# Communications

Designed Catalysts

A Catalyst for the Simultaneous Ring-Opening Metathesis Polymerization/Vinyl Insertion Polymerization**

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Dedicated to Professor Walter Kaminsky on the occasion of his 70th birthday

Both the vinyl insertion polymerization (VIP) of olefins[1–7] and the ring-opening metathesis polymerization (ROMP)[8,9] of cyclic olefins are well-established polymerization techniques based on the insertion of a monomer between a transition metal (ion) and a growing polymer chain. In fact, they are related to each other, since a cationic, VIP-active catalyst may be converted into a ROMP-active catalyst by a simple α-elimination process. In contrast, the reverse process, that is, the α addition of a proton to a metal alkylidene to form a cationic VIP-active species, is much more difficult to accomplish in a controlled way.

The occurrence of both VIP- (Scheme 1 a) and ROMP-derived (Scheme 1 b) structures in poly(NBE) (NBE = norborn-2-ene) was observed already in the early days of polyolefin chemistry and paved the way for identifying and understanding metathesis-based processes.[10,11] Nevertheless, at that time there was no clear evidence for the presence of both structures, that is, both ROMP- and VIP-derived repeat units, within one single polymer chain.[10–14] In fact, because of the high crystallinity of these polymers, it was argued that two different polymers, that is, one VIP- and one ROMP-derived, had formed concomitantly. The first unequivocal evidence for the presence of both ROMP- and VIP-derived structures within one single polymer chain was reported by Farina et al. using Mo- and Re-based initiators;[15,16] they unambiguously assigned characteristic signals
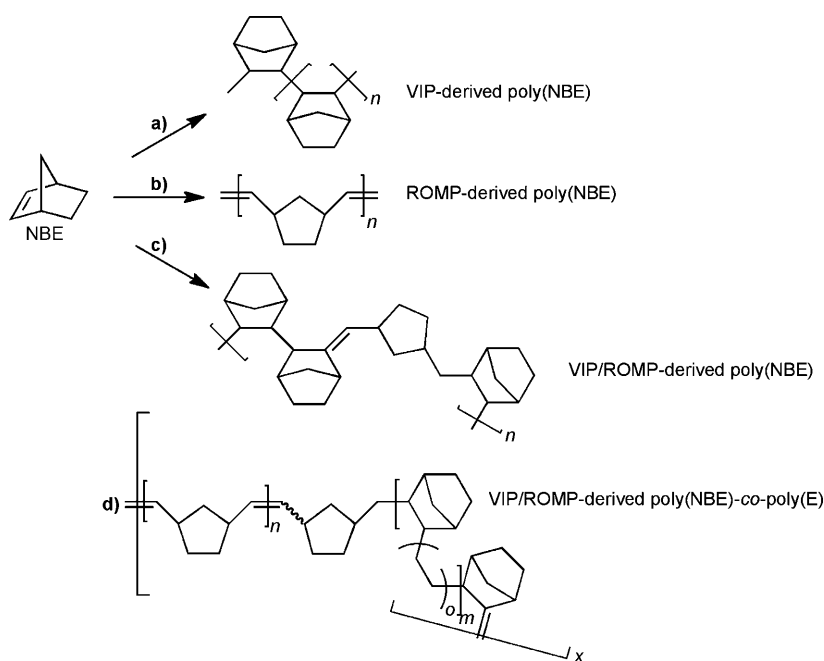
Scheme 1. Different types of poly(NBE) and poly(NBE)-*co*-PE obtained by VIP, ROMP and VIP/ROMP as well as the structure of the target copolymer.

for the quaternary carbon and for the methylene group in VIP/ROMP-derived poly(NBE) (Scheme 1 c).

In fact, the structure of this particular polymer can be explained only by a reversible α-elimination/α-addition process, which permits VIP and ROMP to take place within the same polymer chain. Owing to the relationship between VIP and ROMP, even one single switch between VIP and ROMP, resulting in the synthesis of AB diblock copolymers, has attracted attention. Thus, Grubbs et al. reported on a titanacyclobutane compound active in the ROMP of NBE; upon addition of an alcohol and activation with Et₂AlCl, a cationic species was created that is active in the VIP of ethylene (E), resulting in the synthesis of poly(NBE)ROMP-*b*-poly(E).[17] Kaminsky et al. reported on a controlled switch from VIP to ROMP in the preparation of poly(NBE)VIP-*b*-poly(NBE)ROMP, poly(NBE)VIP-*b*-poly(CPE)ROMP, and poly-(NBE)VIP-*b*-poly(COE)ROMP (CPE = cyclopentene, COE = *cis*-cyclooctene).[18,19]

We aimed at the creation of a Group IV based initiator system capable of forming both VIP- and ROMP-derived structures from a cyclic olefin and also capable of copolymer-

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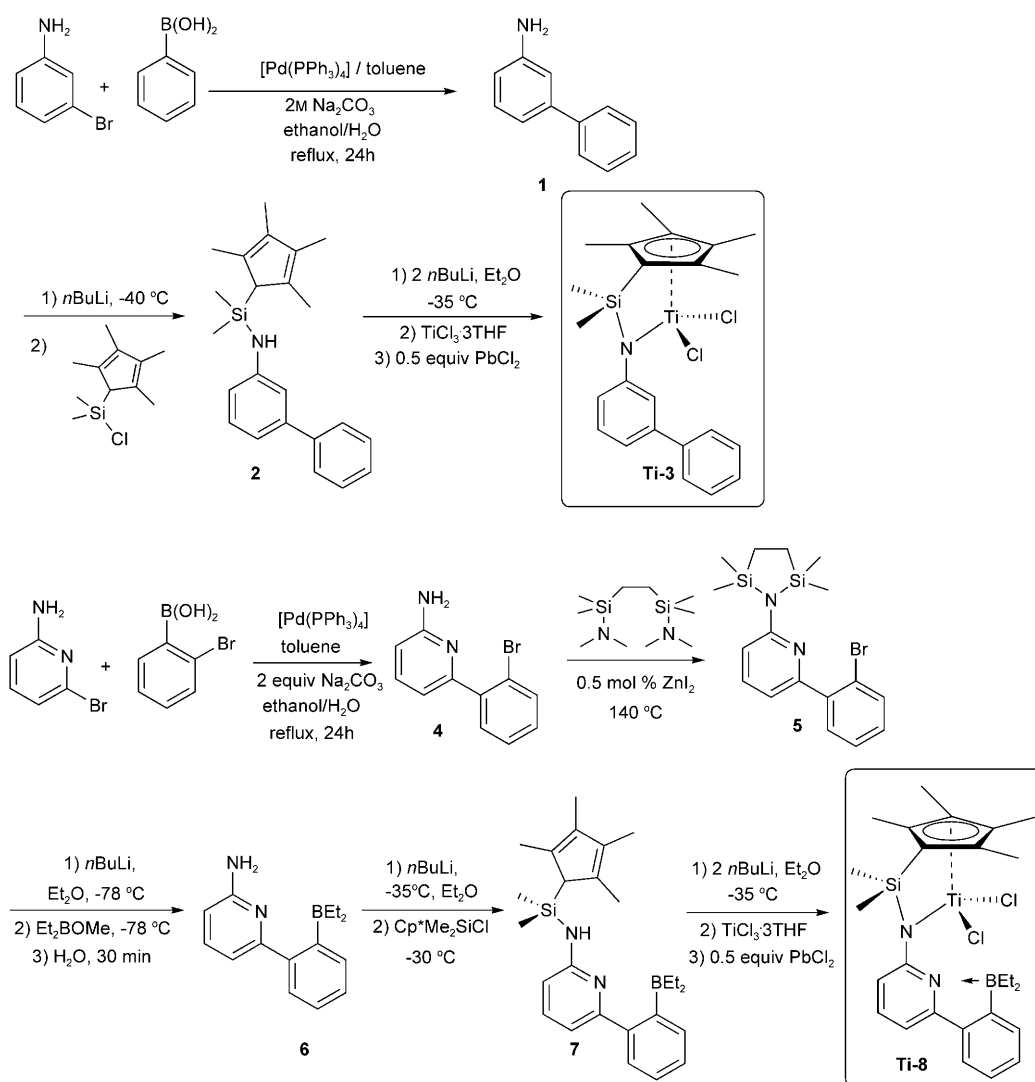Leibniz-Institut für Oberflächenmodifizierung e.V. (Germany)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201004125.

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izing an acyclic olefin to yield high-molecular-weight copolymers with a narrow molecular-weight distribution containing multiple blocks of both ROMP- and VIP-derived structures within one single polymer chain. Such unprecedented polymeric structures, particularly those derived from COE and E, would display features of standard cycloolefin copolymers (COCs)[5] without displaying the standard drawbacks of pure ROMP-derived polymers, that is, lack of stability in the presence of oxygen. Additionally, they would offer the possibility of functionalization through polymer-analogous reactions, for example, halogenation, epoxidation, and vicinal dihydroxylation. In this way, the poor derivatization techniques for standard polyolefins can be bypassed and the copolymerization of functional monomers can be circumvented. Particularly the target homogeneous distribution of the ROMP- and VIP-derived structures along the polymer backbone, rather than an AB-block-copolymer structure, would support these features.

Zirconium and titanium are suitable transition metals for both VIP- and ROMP-active catalysts; in other words, cationic alkyl complexes as well as methylidene complexes of Zr^{IV} and Ti^{IV} exist.[20–23] These metal methylidenes are active initiators in the ROMP of cyclic olefins such as NBE.[24,25] However, an initiator capable of reversibly switching between ROMP and VIP must bear a ligand system that can reversibly abstract a proton from the cationic species and re-add a proton to the metal alkylidene. Preferably, one should have control over this process, for example, by change of temperature. These requirements can be met with a basic auxiliary ligand; however, its reversible protection is required to prevent its irreversible coordination to the cationic metal center.

In view of these requirements, we designed an amine/borane-containing, Ti^{IV}-based, half-sandwich precatalyst with a constrained geometry (**Ti-8**, Scheme 2).

Upon activation, for instance with methylalumoxane (MAO),[26] this highly electrophilic complex was expected to be capable of accomplishing this task. By design, the free pyridyl group should be capable of abstracting a proton, that is, inducing α elimination via a six-membered transition state. The boryl group competes for the free lone pair of electrons; thus the α-elimination process should be temperature dependent. We also synthesized the corresponding amine/borane-free model compound **Ti-3** to illustrate and clarify the role of the amine/borane ligand, respectively.

Upon activation with MAO (**Ti-8**/MAO = 1:1000) and addition of 1000 mol equiv of NBE, pure poly(NBE)$_{ROMP}$ (M_n = 4600 g mol^{-1}, PDI = 1.51, *cis/trans* = 40:60) was obtained at T = 50°C. The ^{1}H and ^{13}C NMR spectra (in C$_6$D$_4$Cl$_2$) show the characteristic signals at δ = 5.41 (C=C$_{trans}$), 5.21 (C=C$_{cis}$), and around 134.0, 134.9 ppm, respectively. As expected a glass transition was observed (T_g = 73°C) and no reflections for crystalline regions could be observed by wide-angle X-ray diffraction (WAXD). However, when the NBE concentration was increased (10000 mol equiv), poly(NBE) containing both VIP- and ROMP-derived repeat units was

Scheme 2. Synthesis of **Ti-3** and **Ti-8**.

obtained. Again, a fully amorphous polymer ($M_n = 10000\ \mathrm{g\,mol^{-1}}$, PDI = 1.47, $T_g = 136\,°C$) was obtained as evidenced by WAXD. To identify the active species, **Ti-8** was mixed with MAO and NBE (1:20:50) in $C_2D_2Cl_4$. In the ^1H NMR spectrum, a doublet at $\delta = 8.01$ ppm ($J = 7$ Hz) corresponding to the $[Ti=CH-c-(1,2-C_5H_8)-CH=CHR]$ moiety[24,25] was observed, which disappeared upon heating above $50\,°C$.

In the copolymerization of ethylene (4 bar) with NBE, **Ti-8** again displayed NBE-concentration-dependent behavior. Thus, a pure VIP-derived E-NBE copolymer was obtained at $T = 50\,°C$ when **Ti-8**/MAO/NBE was used in a ratio of 1:1000:2000 (Table 1, entry 1). However, at a higher NBE concentration (Table 1, entry 2), a fully amorphous polymer

Table 1: **Ti-8**-catalyzed copolymerization of E with NBE or COE; reaction time: 1 h.

Entry	Ti-8/MAO/NBE	T [°C]	A[a]	M_n [g mol^{-1}]	PDI	T_m [°C]	X[b]
1	1:1000:2000	50	64	570000	1.32	116	0
2	1:1000:10000	50	35	1100000	1.05	122	16
3	1:1000:20000	50	50	1540000	1.29	125	25
4	1:2000:10000	70	65	480000	1.94	123	n.a.
5	1:2000:20000	50	115	1180000	1.08	92	71
	Ti-8/MAO/COE	T [°C]	A[a]	M_n [g mol^{-1}]	PDI	T_m [°C]	X[b]
6	1:1000:2000	50	64	1500000	1.14	129	0
7	1:1000:10000	50	12	800000	1.22	145	42
8	1:2000:10000	70	34	490000	2.5	142	8

[a] Activity in $\mathrm{kg\,mol^{-1}\,bar\,h^{-1}}$. [b] The mol% of poly(NBE)$_{ROMP}$ and poly(COE)$_{ROMP}$, respectively; n.a.: not analyzed.

was obtained containing multiple blocks of both ROMP- and VIP-derived NBE units (poly(NBE)$_{ROMP}$/poly(NBE)$_{VIP}$/poly(E) = 1:1:4). A further increase in NBE concentration resulted in a further increase in the proportion of ROMP-derived poly(NBE) units (poly(NBE)$_{ROMP}$/poly(NBE)$_{VIP}$/poly(E) = 2:1:5), and in a further increase in the molecular weight (Table 1, entry 3). It is important to emphasize that both the ROMP- and VIP-derived poly(NBE) sequences occur within the same polymer chain, as suggested by the narrow polydispersity index of the polymers (PDI $\leq$ 1.3, Table 1), the absence of any additional peaks in the gel permeation chromatogram that could be assigned to poly-(NBE)$_{ROMP}$, the absence of a glass transition attributable to a poly(NBE)$_{ROMP}$ homopolymer, and the fact that no high T_m values were found like those usually observed for cyclic olefin copolymers.

An increase in reaction temperature to $70\,°C$ resulted in a decrease in M_n and in an increase in PDI (Table 1, entry 4). This is attributed to a higher fraction of unprotected pyridyl moieties which directly results in an increase in α elimination. Consequently, the concentration of intermediary titanium alkylidenes is higher; however, these ultimately react with E to form titanium methylidenes, which decompose at this temperature (vide supra). This side reaction also accounts for the observed activities, which are lower than those obtained with similar Ti(Cp*SiMe$_2$NR) systems.[3] A further increase in NBE concentration increased the poly(NBE)$_{ROMP}$ fraction within the polymer to 71 mol%. Consequently, T_g decreased

to $92\,°C$. The role of MAO becomes obvious when one compares entries 3 and 5 in Table 1. An increase in MAO concentration results in an increase in activity (better stabilization of the cationic species), a decrease in PDI (better stabilization of the cationic species, reduced chain transfer), and a increase in the poly(NBE)$_{ROMP}$ content. There is a simple explanation: α elimination results in pyridinium moieties which react irreversibly with MAO to form methane and a titanium alkylidene. The latter gives rise to a polymer with a higher poly(NBE)$_{ROMP}$ content but also a lower M_n value, since the reaction of the titanium alkylidene with ethylene cleaves the polymer chain from the metal center.

To support these findings and identify the actual structure of the polymer, we compared the ^{13}C NMR spectra of poly(NBE)$_{ROMP}$-co-poly(NBE)$_{VIP}$-co-poly(E) polymers with those of pure ROMP-derived poly(NBE) as well as of poly(NBE)$_{ROMP}$-alt-poly(E$_3$) formed by the alternating ring-opening metathesis copolymerization of NBE with COE (Figure 1).[27,28] Poly(NBE)$_{ROMP}$-alt-poly(E$_3$) mimics one ROMP-derived poly(NBE) repeat unit followed by three ethylene units. No signals were found for poly-(NBE)$_{ROMP}$-poly(E), that is, $-CH=CH-c-(1,2-C_5H_8)-CH=CH-(CH_2)_n-$ sequences. The signals at $\delta = 47.5$ and 41.3 ppm correspond to the alternating, isotactic VIP-derived E-NBE diads.[29–34] In addition, E-NBE-E-E sequences become visible. The signals at $\delta = 46.8$ and 41.1 ppm correspond to the alternating, syndiotactic VIP-derived E-NBE sequences, while the signal at $\delta = 32.6$ ppm stems from alternating E-NBE and isolated NBE sequences. Finally, the signal at $\delta = 29.4$ ppm can be attributed to homo-poly(E) sequences. The most important signals, however, are found at $\delta = 133.9, 132.9\ 42.9, 42.7, 42.5, 41.8, 41.1, 38.5, 38.3,$ and 33.2 ppm. These can be assigned unambiguously to poly-(NBE)$_{ROMP}$-alt-poly(NBE)$_{VIP}$ sequences and provide clear evidence for the incorporation of the poly(NBE)$_{ROMP}$ units into the polymer main chain. No signals indicative of a 1,7-connectivity of poly(NBE)$_{VIP}$ sequences were observed.[35,36]

These findings exclude the presence of the two polymers poly(NBE)$_{ROMP}$ and poly(NBE)$_{VIP}$-co-poly(E) as well as the following alternative pathway: Poly(NBE)$_{ROMP}$ could form by initial α elimination followed by cleavage of the titanium alkylidene by E, which would result in a vinyl-terminated polymer. This macromonomer could then copolymerize with NBE and E. In fact, our data support the reaction mechanism shown in Scheme 3: Reaction of a cationic VIP-active species with NBE, followed by α elimination produces a disubstituted titanium alkylidene whose formation is favored over the formation of a monosubstituted alkylidene from the α elimination after E insertion. High concentrations of NBE promote both the α elimination and the ROMP of this monomer. The proton stays, at least for a certain time, at the pyridine moiety and can be donated back to the titanium
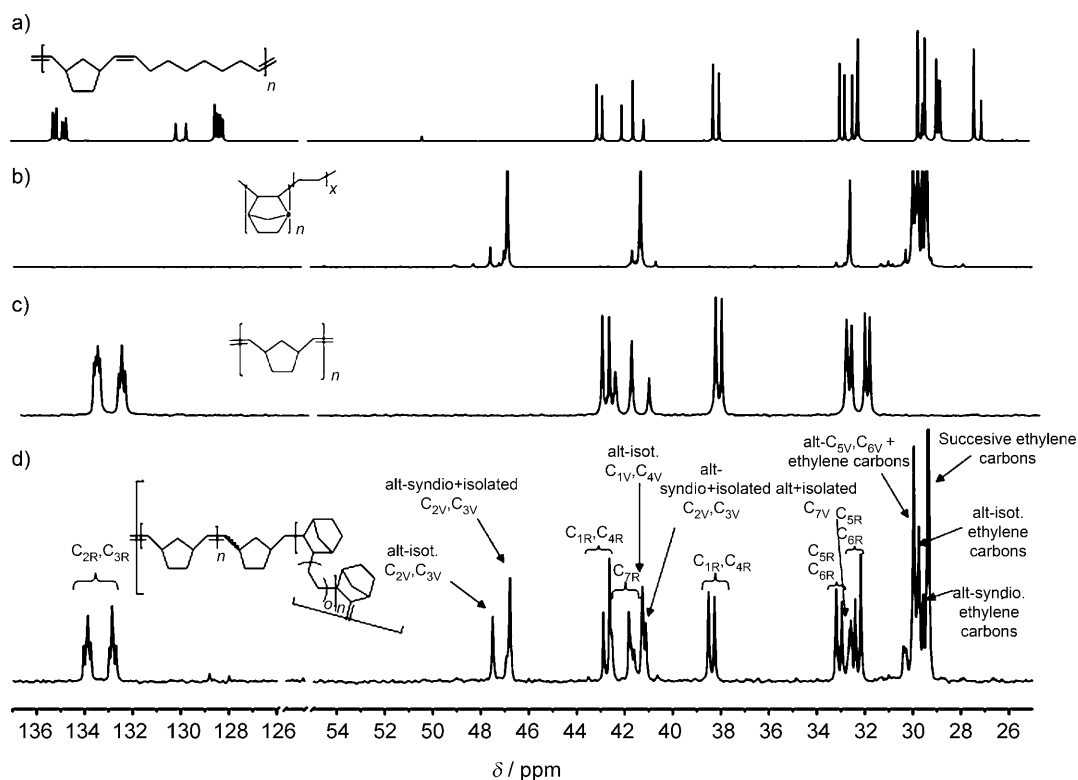
Figure 1. ^{13}C NMR spectra (in $C_2D_2Cl_4$) of poly(NBE)$_{ROMP}$ (c), poly(NBE)$_{ROMP}$-*alt*-poly(E$_3$) (a), **Ti-8**-derived poly(NBE)$_{ROMP}$-*co*-poly(NBE)$_{VIP}$-*co*-poly(E) (d), and poly(NBE)VIP-*co*-ploy(E) (b). alt-syndio: alternating, syndiotactic; alt-isot.: alternating, isotactic; V: VIP product; R: ROMP product.

Scheme 3. Proposed mechanism for the **Ti-8**-catalyzed formation of poly(NBE)$_{ROMP}$-*co*-poly(NBE)$_{VIP}$-*co*-poly(E).

not the most favorable and requires, as observed, high concentrations of NBE to stabilize the titanium alkylidene. The proposed structure of poly(NBE)$_{ROMP}$-*co*-poly(NBE)$_{VIP}$-*co*-poly(E) is shown in Scheme 1 d.

If all that is true, then the homopolymerization of COE as well as its copolymerization with E should give similar results. In fact, the homopolymerization of COE by **Ti-8** activated by MAO (**Ti-8**/MAO/COE = 1:1000:1000) at 50°C resulted in the formation of pure ROMP-derived poly(COE) ($M_n = 115\,000$ g mol^{-1}, PDI = 1.48, $T_g = -54$°C). Both the ^{1}H and ^{13}C NMR spectra (in $C_6D_4Cl_2$) show the characteristic signals at $\delta = 5.39$ (C=C$_{trans}$), 5.34 (C=C$_{cis}$) and 127.7, 130.8 ppm (*cis/trans* $\approx$ 50:50). Similarly, the

alkylidene to re-establish the VIP-active species. At this point, an NBE monomer can insert again, most probably followed by E insertion. As one might expect, this process is

copolymerization of E with COE at a **Ti-8**/MAO/COE ratio of 1:1000:2000 (Table 1, entry 6) gave crystalline poly(COE)$_{VIP}$-*co*-poly(E) ($T_m = 129°C$). An increase in the COE concentration (Table 1, entry 7) again resulted in the formation of poly(COE)$_{ROMP}$-*co*-poly(COE)$_{VIP}$-*co*-poly(E) ($T_m = 145°C$) in a ratio of 8:1:10, that is, with a very high content of ROMP-derived poly-(COE). The unimodal, comparably narrow molecular-weight distribution (PDI = 1.22), the different *cis/trans* ratios, and the fact that no glass transition for poly(COE)$_{ROMP}$ was observed strongly suggest that the multiple poly(COE)$_{ROMP}$ blocks are part of the polymer chain and do not form a second, separate purely ROMP-derived polymer.
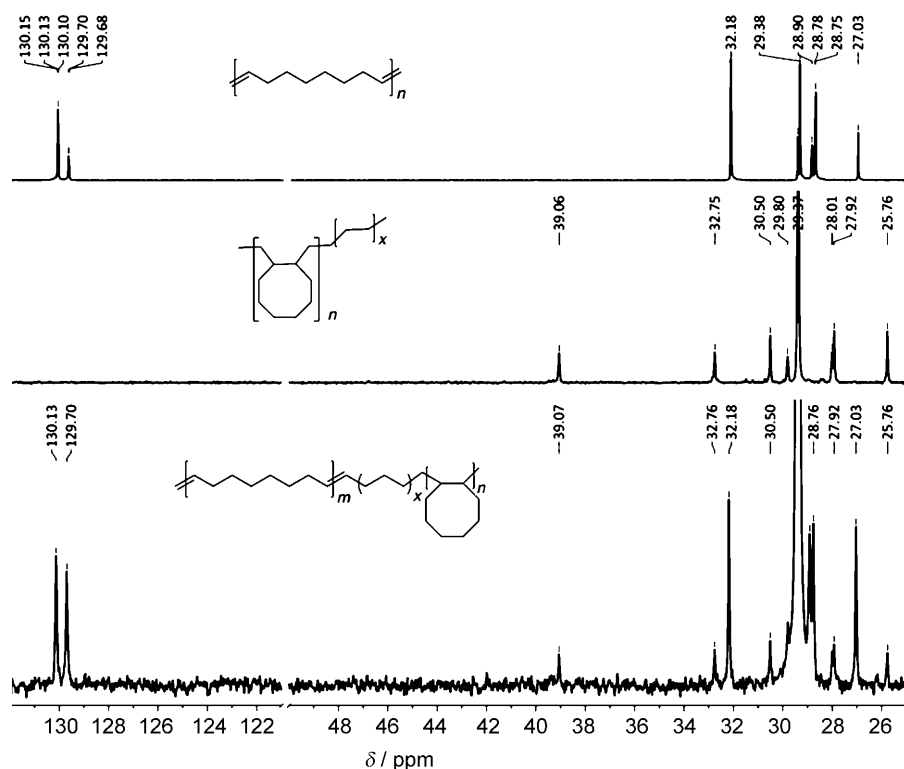
Figure 2 shows the ^{13}C NMR spectra of poly(COE)$_{ROMP}$-*co*-poly-(COE)$_{VIP}$-*co*-poly(E), a ROMP-derived poly(COE), and a VIP-derived poly(COE)$_{VIP}$-*co*-poly(E). Signals of both the ROMP- ($\delta = 130.1, 129.7, 32.2, 29.4, 28.8,$ and 27.0 ppm) and VIP-derived polymer at $\delta = 39.0, 32.8, 30.5, 29.8, 29.1, 28.0, 27.9, 25.8$ ppm are visible; however, owing to additional signals of olefins arising from α elimination, the overall *cis/trans* ratio of the double bonds is about 1:1 as compared to a value of 3:7 for pure **Ti-8**-derived poly(COE)$_{ROMP}$. An increase in the **Ti-8**/MAO ratio (1:2000, Table 1, entry 8) and in the reaction temperature to $T = 70°C$ resulted in the formation of poly(COE)$_{ROMP}$-*co*-poly(E) (poly(COE)$_{ROMP}$/poly(E) = 1:16). The absence of any additional peaks apart from those for linear poly(E) and poly(COE)$_{ROMP}$ in the ^{13}C NMR spectrum suggests a highly linear structure for the poly(E)-derived blocks.

The central role of the auxiliary pyridine ligand becomes apparent when the above-described homo- and copolymerizations are carried out with **Ti-3** instead of **Ti-8**. Thus, **Ti-3** copolymerizes NBE and E in the same way as other (η^5-cyclopentadienyl)silylamido titanium(IV) catalysts:[5,37] only

Figure 2. ^{13}C NMR spectra (in C$_2$D$_2$Cl$_4$) of **Ti-8**-derived poly(COE)$_{ROMP}$-*co*-poly(COE)$_{VIP}$-*co*-poly(E) (bottom), poly(COE)$_{VIP}$-*co*-poly(E) (middle), and poly(COE)$_{ROMP}$ (top).

poly(NBE)$_{VIP}$-*co*-poly(E) ($300000 < M_n < 1400000$ g mol^{-1}; $1.07 < PDI < 1.56$) was obtained (Table 2, entries 1–4). Under none of the applied reaction conditions, including those used for **Ti-8**, were ROMP-derived structures observed. The same holds for the copolymerization of E with COE (Table 2, entries 5 and 6).

In summary, we have described a catalytic system capable of synthesizing copolymers of E with cyclic olefins that contain both ROMP- and VIP-derived structures within one polymer chain. We are currently exploring the limits of this methodology in terms of monomers and the special properties of the copolymers obtained.

Table 2: **Ti-3**-catalyzed copolymerization of E with NBE or COE; reaction time: 1 h, 4 bar, T = 50°C.

Ti-3/MAO/NBE	χ_{NBE}[a]	A[b]	M_n [g mol^{-1}]	PDI	
1:1000:2000	3.3	66	1 400 000	1.07	
1:1000:5000	10	300	470 000	1.53	
1:2000:10000	16	745	300 000	1.38	
1:2000:20000	19	410	320 000	1.56	
Ti-3/MAO/COE	χ_{COE}[a]	A[b]	M_n [g mol^{-1}]	PDI	T_m [°C]
1:1000:2000	1	170	2 500 000	1.07	122
1:2000:10000	16	670	1 750 000	1.21	119

[a] Amount of cyclic olefin (mol%) in the copolymer. [b] Activity in kg mol^{-1} bar h.

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