 DOI: 10.1002/masy.201051007

Alternating Ring-Opening Metathesis Copolymerization of Norborn-2-ene with *cis*-Cyclooctene and Cyclopentene

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Summary: Ru-alkylidenes based on unsymmetrical imidazolin-2-ylidenes, were used for the alternating copolymerization of norborn-2-ene (NBE) with *cis*-cyclooctene (COE) and cyclopentene (CPE), respectively. Alternating copolymers, i.e., poly(NBE-*alt*-COE)$_n$ and poly(NBE-*alt*-CPE)$_n$ containing up to 97 and 91% alternating diads, respectively, were obtained. The copolymerization parameters of the alternating copolymerization of NBE with CPE under the action of different initiators were determined using a first order Markov model. Hydrogenation of poly(NBE-*alt*-COE)$_n$ yielded a fully saturated, hydrocarbon-based polymer.

Keywords: copolymerization; polyolefins; ring-opening metathesis polymerization; synthesis

Introduction

The *alternating* copolymerization of two different monomers is still a challenging task. For an alternating copolymerization to be accomplished by ROMP, a situation has to be created where the insertion of a monomer A into the living metal alkylidene is favored in case a second, different monomer B was inserted in the previous step and where insertion of a certain monomer A or B is strongly disfavored in case the same monomer was inserted in the preceding step. Consequently, reports on the alternating copolymers in general as well as on copolymerizations accomplished via metathesis copolymerization of two different monomers are comparably rare.[1–9] We addressed this task by using Grubbs- or Grubbs-Hoveyda-type initiators. Generally, their selectivity and reactivity is governed by the nature of the N-heterocyclic carbene (NHC),[10–25] the alkylidene[26–37] or the (pseudo)halide ligands.[38–48] We prepared a series of novel initiators for the synthesis of alternating copolymers based on Grubbs-type initiators containing unsymmetrical NHCs.[24,49] and checked for their capability to copolymerize norborn-2-ene (NBE) and *cis*-cyclooctene (COE) as well as NBE and cyclopentene (CPE) in an alternating way.

Results and Discussion

A series of different Ru-alkylidenes (Grubbs-type initiators) based on unsymmetrical NHCs were used for the alternating copolymerization of NBE with COE and CPE, respectively. Their structure is shown in Figure 1.

We used initiators **1**-**9** in the copolymerization of NBE with COE and CPE, respectively. Using a NBE:COE ratio of 1:50, the corresponding copolymers poly(NBE-*alt*-COE)$_n$ contained 95-97%

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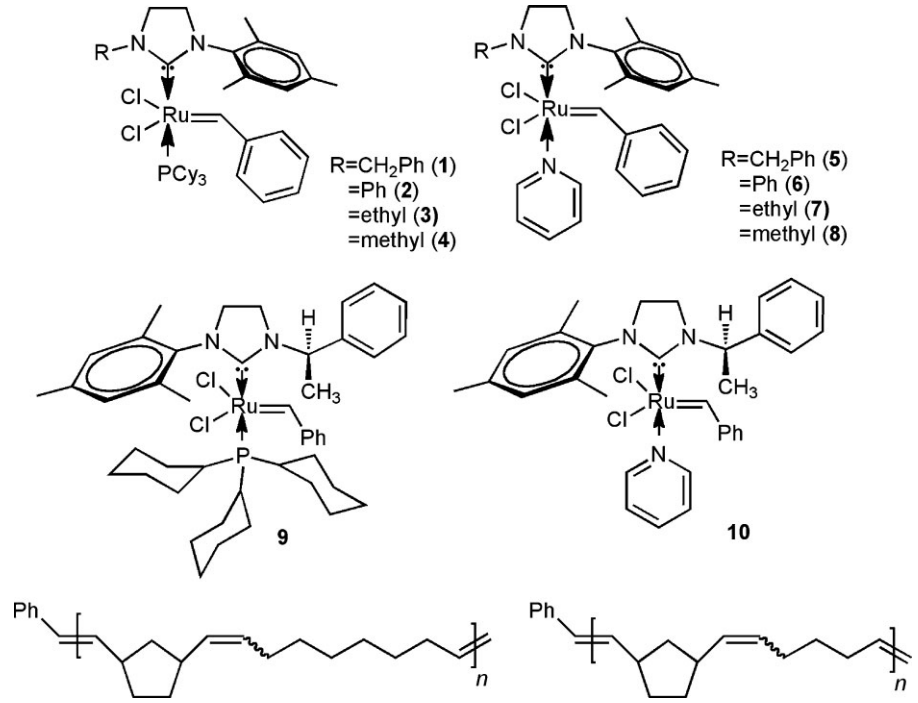

Figure 1.
Structure of initiators **1-10** and of poly(NBE-*alt*-COE)$_n$ (bottom, left) and poly(NBE-*alt*-CPE)$_n$ (bottom, right).

alternating diads (Table 1). In contrast, using a ratio of NBE:CPE of only 1:7, the poly(NBE-*alt*-CPE)$_n$ copolymers containing 79-91% of alternating diads were obtained (Table 2). This percentage of alternating units is among the highest values found so far.[4] This is of particular interest, since CPE usually displays a rather limited propensity to undergo ROMP[50] and homopolymerization of CPE is often counterbalanced by backbiting, yielding cyclic, low molecular weight polymers.[51] The structures of the two alternating copolymers are shown in Figure 1, a representative ^{13}C-NMR spectrum is shown in Figure 2.

Hydrogenation of poly(NBE-*alt*-COE)$_n$ with *p*-toluenesulfonylhydrazide in hot xylene yielded a fully saturated, hydrocarbon-based polymer whose backbone

Table 1.
Results of the alternating copolymerization of NBE with COE.

initiator	*cis* (%)[a]	alternating diad (%)[a]	M_n (g/mol)	PDI[b]
1	61	95	5.5×10^5	2.0
2	60	96	7.6×10^5	1.9
3	61	97	8.0×10^5	1.6
5	61	97	6.0×10^5	1.9
6	59	96	7.8×10^5	1.8
7	62	97	1.3×10^6	1.4
8	64	96	1.5×10^6	1.6
9	50	97	4.0×10^4	2.19
10	50	97	1.4×10^5	1.59

Initiator:NBE:COE = 1:2000:100000.[a]by ^{13}C-NMR,[b]by GPC.

Table 2.
Results of the alternating copolymerization of NBE with CPE.

initiator	alternating diad (%)[a]	M_n (g/mol)	PDI[b]
1	79	1.0×10^4	1.9
2	90	2.5×10^4	2.3
3	90	4.4×10^4	1.9
5	85	2.0×10^4	1.9
6	91	5.4×10^4	2.4
7	91	3.4×10^4	2.6
8	86	2.0×10^4	1.9

Initiator:NBE:CPE = 1:2000:14000.[a]by ^{13}C-NMR,[b]by GPC.

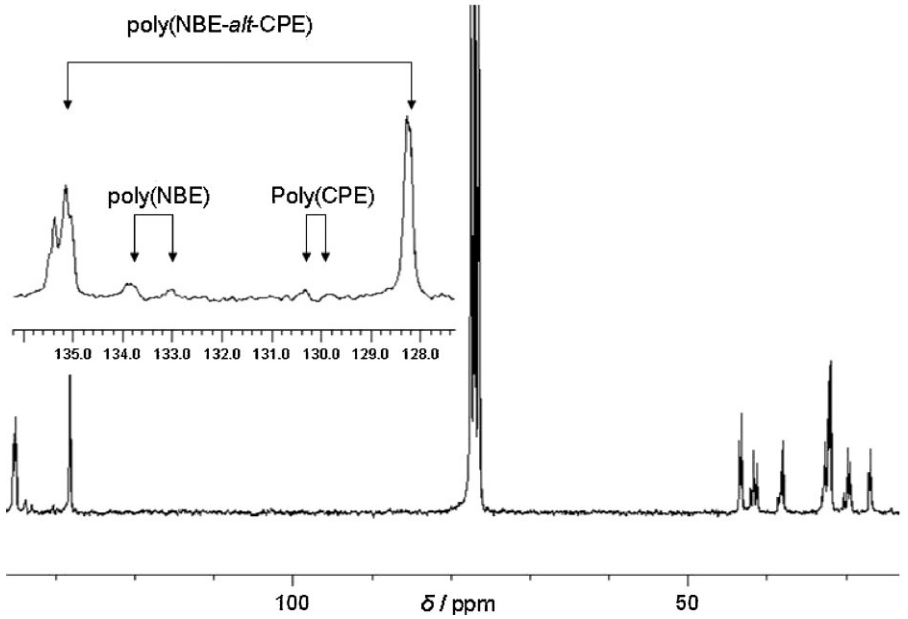

Figure 2.
^{13}C-NMR of poly(NBE-*alt*-CPE)$_n$.

Table 3.
Copolymerization parameters obtained with initiators **1-8** in the alternating copolymerization of NBE (1) with CPE (2).

initiator	1	2	3	5	6	7	8
r_1	1.4	1.2	1.2	1.4	1.2	1.2	1.5
P_{12}	0.83	0.85	0.85	0.83	0.85	0.85	0.82
$r_2\ 10^{-3}$	43	6.3	6.4	18	4.8	4.3	14
P_{21}	0.77	0.96	0.96	0.88	0.97	0.97	0.91

formally consists of CPE (1,3-insertion) followed by an even number (10) of carbon units and that may hardly be realized by any other polymerization method.[52]

From the ^{13}C-NMR spectra, we were able to extract the copolymerization parameter *r*. A first-order Markov model ultimately leading to the Mayo-Lewis equation[53] was applied. In this case, an *r*-value for each monomer is obtained. Thus, $r_1 = ([1/P_{12}]\text{-}1)([\text{CPE}]/[\text{NBE}])$ and $r_2 = ([1/P_{21}]\text{-}1)([\text{NBE}]/[\text{CPE}])$ with P_{12} and P_{21} being the reactivity probabilities for CPE to insert into a growing chain with a terminating NBE and vice versa. Again, the results are summarized in Table 3. Both P_{12} and P_{21} can be retrieved from ^{13}C-NMR.

Conclusion

In summary, we significantly extended the number of Ru-alkylidene based metathesis initiators which allow for the synthesis of highly alternating copolymers of norborn-2-ene with *cis*-cyclooctene and cyclopentene, respectively. In terms of initiation efficiency, the pyridine derivatives turned out to be superior over the parent PCy_3-based compounds. A high *cis*-content was observed in poly(NBE-*alt*-COE)$_n$ prepared by any of the initiators used here. Hydrogenation of the alternating copolymers allows for creating model systems for poly(olefin) chemistry, e.g., for the determination of chemical shifts in 1-olefin

polymerization-derived copolymers of cyclopentene and ethylene.

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