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Terpolymerization of Linear and Alicyclic α-Olefins with Norbornene and Ethylene by *ansa*-Metallocene Catalysts[†]

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ABSTRACT: Ethylene−norbornene (E−N) terpolymerization experiments using the linear olefin 1-octene (O) or the alicyclic vinylcyclohexane (VCH) were conducted with two different *ansa*-metallocene compounds $Zr(\eta^5:\eta^5\text{-}C_5H_4CPh_2C_{13}H_8)Cl_2]$ (**1**) and $[Zr\{(\eta^5\text{-}2,5\text{-}Me_2C_5H_2)_2CHMe\}Cl_2]$ (**2**). The terpolymers obtained were investigated in detail by determining microstructure and termonomer contents by ^{13}C NMR, molar masses, and thermal properties. Chain end group analysis gave insight into factors that influence termonomer insertion and chain termination. Terpolymer molar masses were lower than those of the corresponding copolymers, those from **1** being higher than those from **2**. This is related to the lower tendency of catalyst **1** to give β-H elimination at a last enchained E unit as revealed from the low amount of vinyl chain end groups in ^1H NMR spectra. In VCH terpolymers from catalyst **1**, only vinylene end groups, arising from 2,1 VCH insertions after one last inserted E unit, are present. This along with the lower activity reveals that VCH insertion is more difficult with this catalyst than with catalyst **2**. Furthermore, all experiments showed that in general VCH is more difficult to coordinate to an active catalyst than O. While catalyst **1** provides higher molar masses, catalyst **2** enables to reach higher activities, higher N and termonomer contents, and higher T_g values. Finally, it was found that termonomer content greater than 3 mol % clearly affects T_g values. Thus, preparation of norbornene−ethylene−α-olefin terpolymers with high T_g and attractive molar masses was achieved in high yield by metallocene catalysts.

Introduction

Cyclic olefin copolymers (COC), produced by copolymerization of ethylene with cyclic olefins, are materials of high commercial interest successfully used for applications in optics, capacitor films, food and drug packaging, medical and diagnostic containers. The copolymerization of ethylene (E) and norbornene (N) by *ansa*-metallocene-based catalysts was first reported by Kaminsky et al.,[1] generating a new class of cyclic olefin based polymers with unique properties, which were studied in detail over the last two decades.[2−6] Both academic and industrial groups have focused their research interest in COC. TOPAS Advanced Polymers (formerly part of Ticona) and Mitsui have independently developed commercial grades of these copolymers named as TOPAS and APEL, respectively.[7]

Ethylene copolymers with more than 20 mol % of norbornene are amorphous thermoplastic materials with a broad range of outstanding properties like excellent moisture barrier, high glass transition temperatures up to 220 °C, thermoformability, stiffness, dead-fold characteristics, remarkable biocompatibility, and chemical inertness. Copolymer properties, which are controlled by cyclic comonomer content, sequence distribution, and the stereochemical placement of norbornene units, are tightly connected to the structure of the catalyst employed.

One possibility to further widen the application of COC is the introduction of a third monomer. The opportunity of incorporating other olefins (as third monomer) into the E−N backbone may lead to improvements in the mechanical or other physical properties of the polymer. Despite the potential of this class of polymers only a limited number of reports can be found in literature on terpolymerization reactions with ethylene and norbornene.[8]

As a promising approach to further expand the material performance of COC, the introduction of a termonomer, either a linear α-olefin as 1-octene (O) or an alicyclic α-olefin like vinylcyclohexane (VCH), was considered herein. The presence of a longer linear α-olefin or of a sterically demanding α-olefin within the E−N copolymer backbone could result in a distinct change of polymer physics and therefore improve the commercial applicability of the material. Thus, the present work deals with the synthesis and detailed structural, molecular, and thermal characterization of terpolymers of ethylene and norbornene with third monomers such as 1-octene and vinylcyclohexane to obtain poly(E-*ter*-N-*ter*-O) and poly(E-*ter*-N-*ter*-VCH), respectively.

Terpolymerization reactions were investigated by using *ansa*-zirconocene based precursors activated with methylaluminoxane (MAO). $[Zr(\eta^5:\eta^5\text{-}C_5H_4CPh_2C_{13}H_8)Cl_2]$ (**1**) and $[Zr\{(\eta^5\text{-}2,5\text{-}Me_2C_5H_2)_2CHMe\}Cl_2]$ (**2**) were selected (Figure 1). Complex **1** belongs to the class of C_s-symmetric metallocenes which is a highly studied group of metallocenes, leading to high molar mass syndiotactic polypropylene for example,[9] complex **2** is known to show excellent activity for the copolymerization of ethylene and a bulky comonomer such as norbornene.[10] Even though they have different symmetry and different structural characteristics they are representative examples of catalysts which would have the potential of providing terpolymers with suitable molar masses and comonomer contents. The influence of termonomer concentration, at

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[†] Dedicated to Dr. Francesco Di Colo, who unexpectedly and sadly passed away.

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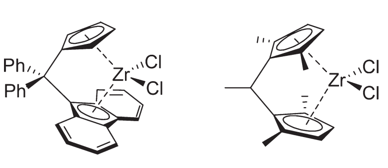
elevated polymerization pressure and high temperatures, on polymerization behavior was investigated. Polymer analysis, as there is determination of microstructure, termonomer content, molar mass, thermal properties, and analysis of chain end groups, gave insight into factors that influence termonomer insertion and chain termination.

Results and Discussion

The two catalyst precursors were selected as two representative *ansa*-metallocenes leading to E−N copolymers with high molar mass (**1**) and with excellent activity (**2**). Terpolymerization series were carried out in a lab-scale autoclave at a temperature of 50 up to 80 °C. High [N]/[E] molar ratios in feed were considered to achieve synthesis of terpolymers having more than 30 mol % of norbornene content and thus materials with high glass transition temperatures. The [N]/[E] ratio was kept constant at 4, 8, and 12. Termonomer concentration was varied as much as possible trying to attain terpolymers with termonomer content as high as possible and, at the same time, molar masses (M_w) possibly higher than 60000 g mol^{-1}. In particular, for the synthesis of poly(E-*ter*-N-*ter*-O), polymerization temperature was set at 70 °C, and a range of feed composition was investigated at constant ethylene pressure of 5.0 bar. For the synthesis of poly(E-*ter*-N-*ter*-VCH), ethylene pressure was varied within a range of 2.5 to 5.0 bar and temperature was set from 50 to 80 °C to test whether altering polymerization temperature and pressure would have an impact on molar masses and termonomer incorporation. Microstructure and norbornene content in the copolymers were determined by means of ^{13}C NMR spectroscopy. Molar masses and glass transition temperatures (T_gs) were determined by SEC and DSC measurements, respectively. Selected results of the terpolymerization reactions of E and N with 1-octene or vinylcyclohexane by means of MAO-activated metallocenes **1** and **2** are reported in Tables 1 and 2, respectively. For comparison the results of E−N copolymerization under identical conditions are also included in the tables.



1 **2**

Figure 1. Studied *ansa*-zirconocene-based precursors used in terpolymerization.

Activities. Activities are expected to drop with increasing N amount in the feed, which is indeed the case for E−N copolymerization performed with both catalytic systems. Catalyst **2** is more active than **1** under identical conditions (activities of entries 6 and 7 are higher than those of 1 and 2 in Table 1). The results become more complex looking at terpolymerization experiments. Under the conditions employed, there is a dependence of the catalytic activity of **1** on [Al]/[Zr] ratio, catalyst and termonomer concentrations (entry 4 vs 1), that makes the comparisons not straightforward. However, it appears that addition of octene increases activity of catalyst **1** and at the same time lowers polymer molar mass (entry 5 vs 2). In the case of catalyst **2**, addition of octene decreases both activity and polymer molar mass (entry 11 vs 6). Regarding the synthesis of poly(E-*ter*-N-*ter*-VCH), polymerization activities of both catalysts do not

Table 1. Ethylene/Norbornene/1-Octene Terpolymers Using [Zr(η^5:η^5-$C_5H_4CPh_2C_{13}H_8$)Cl_2] (1) and [Zr{(η^5-2,5-$Me_2C_5H_2$)$_2$CHMe}Cl_2] (2)

entry[a]	catalyst	[Al]/[Zr]	N/E/O[b]	yield, g	activity[c]	N,[d] mol %	O,[d] mol %	T_g,[e] °C	M_w[f] × 10^{-3}	M_w/M_n[f]
1	**1**	4000	8/1/0	7.2	1920	46		124	784	2.0
2	**1**	4000	12/1/0	6.0	1600	49		131	759	2.1
3	**1**	4000	4/1/1	6.1	4067	39	4	80	155	2.0
4	**1**	7200	8/1/1	6.8	4072	44	2	118	144	2.1
5	**1**	4000	12/1/0.5	31.0	5317	49	2	143	93	1.9
6	**2**	4000	8/1/0	33.0	8800	54		148	160	2.1
7	**2**	4000	12/1/0	7.6	2027	56		161	188	3.1
8	**2**	4000	4/1/1	12.4	4831	44	5	99	39	2.0
9	**2**	3200	7/1/0.5	6.8	2720	57	2	155	88	2.3
10	**2**	4800	8/1/0.5	7.3	3485	56	2	155	82	2.3
11	**2**	4000	8/1/1	15.6	3343	57	4	150	47	2.7

[a] Polymerization conditions: [catalyst] = 10−30 μM; ethylene pressure = 5.0 bar; temperature = 70 °C ; time = 10−15 min; volume = 0.3 L. [b] Feed molar ratio. [c] Activity in kg polymer mol^{-1} h^{-1} p^{-1}. [d] Norbornene and 1-octene mole percent in terpolymer determined by ^{13}C NMR. [e] Determined by DSC. [f] Determined by SEC in *o*-dichlorobenzene by using standard polystyrene calibration.

Table 2. Ethylene/Norbornene/Vinylcyclohexane Terpolymers Using [Zr(η^5:η^5-$C_5H_4CPh_2C_{13}H_8$)Cl_2] (1) and [Zr{(η^5-2,5-$Me_2C_5H_2$)$_2$CHMe}Cl_2] (2)

entry[a]	catalyst	N/E/VCH[b]	p_E, bar	T, °C	yield, g	activity[c]	N,[d] mol %	VCH,[d] mol %	T_g,[e] °C	M_w[f] × 10^{-3}	M_w/M_n[f]
1	**1**	8/1/0	5	70	7.2	1920	46		124	784	2.0
2	**1**	12/1/0	5	70	6.0	1600	49		131	759	2.1
12	**1**	4/1/8	2.5	70	14.7	4697	34	3	74	52	2.2
13	**1**	8/1/8	2.5	80	6.6	2109	44	2	115	51	2.3
14	**1**	10/1/4	5	50	11.4	1824	45	1	117	163	2.4
15	**1**	12/1/4	3	70	3.1	1378	52	1	137	156	3.1
6	**2**	8/1/0	5	70	33.0	8800	54		148	160	2.1
7	**2**	12/1/0	5	70	7.6	2027	56		161	188	3.1
16	**2**	8/1/4	5	70	10.1	2693	51	2	145	33	1.9
17	**2**	8/1/8	5	70	26.5	7067	51	3	121	16	1.9
18	**2**	8/1/4	5	50	11.7	2340	51	3	120	30	1.9
19	**2**	12/1/4	5	50	7.9	1580	56	2	148	35	2.0
20	**2**	12/1/4	5	70	29.1	5169	53	1	147	29	1.9
21	**2**	12/1/4	3	70	20.0	8889	62	1	162	25	1.8

[a] Polymerization conditions: [Catalyst] = 10 − 17 μM; [Al]/[Zr] = 4000; time = 15 min; volume = 0.3 L. [b] Feed molar ratio. [c] Activity in kg polymer mol^{-1} h^{-1} p^{-1}. [d] Norbornene and vinylcyclohexane mole percent in terpolymer determined by ^{13}C NMR. [e] Determined by DSC. [f] Determined by SEC in *o*-dichlorobenzene by using standard polystyrene calibration.

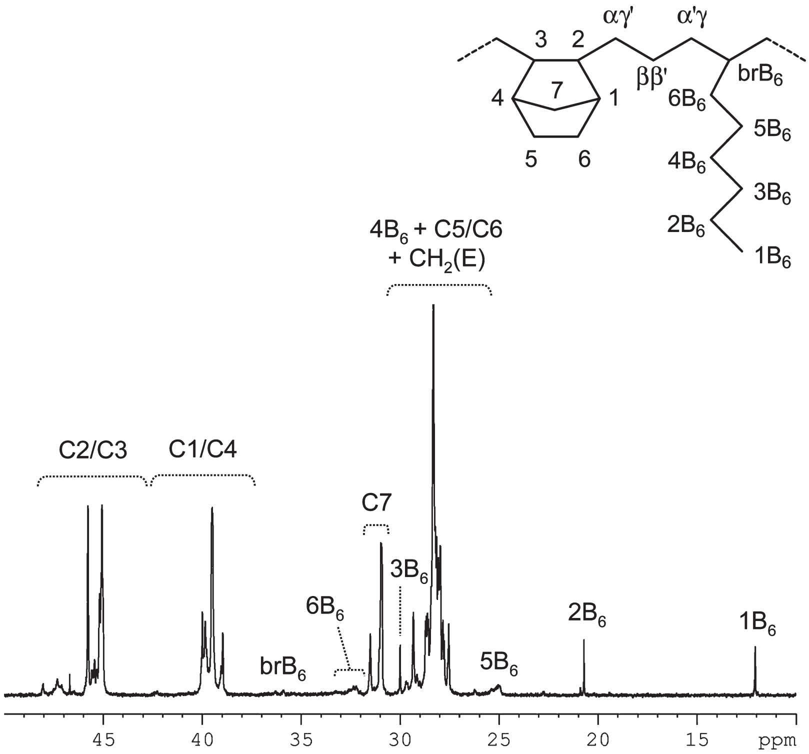


Figure 2. ^{13}C NMR spectra (108.58 MHz, $C_2D_2Cl_4$, 103 °C) of poly(E-*ter*-N-*ter*-O) sample prepared by **1** (Table 1, entry 3).

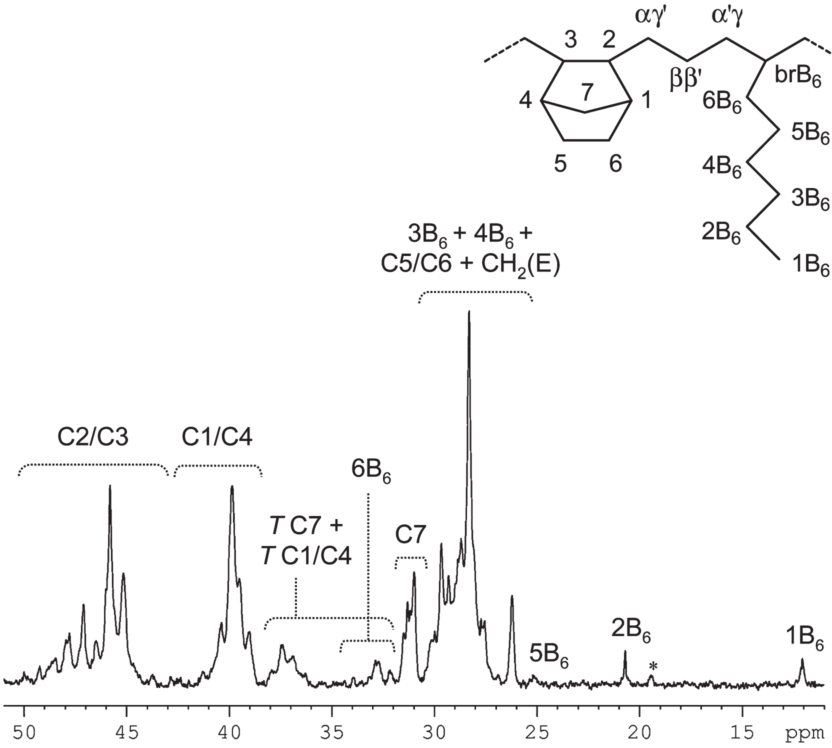


Figure 3. ^{13}C NMR spectra (108.58 MHz, $C_2D_2Cl_4$, 103 °C) of poly(E-*ter*-N-*ter*-O) sample prepared by **2** (Table 1, entry 8).

vary considerably with changing termonomer concentration. Lowering the reaction temperature from 70 to 50 °C led to a decrease in catalyst activity (Table 2, entries 20 vs 19).

Microstructure. Terpolymers were analyzed by ^{13}C NMR spectroscopy to evaluate the monomer content and eventually the terpolymer microstructure. In case of E−N copolymers, the assignment of stereosequences allows to determine the polymer microstructure, which is dominated by metallocene symmetry and ligand type. In general, *ansa*-metallocenes with C_s symmetry generate random copolymers containing short norbornene homosequences (diads and triads). Poly(E-*co*-N) prepared with C_s-symmetric catalyst **1** performed at a [N]/[E] molar feed ratio of 8 showed a N incorporation of 44 mol %. The analysis of various stereosequences resulted to contain both *racemic* and *meso NN* dyads in a nearly 1:1 ratio. The complete analysis of the spectra at tetrad level[11] revealed that catalyst **1** has a marked

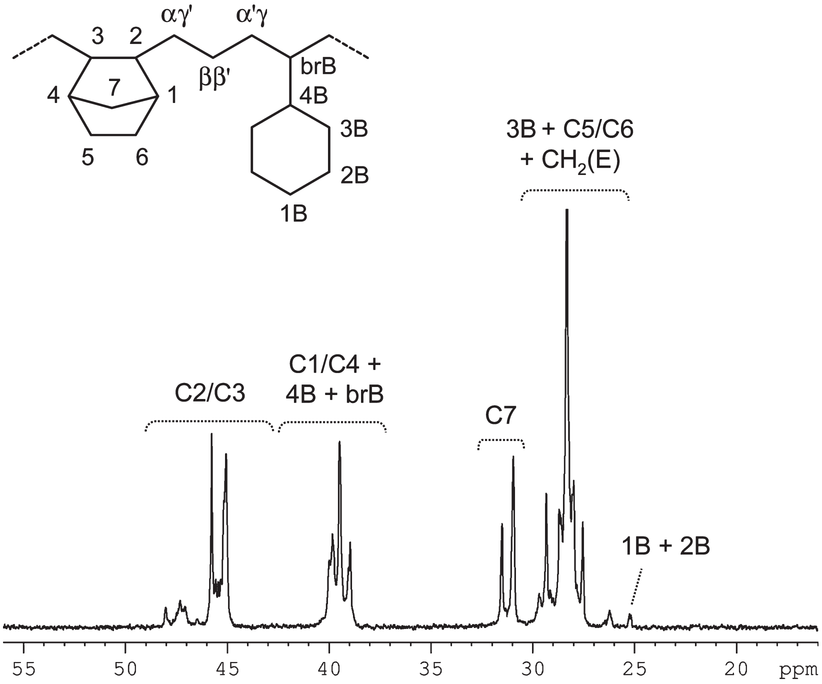


Figure 4. ^{13}C NMR spectra (108.58 MHz, $C_2D_2Cl_4$, 103 °C) of poly(E-*ter*-N-*ter*-VCH) sample prepared by **1** (Table 2, entry 14).

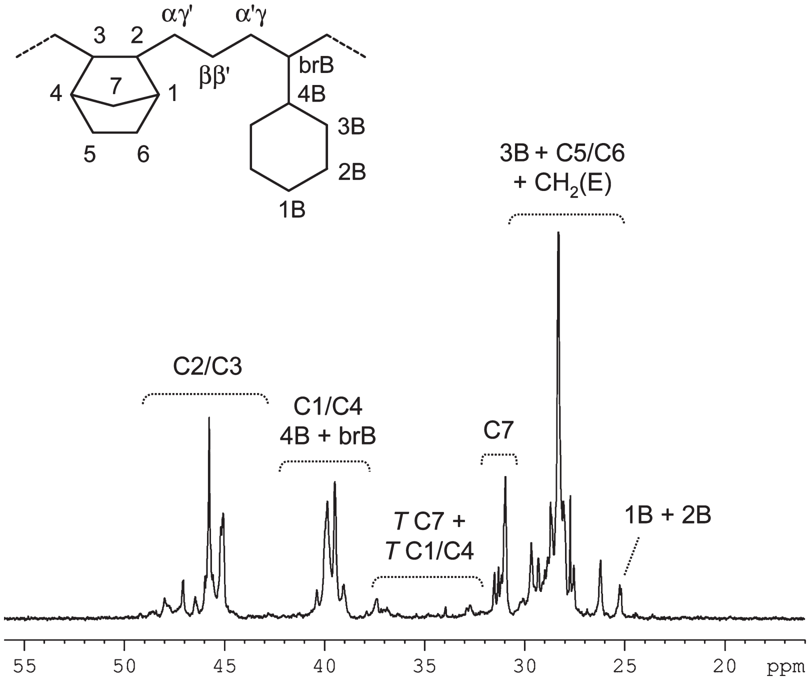


Figure 5. ^{13}C NMR spectra (108.58 MHz, $C_2D_2Cl_4$, 103 °C) of poly(E-*ter*-N-*ter*-VCH) sample prepared by **2** (Table 2, entry 18).

selectivity for producing E−N copolymers with high amount of *ENEE* (30 mol %) and *NEEE* (16 mol %) isolated norbornene units, and gave a low amount of stereosequences containing *NNEN* (5.2 mol %) and *NNNE* (3.8 mol %) tetrads.

On the other hand the C_1-symmetric precursor **2** produced poly(E-*co*-N) with greater norbornene incorporation compared to **1**, as a consequence of its comparatively lower steric hindrance at the active site.[10] Poly(E-*co*-N) prepared with similar feed ratio of [N]/[E] = 8 showed a N content of 54 mol %, demonstrating a higher selectivity for producing *meso NN* dyads (*meso*/*racemic* = 3.7). Conversely to **1**, the analysis of the E−N copolymer microstructure from catalyst **2** showed a lower amount of isolated norbornene units *ENEE* (15 mol %) and *NEEE* (8.1 mol %), and a significant amount of *NNEN* (16.2 mol %) and *NNNE* (6.5 mol %) short microblocks. It should be pointed out that terpolymers with high norbornene content gave rise to rather complicated spectra owing to an overlapping between E−N backbone resonances and signals attributed to 1-octene or to vinylcyclohexane. Secondary and tertiary carbons were identified with the help of DEPT 135 experiments.

The ^{13}C NMR spectra of poly(E-*ter*-N-*ter*-O) and poly(E-*ter*-N-*ter*-VCH) are depicted in Figures 2, 3 and 4, and 5, respectively. Figures 2 and 4 show the spectra of samples performed using catalyst **1**, while Figures 3 and 5 show those for samples prepared from **2**. A general structure for terpolymers,

Table 3. Assignment of ^{13}C NMR Chemical Shifts for Carbons of 1-Octene and Vicinal Ethylene Units in Poly(E-*ter*-N-*ter*-O)

assignment			ref 12
carbon	DEPT[a]	chemical shift[b]	chemical shift[c]
$1B_6$	p	11.9−12.1	12.0−12.2
$2B_6$	s	20.5−20.9	20.7−21.0
$\beta\beta'$	s	22.7	22.2−23.1
$5B_6$, $\beta'\delta$	s	24.9−25.4	24.7−25.5
$4B_6$	s		27.6−28.2
$3B_6$	s	30.0	30.0−30.2
$6B_6$, $\alpha'\delta$	s	32.1−32.6	32.4−32.7
$\alpha'\gamma$	s	33.1−33.4	32.8−33.7
brB_6	t	36.3	33.9−33.7

[a] DEPT experiment results: p = primary carbon atom, s = secondary carbon atom, and t = tertiary carbon atom. [b] Chemical shift referred to HMDS. [c] Chemical shift estimation relative to HMDS at 2.03 ppm.

along with the relative labeling of carbon atoms, is also included in the figures. The labeling of carbons in these structures are based on common nomenclature used in the literature.

Concerning 1-octene, the ^{13}C NMR spectrum of a sample containing 4 mol % of termonomer synthesized by catalyst **1** is shown in Figure 2. The peak assignments were based taking into account DEPT experiments and literature data on poly(E-*co*-O).[12,13] Chemical shift assignments for carbons of 1-octene and ethylene units next to O in the terpolymers are reported in Table 3, the assignment of E-O copolymers published earlier are also enclosed.[12] As apparent in Figure 2, signals appearing between 11.9 and 12.1 ppm were attributed to the methyl carbon $1B_6$. Peaks from 20.5 to 20.9 ppm were attributed to the $2B_6$ carbon. The signals in the 24.9−25.4 ppm region should be corresponding to the side chain methylene carbon $5B_6$ and secondary carbon atoms $\beta'\delta$. The signal of $4B_6$ carbon was located in the complex cluster of peaks between 27.5 and 29.7 ppm, within the same interval the E and C5/C6 resonances of N are also to be found. The peak at 30.0 ppm was identified as the side chain methylene carbon $3B_6$. The small signals appearing in the region from 32.1 to 33.4 ppm were attributed to the $6B_6$ carbon of the O units along with signals assigned to $\alpha'\gamma$, $\alpha'\beta$ and $\alpha'\delta$ carbons of the main chain. The peaks around 36.3 ppm, observed only in samples performed at lower [N]/[E] feed ratios, were assigned to the branching methine carbons brB_6. It is worth noting that terpolymers prepared with precatalyst **2** gave rise to terpolymers with more complex ^{13}C NMR spectra (Figure 3) owing to numerous overlapping peaks coming from the E−N backbone microstructure obtained with this catalyst. Thus, signals corresponding to the side chain methylene carbons of the O units were hardly detected.

The content of ethylene, norbornene, and 1-octene in terpolymers was quantitatively evaluated on the basis of integration values of signals diagnostic for each monomer unit: the methyl carbon atom $1B_6$ of 1-octene, which appears in a window of the spectra free from other signals, allowed to calculate the O content in terpolymers according to eq 2; the signals of C2/C3 carbons of norbornene units between 42.6 and 49.2 ppm allowed to estimate the N content (eq 1); the peak intensities of signals diagnostic for ethylene units, in the range from 30.6 to 24.3 ppm, accounted for the overlapping with 1-octene ($3B_6$, $4B_6$, and $5B_6$) and norbornene signals (C5/C6) and were calculated by means of eq 4.

As far as vinylcyclohexane is concerned, the ^{13}C NMR spectra of poly(E-*ter*-N-*ter*-VCH) performed using catalysts **1** and **2** are shown in Figures 3 and 4, respectively. Resonances were assigned by comparing signals of terpolymers with different VCH content to literature data of poly(E-*co*-VCH).[14] Resonances ascribed to VCH insertion were attributed to the distinctive cyclohexyl carbons 1B and 2B in the region from 24.9 to 25.2 ppm. The methylene carbon 3B and the branching methine carbons brB were located in the cluster of peaks in the ranges 27.5−29.7 and 38.9−40 ppm, respectively. The weak signals appearing between 41.6 and 42 ppm, observed only in samples synthesized at lower N/E feed ratios, were assigned to the cyclohexyl carbon atom 4B. The termonomer content was quantitatively evaluated on the basis of integration value of signals diagnostic for vinylcyclohexane units that are the cyclohexyl carbons 1B and 2B (eq 6), while the peak intensities of signals diagnostic for ethylene units, in the range from 34.3 to 26.2 ppm, accounted for the overlapping with vinylcyclohexane ($3B_6$) and norbornene signals (C5/C6) and were calculated by means of eq 8.

The 1-octene content in the terpolymers was found to be between 2 and 5 mol % (Table 1). As apparent in the table the 1-octene incorporation increases upon increasing [O] in the feed in case of catalyst **2**. Conversely, polymers from **1** showed the maximum O incorporation level of 4 mol % only at low [N]/[E] molar feed ratio of 4/1. By increasing the molar ratio of norbornene and ethylene in the feed in the composition range [N]/[E] between 8 and 12, O incorporation level seemed to reach a constant O value, around 2 mol %, suggesting that the [N]/[E] molar feed ratio is likely to affect the incorporation efficiency of 1-octene into the terpolymer.

In general, catalysts **1** and **2** behave similarly with respect to VCH incorporation. The insertion of VCH is much more difficult compared to ethylene and norbornene and varied slightly with an increase in the termonomer feed concentration. As observed for 1-octene, the incorporation of VCH is clearly dependent on the [N]/[E] molar feed ratio and the maximum value of 3 mol % was reached only at low [N]/[E] feed ratios (Table 2). Nevertheless, it is worth pointing out that 1-octene incorporation was preferred over that of vinylcyclohexane as a 4−8 times higher VCH concentration was needed to account for the same termonomer level. This fact indicates that the VCH incorporation was not so efficient as that of 1-octene, and the preparation of terpolymers with VCH content higher than 3 mol % is difficult with these catalysts even if the terpolymerizations are conducted at higher VCH/E molar ratios. Finally, comparing polymers prepared at different temperatures a slight increase in VCH incorporation was noticed at lower temperature.

As in the copolymerization, the N content in the terpolymers increases with increasing N molar ratio in feed. Terpolymers displayed tunable N content between 33 and 52 mol % from catalyst **1** (Table 2 entries 12 − 15) and between 44 and 62 mol % from catalyst **2** (Table 1 entry 8 − Table 2 entry 21). The N content in the terpolymers was not appreciably influenced by changing the amount of octene in the feed, while high concentration of VCH, required for third monomer incorporation similar to 1-octene, leads to a partial competition between VCH and N that makes in case of catalyst **2** the total amount of N incorporated in poly(E-*ter*-N-*ter*-VCH) lower (see Table 2 entries 6 vs 17 and 7 vs 20).

The presence of signals ascribed to branching methine carbons, in the case of poly(E-*ter*-N-*ter*-O), suggested the termonomer being statistically distributed along the polymer chain. Probably, VCH is also statistically distributed along the polymer chain. Finally, there is no evidence that the distribution of stereosequences is influenced by the presence of termonomer.

Molar Masses. A comparison of molar masses of terpolymers, determined by SEC, revealed that those from catalyst **1** are significantly higher than those obtained with catalyst **2**. The highly nucleophilic and sterically encumbered coordination of a cyclic olefin such as N mitigates chain transfer

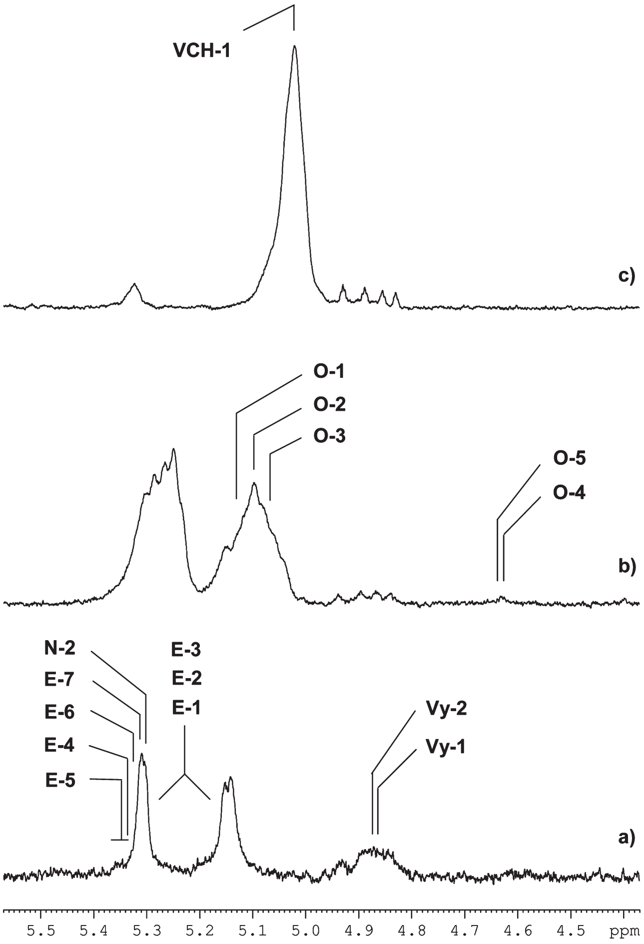


Figure 6. Expansions of the region between 4.4 and 5.6 ppm of ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by **1**: (a) poly(E-*co*-N) (Table 1, entry 2); (b) poly(E-*ter*-N-*ter*-O) (Table 1, entry 3); (c) poly(E-*ter*-N-*ter*-VCH) (Table 1, entry 14).

processes for stereoelectronic reasons, and thus often at high N feed concentrations molar masses are higher (see entry 7 vs 6). Terpolymers obtained by both **1** and **2** showed relatively low M_w values compared to those of E−N copolymers obtained under similar conditions. The dependence of molar masses on the termonomer feed concentration clearly shows O and VCH to behave as chain termination/transfer agents, that is they act as reagents which both terminate and facilitate reinitiating of a growing polymer chain. In case of 1-octene, the higher the concentration of termonomer, the lower the M_w values of the resulting terpolymers (e.g., Table 1 entries 6, 10, and 11) in agreement with the general observation that the introduction of α-olefins in copolymerization reaction leads to a decrease of molar masses.[14−16] Comparatively much higher VCH feed concentration was required for terpolymers with similar termonomer incorporation level and lower M_w values. Thus, probably O is easier to coordinate than VCH, but after coordination and/or insertion VCH causes easier chain termination. Finally, by lowering the reaction temperature higher M_w values could be observed, indicating the contribution of other chain termination reactions as those related to ethylene whose rates of reaction are different at different temperatures.

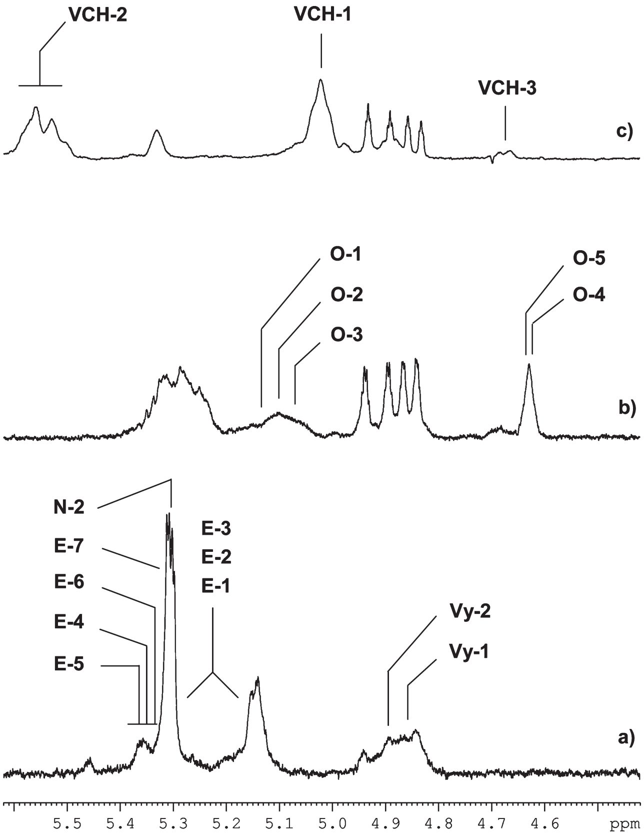
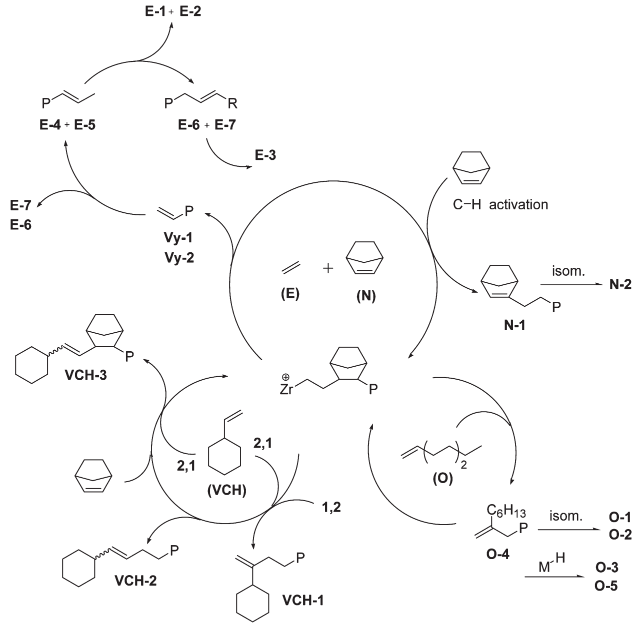


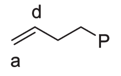
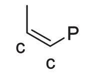
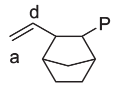
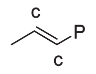
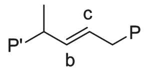
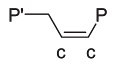
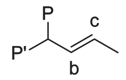
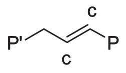
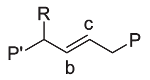
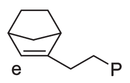
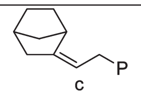
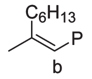
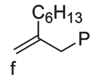
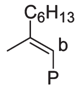
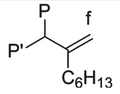
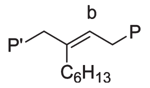
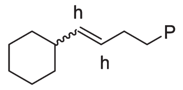
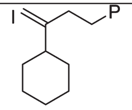
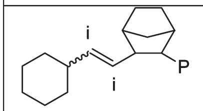
Figure 7. Expansions of the region between 4.4 and 5.6 ppm of ^{1}H NMR spectra (400 MHz, $C_2D_2Cl_4$, 103 °C) of polymers prepared by **2**: (a) poly(E-*co*-N) (Table 1, entry 6); (b) poly(E-*ter*-N-*ter*-O) (Table 1, entry 8); (c) poly(E-*ter*-N-*ter*-VCH) (Table 1, entry 18).

Scheme 1. Possible Paths Leading to the Terpolymer Chain Unsaturations in Table 1



Chain End Analysis. The chain end analysis of the terpolymers could be useful to provide direct evidence for the reactions responsible for chain growth termination. In a given catalytic system the possible chain transfer pathways are primarily indicated by the relative amount of typical unsaturated end group signals, originating from a first event of *β*-H transfer to the metal or to the monomer. Figures 6 and 7 show proton spectra expansions of the olefinic region of poly(E-*ter*-N-*ter*-O), poly(E-*ter*-N-*ter*-VCH), and those of E−N copolymers prepared under identical polymerization conditions produced with catalysts **1** and **2**, respectively.

Table 4. ^{1}H NMR Data Relative to the Various Chain Unsaturations in the Investigated Terpolymer Samples[a]

Structure	Notation	^{1}H NMR (ppm)	Structure	Notation	^{1}H NMR (ppm)
	**Vy-1**	a: 4.80 – 4.93 d: *5.72*		**E-4**	c: *5.28 – 5.32*
	**Vy-2**	a: 4.74 – 4.85 d: *5.69*		**E-5**	c: *5.29 – 5.33*
	**E-1**	b: *5.03* c: *5.22*		**E-6**	c: *5.26*
	**E-2**	b: *5.08* c: *5.24*		**E-7**	c: *5.30*
	**E-3**	b: *5.03* c: *5.22*			
	**N-1**	e: *5.50*		**N-2**	b: *5.30*
	**O-1**	b*: 5.03*		**O-4**	f: *4.60*
	**O-2**	b: *5.01*		**O-5**	f: *4.65*
	**O-3**	b: *5.00*			
	**VCH-1**	h: 4.99		**VCH-3**	l: 4.61 – 4.67
	**VCH-2**	i: 5.48 – 5.61			

[a] The chemical shifts in italics outline a slight difference between those observed in our terpolymers and those of poly(E-*co*-O)[17] and poly(E-*co*-N)[18] in the literature.

The spectra show the existence of various structural types of olefinic double bonds, associated with the presence of both terminal and internal unsaturations. The resonances of all these structural units, reported in Scheme 1 and Table 4, were attributed by comparison of spectra of terpolymers with different termonomer content with those of ethylene copolymers, those with N prepared with the same catalysts and those with VCH and O reported in the literature.[16,17] Scheme 1 describes the possible paths leading to terpolymer chain unsaturation with a last-inserted E, O, VCH, or N unit.

As apparent in Figure 6a three different multiplets were detected. The signal in the range between 4.8 and 4.93 ppm was characteristic of the vinyl chain end structure **Vy-1** and **Vy-2**, formed by chain termination via β-H elimination after ethylene insertion. The multiplets centered at 5.14 and 5.31 ppm may arise from the contribution of several concurrent pathways of chain isomerization and allylic chain activation after ethylene insertion, leading to the formation of internal unsaturations depicted in Scheme 1 and well described in ref 17. The peak at 5.3 ppm includes unsaturated norbornenyl chain start **N-2**, originated by C−H bond activation of a norbornene unit and further isomerization.[18] The ^{1}H NMR spectrum of poly(E-*ter*-N-*ter*-O) (Figure 6b) includes structures arising from last-inserted 1-octene units. Chemical shifts of the olefinic region were found to be quite similar to those of E−O copolymers reported in literature.[17] Signals are quite broad probably for the influence of adjacent N units in sequences with different N content or stereo environment. They are related to the β-H elimination after 1-octene insertion, followed by further isomerization of the terminal olefin. The signal at 4.7 ppm was attributed to vinylidene structures **O-5** and **O-4** (Scheme 1). The broad multiplet

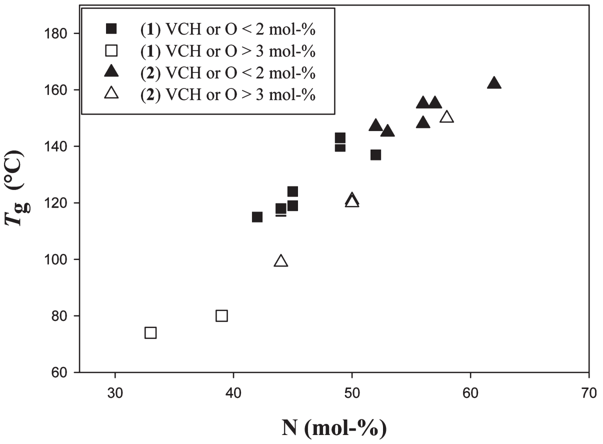


Figure 8. Plot of glass transition temperature (T_g) versus norbornene content in poly(E-*ter*-N-*ter*-O) and poly(E-*ter*-N-*ter*-VCH) terpolymers obtained with **1** and **2**.

centered at 5.09 ppm includes internal unsaturation **O-1**, **O-2**, and **O-3**, resulted from termination and isomerization of a chain with a last inserted 1-octene units. The spectra of poly(E-*ter*-N-*ter*-VCH) (Figure 6c) appear comparatively simpler compared to Figure 6a and Figure 6b. The assignment of the resonances in the olefinic region of the ^{1}H NMR spectra showed some ^{1}H NMR chain-end structures peculiar of last-inserted vinylcyclohexane units, similar to those of poly(E-*co*-VCH) found in literature.[16] The signal at 4.99 ppm was attributed to vinylene chain end structures **VCH-1**. Vinylene end groups result from chain termination via β-H elimination after 2,1-insertion of vinylcyclohexane.

The ^{1}H NMR spectra of polymers prepared by **2** depicted in Figure 7 differ from those of polymers prepared by **1** (Figure 6). In general a higher amount of vinyl chain end structures **Vy-1** and **Vy-2** was observed as a comparison to terpolymers prepared by **1**. Moreover, the spectra of poly(E-*ter*-N-*ter*-O) (Figure 7b) show a strong signal at 4.64 ppm ascribed to vinylidene structures **O-5** and **O-4** along with a broadening and a shift of the multiplets at 5.09 and 5.27 ppm as in the spectra of poly(E-*ter*-N-*ter*-O) prepared by **1** (Figure 6b). In the spectra of poly(E-*ter*-N-*ter*-VCH) (Figure 7c) some additional signals were visible. The small multiplet between 4.61 and 4.67 ppm is characteristic of the vinylidene chain end structure **VCH-3**, formed by chain termination via β-H elimination after 1,2-insertion of vinylcyclohexane. The multiplet between 5.48 and 5.61 ppm should be related to vinylene chain end structures **VCH-2** immediately adjacent to a norbornene unit, arising via β-H elimination after 2,1-insertion of vinylcyclohexane.

These results reflect the relative importance of the various chain transfer pathways that can occur with the two catalytic systems.

Thermal Analysis. DSC thermal analysis of terpolymers prepared with both catalysts **1** and **2** showed single well-defined glass transition temperatures (T_g) and no endothermic peak corresponding to the melting of any crystalline phase was observed. This observation implies a homogeneous terpolymer microstructure with completely amorphous morphology. Glass transition temperatures ranged from 74 °C for terpolymers with low N content to 162 °C for terpolymers with the highest N content.

In Figure 8 the T_g values of all the polymers prepared were plotted as a function of the norbornene incorporation level estimated by ^{13}C NMR spectra. T_g values of terpolymers from **2** in the various series were higher compared to those prepared with **1**, owing to the greater N incorporation capability of catalyst **2**. Glass transition temperatures were clearly a function of N content in the terpolymer and rapidly increase with increasing content of cyclic units as expected from previous results of poly(E-*co*-N).

It is interesting to note a variation of glass transition temperature values with the content of the third monomer, vinylcyclohexane or 1-octene, in the terpolymers. Comparing entry 7 with entries 10 or 19 all having 56 mol % of norbornene incorporated, entries 10 and 19 containing 2 mol % of O and VCH, respectively, a strong decrease of glass transition temperature from 6 to 13 °C was observed. The same trend of lowering of T_g values holds for all the terpolymers prepared having an amount of third monomer incorporated, 1-octene or vinylcyclohexane, equal or higher than 3 mol % and depicted in Figure 8 with non-filled symbols. It is clear that triangles, corresponding to terpolymers prepared with catalyst **2** are located more on the right side of the figure with respect to squares, that is terpolymers prepared with catalyst **1**. This reflects namely the highest N content of terpolymers prepared with **2**. This part of the curve seems to deviate from a straight line, which is connected with the influence of stereosequences on T_g values of copolymers with high N content.[19] Thus, the content of termonomer of 3 mol % seems to be enough to affect the thermal properties of polymers.

Conclusions

Investigation of E–N terpolymerization with the linear O or the alicyclic VCH α-olefin by two different *ansa*-metallocenes **1** and **2** provided insight on the factors that regulate the insertion or the chain termination of the two termonomers. Terpolymerization activities were still high even at the highest co- and termonomer feed ratios used with both catalytic systems. It is worth noting that the synthesis of VCH terpolymers were performed at higher termonomer concentration in order to reach similar termonomer contents. As far as molar masses are concerned terpolymers have lower molar masses than copolymers, and those obtained from **1** are higher than those obtained from **2**. This is related to the lower tendency of catalyst **1** to give β-H elimination at a last enchained E unit as revealed from the low amount of vinyl chain end groups observed in ^{1}H NMR spectra of terpolymers. In co- and terpolymers prepared by **2** there is a prevalence of signals of internal double bonds of the type E-4–E-7 over those E-1–E-3, that is of those not having an adjacent tertiary carbon. Probably, this is a consequence of chain terminations at a Mt-E-E and subsequent isomerization. Differences between the terminations with two catalysts appear also in chain end groups of terpolymers: in those from catalyst **1** are visible namely chain end groups arising from terminations after the termonomer, while in those from catalyst **2** are visible also the vinyl end groups present in the copolymers. The analysis of chain end groups in octene terpolymers do not allow to distinguish whether they occur after a 1,2 or 2,1 insertion. Conversely, in VCH terpolymerization it is evident that chain terminations occur easily after 2,1 insertions. In terpolymers from catalyst **1** only vinylene end groups, arising from 2,1 VCH insertions after one last inserted E unit, are present. This along with the lower activity reveals that VCH insertion is more difficult with this catalyst than with catalyst **2**. This is confirmed also from the proton spectra of these terpolymers, where are visible also vinylene end groups formed after 2,1 VCH insertion after a N last inserted unit. All data confirm that VCH has a lower insertion ability than O in terpolymerization with E and N. Higher chain termination ability of VCH is highly suggested.

Finally, it was found that termonomer contents greater than 3 mol % clearly affect T_g values. By using catalyst **2** it was possible to reach higher activities, higher N and termonomer contents, and higher T_g values, while catalyst **1** provided higher molar masses. In conclusion, we have shown that it is possible to obtain norbornene and α-olefin terpolymers with high T_g, high molar masses and in high yield by metallocene catalysts in conditions close to those industrially used. Molar masses and thermal characteristics can be tuned by selecting the proper metallocene and comonomer structure in order to reach materials with desired properties.

Experimental Section

Materials. All manipulations of air-sensitive compounds were performed under nitrogen using standard Schlenk-line and glovebox techniques. Ethylene and nitrogen were purified by passage through BTS-catalysts and molecular sieves. Toluene was fresh-distilled over Na prior to use. Norbornene (purchased from Aldrich) was distilled from Na and used as stock solution in toluene. 1-Octene (98%, Aldrich) was dried over CaH_2, distilled, and stored over molecular sieves. Vinylcyclohexane (98%, Aldrich) was distilled over Na and stored over molecular sieves. Methylaluminoxane (MAO, 10 wt % solution in toluene, Crompton) was dried before use (50 °C, 3 h, 0.1 mmHg) to remove solvent and unreacted trimethylaluminum (TMA). Complexes **1** and **2** were donated by TOPAS Advanced Polymers GmbH, Frankfurt, Germany. $C_2D_2Cl_4$ was purchased from Cambridge Isotope Laboratories, Inc. and used as received.

Analytical Measurements. NMR spectra were recorded on a Bruker NMR Advance 400 instrument (400 MHz, ^{1}H; 100.58 MHz, ^{13}C: pulse angle = 12.50 μs, acquisition time = 0.94 s, delay = 16 s). For NMR analysis about 100 mg of terpolymer sample was dissolved in $C_2D_2Cl_4$ in a 10 mm NMR tube and transferred to the spectrometer with the probehead preequilibrated at 103 °C. Chemical shifts for ^{1}H were referred to internal solvent resonances (5.86 ppm) and chemical shifts for ^{13}C were referred to hexamethyldisiloxane (HMDS). See Table 4 for ^{1}H NMR data.

On the basis of the peak intensity of carbons in the ^{13}C NMR spectra it was possible to estimate the content of norbornene, ethylene, and 1-octene or vinylcyclohexane in the terpolymers. The composition of poly(E-*ter*-N-*ter*-O) was calculated according to the following equations:

$$\mathrm{N\ (mol\ \%)} = \frac{[\mathrm{N}]}{[\mathrm{N}]+[\mathrm{E}]+[\mathrm{O}]}\times 100 = \frac{\bar{I}_{\mathrm{N}}}{\bar{I}_{\mathrm{N}}+\bar{I}_{\mathrm{E}}+\bar{I}_{\mathrm{O}}}\times 100 \quad (1)$$

$$\mathrm{O\ (mol\ \%)} = \frac{[\mathrm{O}]}{[\mathrm{N}]+[\mathrm{E}]+[\mathrm{O}]}\times 100 = \frac{\bar{I}_{\mathrm{O}}}{\bar{I}_{\mathrm{N}}+\bar{I}_{\mathrm{E}}+\bar{I}_{\mathrm{O}}}\times 100 \quad (2)$$

$$\bar{I}_{\mathrm{N}} = \frac{1}{2}I_{2/3} \quad (3)$$

$$\bar{I}_{\mathrm{E}} = \frac{1}{2}(I_{\mathrm{CH_2}} - 2\bar{I}_{\mathrm{N}} - 3\bar{I}_{\mathrm{O}}) \quad (4)$$

$$\bar{I}_{\mathrm{O}} = I_{1B6} \quad (5)$$

where $I_{2/3}$ is the peak intensity of the methyne carbons C2/C3 in the norbornene units, $I_{\mathrm{CH_2}}$ is the total area of peaks from 30.6 to 24.3 ppm, and $I_{1\mathrm{B}6}$ indicates the peak intensity of the methyl carbon $1\mathrm{B}_6$ in the 1-octene unit. The composition of poly(E-*ter*-N-*ter*-VCH) was calculated as follows:

$$\mathrm{VCH\ (mol\ \%)} = \frac{[\mathrm{VCH}]}{[\mathrm{N}]+[\mathrm{E}]+[\mathrm{VCH}]}\times 100 = \frac{\bar{I}_{\mathrm{VCH}}}{\bar{I}_{\mathrm{N}}+\bar{I}_{\mathrm{E}}+\bar{I}_{\mathrm{VCH}}}\times 100 \quad (6)$$

$$\bar{I}_{\mathrm{N}} = \frac{1}{2}I_{2/3} \quad (7)$$

$$\bar{I}_{\mathrm{E}} = \frac{1}{2}(I_{\mathrm{CH_2}} - 3\bar{I}_{\mathrm{N}} - 2\bar{I}_{\mathrm{VCH}}) \quad (8)$$

$$\bar{I}_{\mathrm{VCH}} = \frac{1}{3}(I_{1\mathrm{B}} + I_{2\mathrm{B}}) \quad (9)$$

where $I_{\mathrm{CH_2}}$ is the total area of peaks from 34.3 to 26.2 ppm while $I_{1\mathrm{B}}$ and $I_{2\mathrm{B}}$ indicate the peak intensity of cyclohexyl carbons 1B and 2B in the vinylcyclohexane unit, respectively.

Differential scanning calorimetry (DSC) measurements were carried out on a Perkin-Elmer Pyris 1 instrument. Terpolymers were analyzed in a temperature range from 50 to 200 °C using heating and cooling rates of 20 °C min^{-1}. T_g values were recorded during a second thermal cycle. Molar masses (M_w) and molar mass distribution (M_w/M_n) were determined by high temperature size exclusion chromatography (SEC) by a GPCV2000 high system from Waters. Measurements were carried out in *o*-dichlorobenzene at 145 °C, a polystyrene standard calibration was used.

Polymerization Procedure. Terpolymerization reactions were carried out in a 1-L Büchi BEP2000 laboratory autoclave with a type-I glass pressure vessel and heat jacket. Before starting the polymerization reaction the reactor was evacuated for 60 min at 80 °C and filled with nitrogen. After cooling down to reaction temperature, the reactor was filled with toluene, norbornene, MAO, and the appropriate amount of third monomer 1-octene or vinylcyclohexane. After thermal equilibration, the reactor system was saturated with ethylene to the desired pressure. The reaction was initiated by injection of the precatalyst dissolved in toluene. The ethylene pressure was kept constant during the polymerization reaction. The terpolymerization was quenched by addition of 2 mL of ethanol, and precipitated in acetone. The terpolymer products were left stirring overnight, filtered, and suspended again under stirring in acetone. At last, the polymer was collected by filtration and dried under vacuum at 70 °C to constant weight.

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