valid at all. Copolymerization of NBE with COE under the action of **2** leads to the complete consumption of NBE (2000 equivalents with respect to **2**) within less than a minute, while homopolymerization of only 10 equivalents of NBE by **2** requires several minutes. This strongly indicates that insertion of one NBE unit into either **1** or **2** is favored when COE has been inserted as the last monomer.

Hamilton et al. explained the alternating copolymerization of NBE and CPE by RuCl$_3$/excess phenol by a solvent-cage effect.[2] In our case, since nonprotic CH$_2$Cl$_2$ was used, a different explanation must be expected. To shed light onto that point, we conducted temperature-dependent NMR experiments to identify the coalescence temperature T_c for the alkylidene proton in **1**, which in turn allows us to estimate the rate constant of rotation of the NHC ligand k_{rot}. T_c was identified by measuring the spectra in 1 °C increments. At $T = T_c = 2\,°C$, k_{rot} was found to be $67\,s^{-1}$, translating into $k_{rot}(22\,°C) \approx 2.7 \times 10^2\,s^{-1}$ using $k_{rot}(2\,°C) = \delta\nu\pi/\sqrt{2}$ ($\delta\nu$ = difference in the chemical shifts of the two alkylidene signals obtained at $T < T_c$).[20] A similar result was obtained from $k_{rot} = \pi(\delta\nu)^2/(2\Delta\nu)$, that is, $k_{rot}(22\,°C) \approx 2.4 \times 10^2\,s^{-1}$ ($\Delta\nu$ = difference in peak width at half peak height between the signal at $T = T_c$ and at $T \gg T_c$). In view of the different factors that govern both the line width at half peak height and $\delta\nu$, a mean value of k_{rot} at $T = 22\,°C$ of $2.6 \times 10^2\,s^{-1}$ appears to be a good approximation. We then determined the rate constants for the homopolymerization of NBE and COE using **1**. (The reactions with initiator **2** were too fast for these investigations.) Homopolymerizations of NBE clearly followed pseudo-first-order kinetics with $k_{p(homo\text{-}NBE)} = 2540\,L\,mol^{-1}\,s^{-1}$. In contrast to the homopolymerization of NBE, the homopolymerization of COE was slow and was characterized by an increase in initiator efficiency over time. A linear increase in initiator efficiency at least within the time investigated (2 h) was observed, leading to the following kinetics: $[COE] = [COE]_0\,e(-k_{p(homo\text{-}COE)}kt^2/2)$ with $k = ([I]_0$ initiation efficiency). This results in $k_{p(homo\text{-}COE)} = 8.3\,L\,mol^{-1}\,s^{-1}$. The value also fits well the value $k_{p(homo\text{-}COE)} = 9.2\,L\,mol^{-1}\,s^{-1}$ assuming an average initiation efficiency of 15% ($T = 22\,°C$). The low values of $k_{p(homo\text{-}COE)}$ relative to $k_{p(homo\text{-}NBE)}$ certainly reflect the lower ring strain of COE. In the copolymerization of NBE with COE, however, the apparent rate constant for the polymerization of NBE, $k_{p,app(copol\text{-}NBE)}$, dramatically increased to $42\,600\,L\,mol^{-1}\,s^{-1}$, while the one for COE increased only slightly to $k_{p,app(copol\text{-}COE)} = 23\,L\,mol^{-1}\,s^{-1}$. In other words, the rate of insertion of COE is enhanced by the presence of NBE, that is, by an NBE–initiator-derived terminus. The rate of insertion for NBE is more dramatically accelerated by the presence of COE, suggesting that a COE–initiator-derived terminus facilitates NBE insertion.

There must be a mechanism that favors NBE insertion into a COE–initiator-derived terminus and vice versa, over homopolymerization of either of the two monomers. A look at the potential reaction pathways provides some interesting mechanistic insights. In a first step, PCy_3 dissociates from **1**, forming a 14-electron intermediate. Addition of the olefin (COE or NBE), formation of the ruthenacyclobutane, and insertion gives the corresponding insertion products **A** (COE-derived) and **B** (NBE-derived, Scheme 2). As can be anticipated, the rotating NHC ligand in **B** imposes significant steric stress onto both the growing polymer chain and any concomitantly formed metallacyclobutane in the case that this ruthenacyclobutane is coordinated *trans* to the NHC (structure **C**). One way to insert a second NBE unit is to realize a ruthenacyclobutane coordinated side-on to the NHC (structure **E**). This may well be regarded to be energetically less favorable and will therefore proceed slowly. The same applies to the insertion of COE into **B**, thus forming **A** (via **D**): again a ruthenacyclobutane coordinated side-on to the NHC might be the alternative and its formation will also proceed rather slowly. Now, structure **A**, however, may insert the more reactive NBE via ruthenacyclobutanes coordinated *trans* or side-on to the NHC (structures **F** and **G**), since the steric demand of the COE terminus building the polymer chain **P** is much lower than that of an NBE terminus. In other words, the steric interaction of the 1-phenylethyl group with a NBE–initiator-derived terminus is the key to the selectivity. Since NHC rotation is relatively fast (vide supra), it is believed to be responsible for creating this situation. However, since $k_{p(homo\text{-}COE)} < k_{p(NBE\text{-}alt\text{-}COE)} < k_{p(homo\text{-}NBE)}$, homopoly-



Scheme 2. Proposed reaction pathway for the alternating ROMP of NBE and COE.

merization of NBE occurs within a reasonable time, while that of COE takes hours. In summary, the overall sequence [**B**→**D**→**A**→**F**, **G**]$_n$ results in the formation of the alternating copolymer. With less reactive (i.e. sterically more demanding) NBE derivatives such as **3**, **5**, and **6** (Table 1) these copolymerizations can be run using monomer ratios of 1:5 or 1:1. These arguments apply assuming that the rate k_{rot} found for **1** would not be totally different from k'_{rot} and k''_{rot} found for the corresponding 14-electron species [$RuCl_2$(NHC)(CHR)] and for the 16-electron species [$RuCl_2$(NHC)(CHR)(alkene)] (**1′**), in which the the phosphine is replaced by an η^2-coordinated alkene (i.e. NBE or COE).

In conclusion, selectivity in copolymerization is believed to result solely from the steric interaction of the 2-phenethyl substituent at the nitrogen of the NHC ligand with the growing polymer chain in combination with favorable values for k_{rot} and $k_{\mathrm{p,app(copol\text{-}NBE)}}$, and $k_{\mathrm{p,app(copol\text{-}COE)}}$. Ruthenacyclobutanes coordinated side-on to the NHC are believed to play a key role. Finally, if such a steric demand is in fact responsible, then [$RuCl_2$(Py)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(CHPh)][17,21] (**7**) based on a six-membered NHC ligand should also show at least some alternating dyads in the copolymerization of NBE and COE, since the mesityl ligands should interact with the growing polymer chain to a larger extent than those in the five-membered NHCs. In fact, this is the case. Thus, 13% of alternating dyads were found in poly(NBE-*co*-COE)$_n$, when a **7**/NBE/COE ratio of 1:2000:100000 was used, while the second-generation Grubbs catalyst [$RuCl_2(PCy_3)(IMesH_2)$(CHPh)] produced only 8% of alternating dyads under these conditions.

Current work focuses on exploiting the general applicability of this concept by using different initiators as well as on investigating the impact on olefin cross-metathesis, enyne metathesis, and cyclopolymerization.

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Keywords: copolymerization · cyclooctene · metathesis polymerization · norbornene · ruthenium

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