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Tuning the Properties of α,ω -Bis(trialkoxysilyl) Telechelic Copolyolefins from Ruthenium-Catalyzed Chain-Transfer Ring-Opening Metathesis Polymerization (ROMP)

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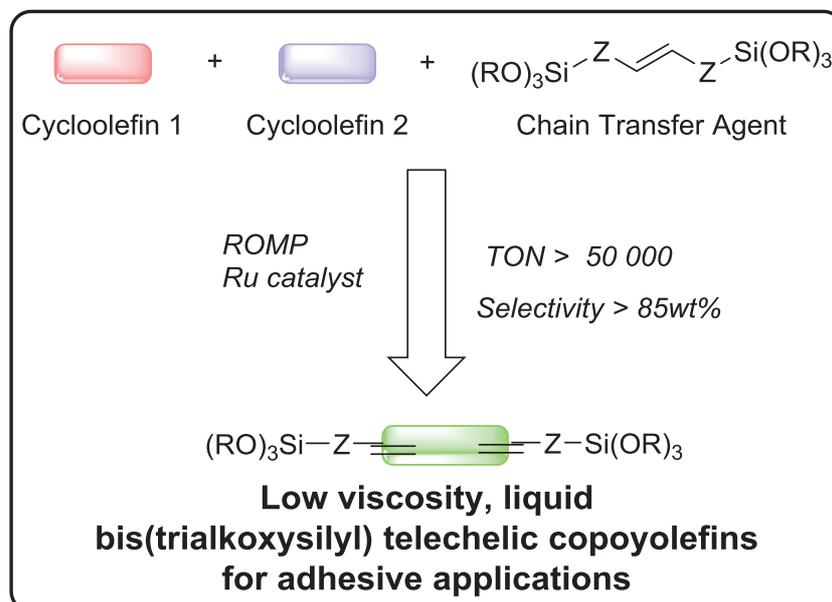
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Abstract

The synthesis of low viscosity liquid α,ω -bis(trialkoxysilyl) telechelic copolyolefins (DF) via ring-opening metathesis polymerization (ROMP)/cross metathesis (CM) is reported. Copolymerization of a norbornene-based olefin (NB-OLF = norbornene (NB), ethylidene norbornene (ENB), methyl 5-norbornene-2-carboxylate (NB^{COOMe}), methyl 5-oxanorbornene-2-carboxylate (oxaNB^{COOMe}), or dicyclopentadiene (DCPD)) with a monocycloolefin (mOLF = cyclooctene (COE), 1,5-cyclooctadiene (COD), or 1,5,9-cyclododecatriene (CDT)) was carried out at 40 °C (except for DCPD at 23 °C) in CH₂Cl₂ for 24 h, using Grubbs' 2nd generation catalyst (**G2**) and the bis(trialkoxysilyl)-functionalized symmetric acyclic alkene (RO)₃Si(CH₂)₃NHC(O)OCH₂CH=CHCH₂OC(O)NH(CH₂)₃Si(OR)₃ (R = Me or Et) as chain-transfer agent (CTA). The catalytic productivity (turnover numbers, TONs, up to 50 000 mol(comonomers).mol(Ru)⁻¹ and 1250 mol(CTA **1**).mol(Ru)⁻¹) and selectivity (> 85wt%; only minor amounts of cyclic non-functionalized copolymers (CNFs) formed) toward the formation of the corresponding DFs were quite high, as evidenced by fractionation experiments and detailed 1D and 2D ¹H and ¹³C NMR spectroscopy and SEC analyses. Thermal and rheological properties of the random copolymers, assessed by DSC and viscosimetric analyses, could be tuned according to the nature and the ratio of comonomers. At 23 °C, P(NB^{COOMe}-*co*-COE) and P(oxaNB^{COOMe}-*co*-COE) synthesized from a 50:50 ratio of comonomers displayed the lowest viscosity. Such silyl-modified polyolefins (SMPOs) are thus foreseeing possible industrial outcomes as one-component adhesives.

Graphical abstract



Introduction

Silyl-modified polymers (SMPs) are commonly used in adhesion of a wide variety of substrates (*e.g.* metal, plastics, glass...).^{1,2,3,4,5} Polycondensation of alkoxy-silyl-functionalized polymers under the action of moisture, arising from the surrounding medium and/or substrates, leads to siloxane-bonded (Si–O–Si) 3D-networks, which afford a cohesive adhesive joint insuring the resistance to the assembly.^{6,7,8,9,10,11,12,13} SMPs are especially valued for their fast curing process, weather resistance and excellent durability of adhesion with limited surface treatment. Also, in regards of current environmental and industrial concerns, SMPs are particularly attractive as water-based and solvent-free adhesives since curing shrinkage – typical of solvent-based adhesives – hardly occurs. One-component adhesives are also highly valuable/preferred because of their easy handling (no mixing of two components is required), making them better positioned on the market.^{14,15} Current academic and industrial efforts aim at elaborating SMPs without the use of isocyanates as precursors to one-component solvent-free adhesives.¹⁶

Over the past few years, we have been developing original strategies towards the synthesis of telechelic polymers as precursors to non-isocyanate PUs (NIPUs) using ring-opening metathesis polymerization (ROMP) of cyclic olefins.^{17,18} Among other routes towards telechelic polyolefins,^{19,20,21,22,23,24,25} ROMP conducted in presence of a difunctional symmetric acyclic alkene chain-transfer agent (CTA) allows α,ω -methacrylate, -epoxide, -carboxylate, -acetoxo, -amino, -carbonate, -hydroxy, -halide and pseudo-halide, or -trialkoxysilyl end-capping of polyolefins.^{26,27,28,29,30,31,32,33,34,35,36}

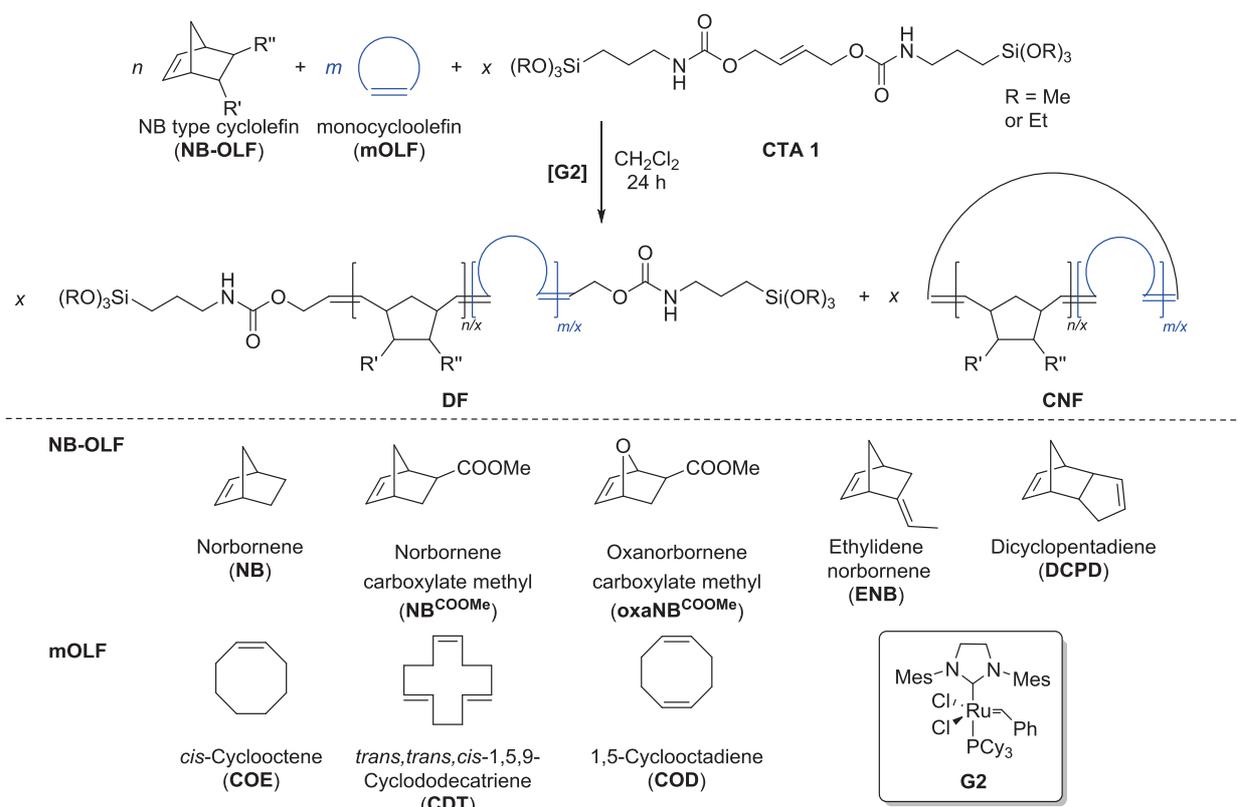
Silyl-modified polyolefins (SMPOs) enable adhesion to olefinic substrates, which is typically difficult due to their non-polar and non-porous surface. Various silyl-functionalized CTAs have enabled the synthesis of diverse SMPOs from metathesis^{37,38,39,40,41,42,43} or other polymerization processes.^{44,45,46,47,48,49,50,51,52} Recently, we have reported the successful ROMP/cross metathesis (CM) of cyclooctene (COE) or 3-alkyl-substituted COEs (3R-COE)

using various mono- or bis(trialkoxysilyl)-functionalized alkenes as CTAs and various Ru-carbene-alkylidene catalysts towards α,ω -bis(trialkoxysilyl)-functionalized poly(cyclooctene)s (PCOEs).^{53,54} Polyolefins synthesized by ROMP using a monocycloolefin (mOLF = COE, 1,5-cyclooctadiene (COD) or 1,5,9-cyclododecatriene (CDT)) are often solid at room temperature due to their high level of *trans* configuration, as favored by metathesis (see the ESI, Table S1, entries 1–3).^{13,55,56,57,58} Similarly, polynorbornene (PNB), poly(ethylidene norbornene) (PENB) and polydicyclopentadiene (PDCPD) synthesized by ROMP are completely amorphous solid materials at room temperature (see the ESI, Table S1, entries 4–6).^{59,60} Only poly(methyl 5-norbornene-2-carboxylate) (PNB^{COOMe}) and poly(methyl 5-oxanorbornene-2-carboxylate) (PoxaNB^{COOMe}) are liquid materials at room temperature, thanks to the pending ester groups ($T_g = -12$ °C and -2 °C, respectively; see the ESI, Table S1, entries 7 and 8). However, the high cost of methyl 5-norbornene-2-carboxylate (NB^{COOMe}) and methyl 5-oxanorbornene-2-carboxylate (oxaNB^{COOMe}), compared to that of COE, CDT, norbornene (NB) or dicyclopentadiene (DCPD), precludes their industrial application.

One requirement of adhesive polymer precursors is to be low viscosity liquids at ambient temperature to ensure effective formulation of adhesives and to maximize contact area and attractive forces between the adhesive and the bonding surfaces.⁶¹ We thus speculated that copolymerizing a NB-based monomer (NB-OLF) with a mOLF would result in low viscosity liquid materials at room temperature, provided the comonomers are suitably chosen. NB-OLF units may induce bending of the *trans*-enriched polyene chain, preventing macromolecules from aligning into crystalline regions, thus resulting in larger amorphous regions and in tuning the T_g of P(NB-OLF-*co*-mOLF) well below room temperature.

While ROMP is well-known for the synthesis of copolymers using Ru-based catalysts,^{selected references:62,63,64,65,66,67,68,69} reports on thermal and rheological properties of these copolymers remain rare.^{70,71,72,73,74} We herein report the first synthesis, thermal and rheological characterizations of α,ω -bis(trialkoxysilyl) telechelic low viscosity liquid copolyolefins

prepared by ROMP/CM using Grubbs 2nd generation (**G2**) catalyst in presence of a bis(trialkoxysilyl)-functionalized alkene CTA, (MeO)₃Si(CH₂)₃NHC(O)OCH₂CH=CHCH₂OC(O)NH(CH₂)₃Si(OMe)₃ (**1**) (Scheme 1). Different couples of comonomers were investigated to first optimize the catalytic productivity and selectivity toward α,ω -bis(trialkoxysilyl)-functionalized copolyolefins. The thermal and rheological properties of the copolyolefins were then investigated.



Scheme 1. Synthesis of copolyolefins by ROMP/CM of NB-OLF and mOLF using **G2**/CTA **1**.

Results and Discussion

Synthesis of bis(trialkoxysilyl) telechelic copolyolefins. The various NB-OLF/mOLF monomer couples (all monomers are commercially available except oxaNB^{COOMe})⁷⁵ were screened in ROMP/CM using CTA **1** (R = Me, Et) and Grubbs' 2nd generation catalyst (**G2**) in CH₂Cl₂. All copolymerizations were carried out at 40 °C, except those involving DCPD which were performed at 23 °C to avoid PDCPD crosslinking (and thus formation of a rigid/i.e. non

liquid (undesirable) PDCPD segment) typically favored at higher temperature (40 °C; see the ESI, Scheme S1).^{76,77,78,79} All reactions were at least duplicated and showed a quite good reproducibility of the conversion and molecular data ($\pm 10\%$). Representative results are summarized in Table 1 (see the ESI, Table S2).

Table 1. Copolymerization of NB-OLF and mOLF catalyzed by **G2** using CTA **1** in CH₂Cl₂ during 24 h.*

Entry	Reaction		[NB-OLF] ₀ /	[CTA 1] ₀	NB-OLF	mOLF	DF	CNF	$M_{n,theo}^c$	$M_{n,NMR}^d$	$M_{n,SEC}^e$	\mathcal{D}_M^e	$M_{n,SEC}^e$	\mathcal{D}_M^e	
	Temp. (°C)	NB-OLF/mOLF	[mOLF] ₀ (equiv vs. G2)	CTA 1-R (equiv vs G2)	Conv. ^a (mol%)	Conv. ^a (mol%)	Sel. ^b (wt%)	Sel. ^b (wt%)	M_n (g.mol ⁻¹) (DF , CNF)				M_n (g.mol ⁻¹) (CNF)		
1	40	NB/COE	1000:1000	OEt	50	100	100	98	2	4100	4100	11 300	1.4	14 000	1.4
2	40	NB/COE	25 000:25 000	OEt	1250	100	100	85	15	4100	4700	21 030	1.6	21 600	1.6
3	40	NB/CDT	25 000:25 000	OEt	1250	100	100	95	5	5100	6000	16 400	1.6	24 200	1.4
4	40	ENB/CDT	1000:1000	OEt	50	100	100	92	8	5600	5000	7300	2.0	11 000	1.9
5	40	ENB/CDT	25 000:25 000	OEt	425	100	100	79	21	16 600	17 100	25 000	1.7	30 000	1.6
6	40	NB ^{COOMe} /COE	1000:1000	OMe	100	100	100	98	2	2600	2700	8800	1.6	10 600	1.5
7	40	NB ^{COOMe} /COE	25 000:25 000	OMe	1250	100	100	98	2	5200	4900	28 100	1.6	43 000	1.4
8	40	oxaNb ^{COOMe} /COE	1 000:1 000	OMe	50	100	100	97	3	3100	3500	3300	1.6	11 900	1.4
9	40	oxaNb ^{COOMe} /COE	25 000:25 000	OMe	1250	100	100	90	10	2900	3700	30 000	1.5	48 000	1.4
10	23	DCPD/COE	1000:1000	OMe	100	100	100	95	5	2400	3100	16 700	1.6	19 000	1.4
11	23	DCPD/COE	25 000:25 000	OMe	1250	96	82	85	15	4300	4900	31 300	1.6	31 500	1.6
12	23	DCPD/CDT	1000:1000	OEt	100	100	100	95	5	2900	4600	7300	1.6	17 900	1.4
13	23	DCPD/CDT	25 000:25 000	OEt	1250	95	75	87	13	3700	4200	31 000	1.9	35 000	1.5
14	23	DCPD/COD	1000:1000	OEt	100	100	100	91	9	2700	3100	14 500	1.9	24 000	1.5
15	23	DCPD/COD	25 000:25 000	OEt	1250	93	85	86	14	4900	5100	35 000	1.8	41 400	1.6

* NB, COE, CDT, DCPD and COD were distilled over CaH₂ prior to use; NB^{COOMe} and ENB were used as received; Reaction time was not optimized. ^a Monomer and CTA conversions as determined by ¹H NMR analysis (refer to the Experimental Section). Full conversion of CTA was observed for all reactions. ^b Weight % of **DF** = difunctionalized copolymer and **CNF** = cyclic nonfunctionalized copolymer determined after weighting the **CNF** recovered following elution of the crude sample through a silica column (refer to the Experimental Section) (Scheme 1). ^c Theoretical molar mass value calculated from $M_{n,theo} = M_{monomer} \times (\text{Conv.monomer} \times$

[monomer]₀) / (Conv.CTA × [CTA]₀), on the basis of the sole formation of functionalized copolymers, i.e. without taking into account any CNF. ^d Experimental molar mass value of the copolymer (**DF** and **CNF**) determined by ¹H NMR analysis (refer to the Experimental Section). ^e Number-average molar mass ($M_{n,SEC}$) and dispersity ($D_M = M_w/M_n$) values determined by SEC vs polystyrene standards (uncorrected M_n values) in THF at 30 °C.

No significant difference between the methoxy- or ethoxy-silyl derivatives of CTA **1** was observed throughout the experiments. For NB/COE, NB/CDT, ENB/CDT, NB^{COOMe}/COE and oxanB^{COOMe}/COE copolymerizations performed at 40 °C, a high productivity of **G2** catalyst with remarkable TONs of ROMP up to 50 000 and TONs of CM up to 1250 was reached with larger loading of comonomers and CTA **1** (Table 1, entries 1–9). Copolymerization of DCPD with COE, CDT or COD carried out at 23 °C (Table 1, entries 10–15) gave copolymers fully soluble in CH₂Cl₂, consistent with the absence of PDCPD cross-linking (see the ESI, Scheme S1). As expected, TONs recorded from DCPD copolymerizations performed at 23 °C were, regardless of the comonomers couple, generally lower than those of other monomers' copolymerization performed at 40 °C, because of the lower reaction temperature which altered the catalytic productivity. As reported for the ROMP of COE using bis(trialkoxysilyl) difunctionalized olefin CTAs,⁵⁴ the desired difunctional random copolymers (**DFs**) were recovered as the major product (typically 85–98wt%), along with only minor (typically < 15wt%) cyclic nonfunctional copolymers (**CNFs**) side products (Scheme 1). Larger **CNF** contents were recorded for higher reagent loadings, in line with a then greater deactivation of the catalyst promoted by larger amounts of trace impurities^{54,lxxx} (Table 1, entries 1 vs 2; 4 vs 5; 8 vs 9; 10 vs 11, 12 vs 13, and 14 vs 15). The selectivity of the **G2**/CTA **1** catalytic system towards the formation of essentially **DF** copolyolefins was thus generally the same, regardless of the comonomers' nature. Note that the random nature of the copolymers is inherent to the ROMP/CM/RCM process and to the simultaneous introduction of both comonomers, and it is evidenced by the matching of the glass transition temperature values calculated from the Flory-Fox equation and measured by DSC analyses (Table 2, Fig. 5, vide infra).

The molar mass values determined by ¹H NMR analyses ($M_{n,NMR}$) for all copolymers remained in fair agreement with the calculated ones determined from the consumption of the monomers and CTA ($M_{n,theo}$), thus highlighting the fair control of the polymerization; this is in

line with our previous observations in the ROMP/CM of COE promoted by **G2/CTA 1-OMe**.⁵⁴ The dispersities were all monomodal and moderately narrow ($D_M = 1.4\text{--}1.9$; see the ESI, Fig. S1).^{28,34,68-73} The molar mass values measured by SEC analyses ($M_{n,SEC}$ values) were always higher than the corresponding $M_{n,NMR}$ and $M_{n,theo}$ data. This may result from the difference between the copolymers' hydrodynamic radius and that of polystyrene standards used for calibration, and/or from the possible adsorption of the copolymers on the SEC column's support which may differ from one set of chemically different comonomers to another and from one molar mass of the copolymer to another; yet, this difference increased with loadings of comonomers up to 100 000. **Erreur ! Signet non défini.**^{lxxxi} The molar mass values of CNFs measured by SEC were often higher than those of the crude copolymers (**DF** and **CNF**), suggesting higher molar mass of CNFs vs that of **DFs**.^{lxxxi}

Structural characterization of the copolyolefins. All crude copolyolefins and their corresponding isolated **CNF** copolymers were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR and FTIR spectroscopies, showing the expected chemical structure and, most importantly, their chain-end functional groups (see the ESI, Fig. S2–S30). A representative ^1H NMR spectrum of a P(NB-*co*-COE) random copolymer prepared from CTA **1-OEt** at $[\text{NB}]_0/[\text{COE}]_0/[\mathbf{1}]_0/[\mathbf{G2}]_0 = 1000:1000:50:1$ (Table 1, entry 1) is illustrated in Fig. 1. Besides the main chain signals ($\text{H}^{10}\text{--}\text{H}^{17}$; note that NB and COE repeating units' signals are undistinguishable in **DF** and **CNF**), typical resonances of the triethoxysilyl propyl urethane end-groups of P(NB-*co*-COE) **DF** ($\text{H}^1\text{--}\text{H}^9$) are clearly observed. The corresponding $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum confirmed the presence of this functional group on each copolyolefin chain-end (Fig. 2). Also, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of isolated P(NB-*co*-COE) **CNF** only displayed, as expected, the signals for the main chain moieties and no signals for any terminal end-capping group (see the ESI, Fig. S31–S32).

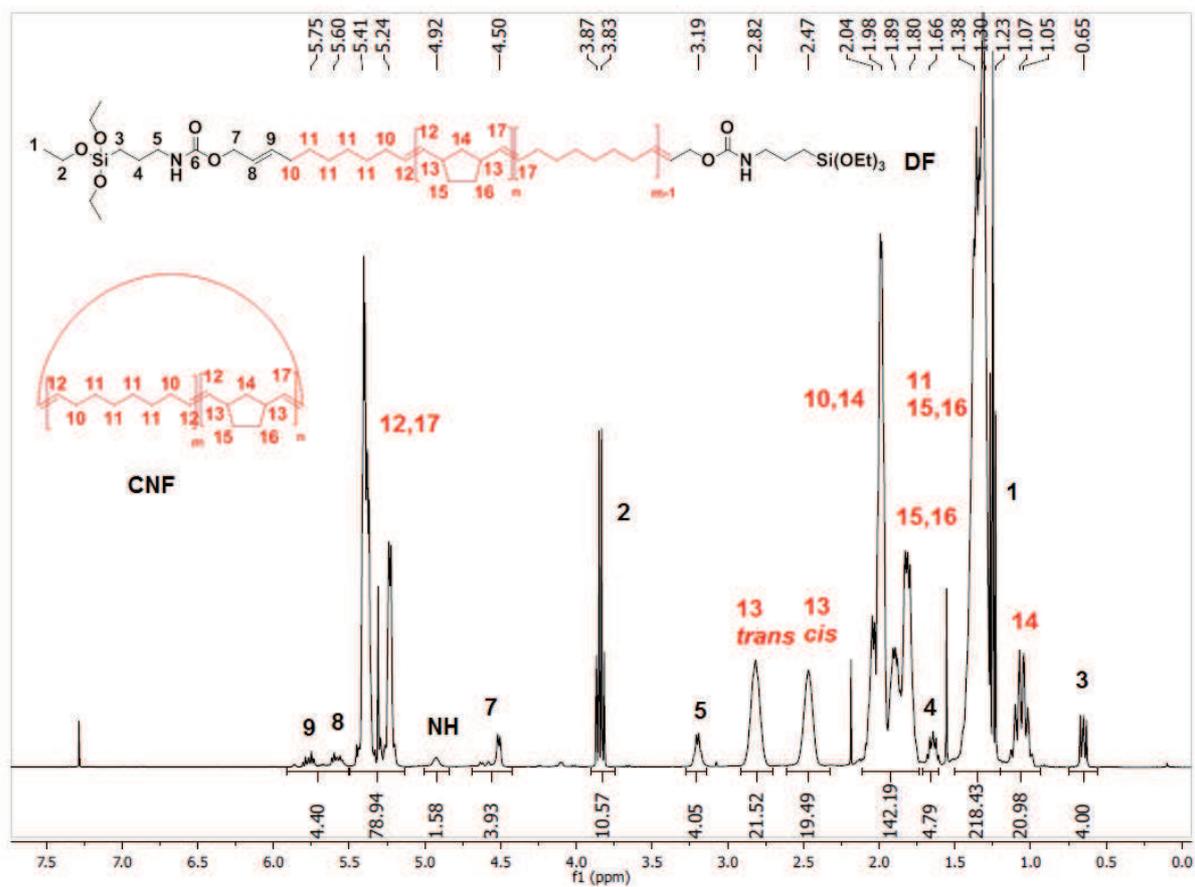


Fig. 1. ¹H NMR spectrum (400 MHz, CDCl₃, 23 °C) of a crude P(NB-co-COE) copolymer (Table 1, entry 1).

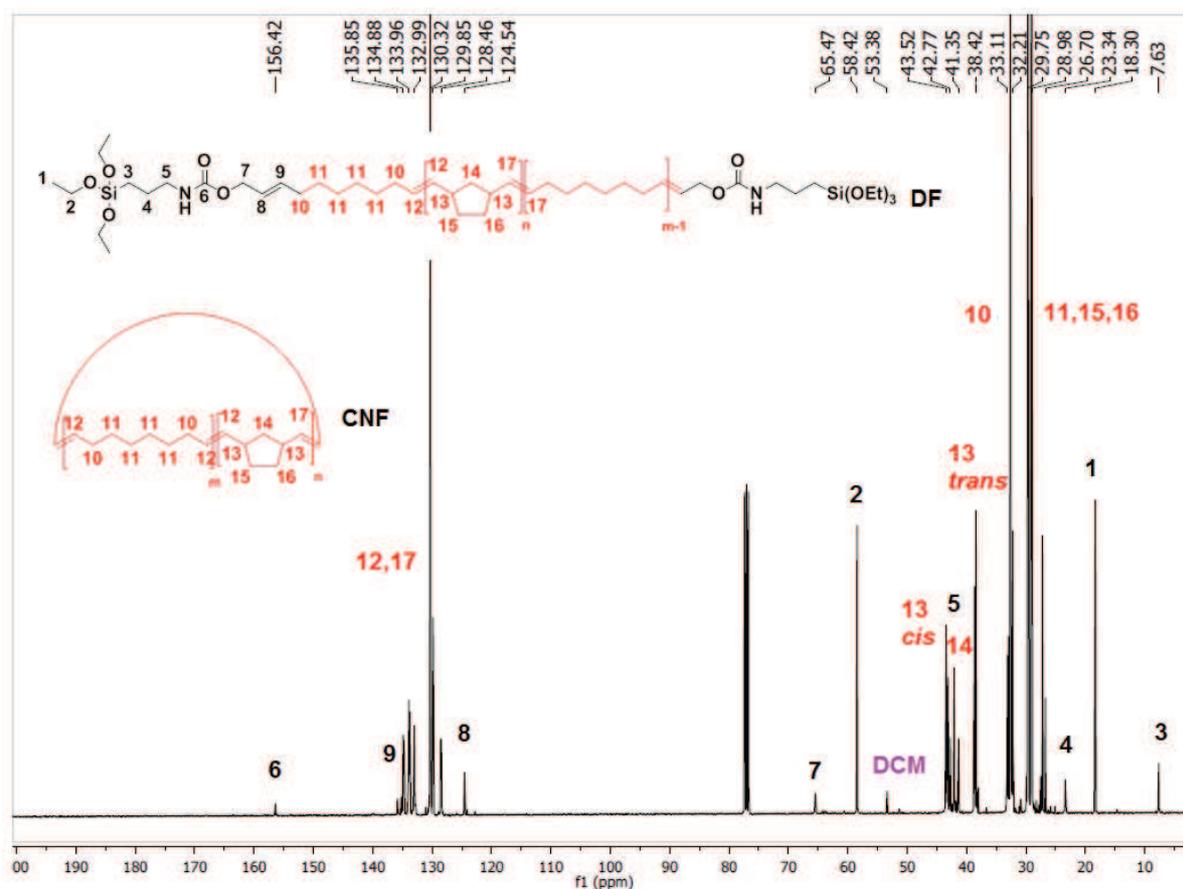


Fig. 2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100 MHz, CDCl_3 , 23 °C) of a crude P(NB-*co*-COE) copolymer (Table 1, entry 1).

Closer insight into the molecular structure of the copolymers was gained through HMBC (heteronuclear multiple bond correlation) NMR spectroscopy. This analysis enable unambiguously identification of the nature of the ultimate monomer unit bearing the trialkoxysilyl end-group. Considering a typical HMBC spectrum illustrated with a P(NB-*co*-COE) copolymer prepared from $[\text{NB}]_0/[\text{COE}]_0/[\mathbf{1-OEt}]_0/[\mathbf{G2}]_0 = 1000:1000:50:1$ (Fig. 3, see the ESI, S33), if COE was the monomer unit flanked by the end-capping group, the methine hydrogens H^8 and H^9 would display correlations with the COE methylene carbons C^{10} and C^{11} (negative signals on the distortionless enhancement by polarisation transfer (DEPT) spectrum). Alternatively, if NB was the monomer unit adjacent to the $-\text{CH}_2\text{OC}(\text{O})\text{NH}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ terminus, H^8 and H^9 would then exhibit correlations with the methine carbon C^{12} (positive

signal on the DEPT spectrum). The correlation signals observed between the methine hydrogens H⁸, H⁹ and C¹⁰, C¹¹ (CH₂ on COE units) and not with C¹² (CH on NB units) revealed that, using an equimolar mixture of NB and COE in the ROMP/CM with CTA **1-OEt**, COE is the only unit adjacent to the alkoxyethyl end-capping group of the macromolecular chain. This indicates that CM using CTA **1** is selective towards COE units. A similar affinity in the CM of CTA **1** towards COE and CDT, rather than NB, NB^{COOMe} or ENB units, was observed in the copolymerization of other sets of monomers, respectively (NB/CDT, ENB/CDT and NB^{COOMe}/COE; see the ESI, Fig. S37–S42). This selectivity in the CM towards COE and COD possibly arises from steric hindrance around the C=C double bonds of NB related units.

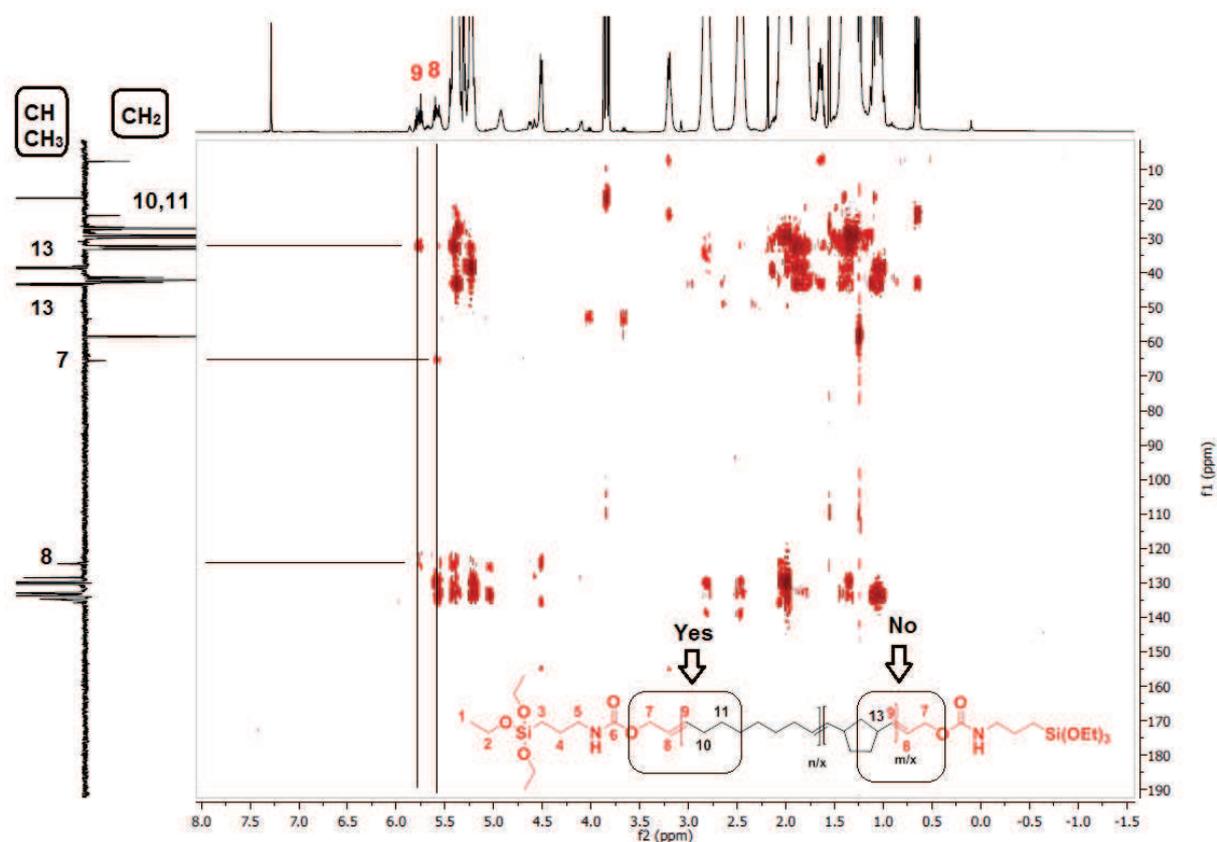


Fig. 3. ¹H-¹³C{¹H} HMBC (DEPT) NMR spectrum (400 MHz, CDCl₃, 23 °C) of a crude P(NB-*co*-COE) copolymer (Table 1, entry 1; see the ESI, Fig. S33 for complete assignment).

The reactivity of CTA **1** in the CM of oxaNB^{COOMe}/COE was different: the HMBC spectrum of P(oxaNB^{COOMe}-*co*-COE) ([oxaNB^{COOMe}]₀/[COE]₀/[**1**]₀/[**G2**]₀ = 1000:1000:50:1; Table 1, entry 8; Fig. 4) showed correlations of H⁷ and H⁸ not only with C⁹ and C¹⁰ (CH₂ of COE units) but also with C¹¹ and C¹² (CH on oxaNB units). Hence, the copolymerization of an equimolar mixture of oxaNB^{COOMe} and COE afforded a copolymer with both monomer units indifferently adjacent to the end-capping group of the macromolecular chain. The CM process using CTA **1** was thus, with this set of olefins, similarly efficient toward oxaNB units and COE units, and more efficient than with NB units. We assume that the oxygen in oxaNB units modulates the electronic density of C=C double bonds, thus increasing the efficiency of CM.^{lxxxii}

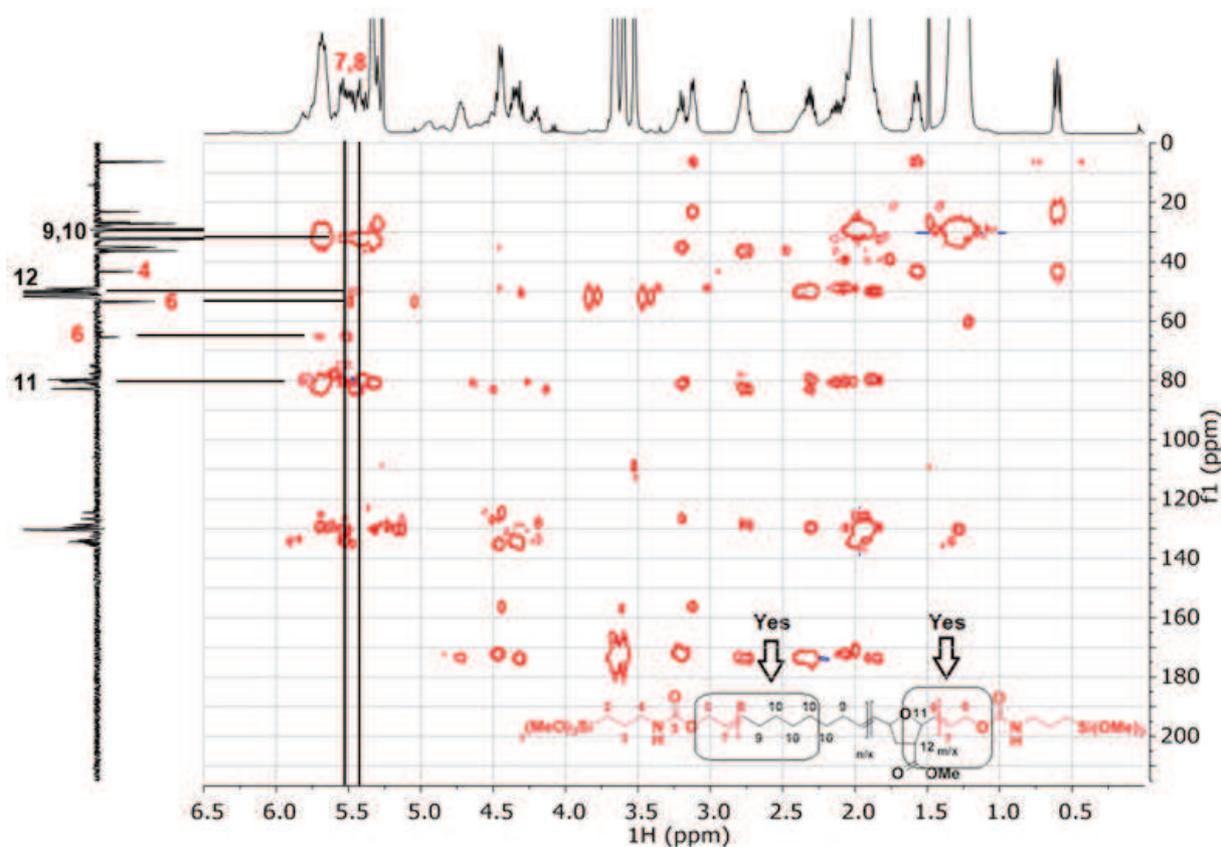


Fig. 4. ¹H-¹³C (DEPT) HMBC NMR spectrum (400 MHz, CDCl₃, 23 °C) of a crude P(oxaNB^{COOMe}-*co*-COE) copolymer (Table 1, entry 8; the spectrum with assignments of all signals is reported in Fig. S40).

FTIR analyses of the copolymers displayed the expected characteristic absorptions, in particular the Si–O–C (1103, 1078, 739 cm^{-1}), NH (3356 cm^{-1}), C=O (1726.3 cm^{-1}) and C–N (1500 cm^{-1}) bands (see the ESI, Fig. S4,S7,S10,S15,S20,S25,S28,S41).

Thermal properties of bis(trialkoxysilyl) telechelic copolyolefins. The NB-OLF/mOLF ratio was next varied from 10:90 to 90:10 for the different sets of comonomers so as to better evaluate the impact on the physical state and thermal properties of the resulting α,ω -bis(trialkoxysilyl) telechelic copolyolefins (Table 2).

Table 2. Apparent physical state and thermal transition temperatures of α,ω -bis(trialkoxysilyl) telechelic copolyolefins synthesized by ROMP/CM using CTA **1** and **G2** in CH_2Cl_2 for 24 h with $[\text{Comonomers}]_0/[\text{CTA}]_0/[\text{G2}]_0 = 2000:100:1$.^a

Entry	NB-OLF/mOLF	[NB-OLF] ₀ : [mOLF] ₀	$M_{n,\text{NMR}}^{\text{b}}$ ($\text{g}\cdot\text{mol}^{-1}$)	Apparent physical state at 23 °C	T_g^{c} exp (°C)	T_g^{d} Calc. (°C)	T_m^{c} (°C)	T_c^{c} (°C)
1	NB/COE	70:30	4400	Liquid	−14	−12	-	-
2	NB/COE	50:50	4100	Liquid	−50	−35	-	-
3	NB/COE	30:70	4100	Solid	<i>n.o.</i>	−54	43	24
4	NB/CDT	90:10	2300	Liquid	−37	-	-	-
5	NB/CDT	70:30	2500	Liquid	−76	-	-	-
6	NB/CDT	50:50	6000	Liquid	<i>n.o.</i>	-	19	−3
7	NB/CDT	30:70	2500	Viscous	<i>n.o.</i>	-	24	12
8	NB/CDT	10:90	2500	Viscous	<i>n.o.</i>	-	26	14
9	ENB/CDT	70:30	5500	Liquid	<i>n.o.</i>	-	10	−18
10	ENB/CDT	50:50	5000	Liquid	−56	-	11	−21
11	ENB/CDT	30:70	5900	Viscous	<i>n.o.</i>	-	25	2
12	NB ^{COOMe} /COE	90:10	2200	Liquid	−36	−21	-	-

13	NB ^{COOMe} /COE	70:30	2800	Liquid	-50	-36	-	-
14	NB ^{COOMe} /COE	50:50	2100	Liquid	-63	-50	-	-
15	NB ^{COOMe} /COE	30:70	2500	Viscous	-76	-62	23	5
16	NB ^{COOMe} /COE	10:90	2300	Solid	<i>n.o.</i>	-73	39	24
17	oxaNb ^{COOMe} /COE	90:10	3500	Liquid	-21	-12	-	-
18	oxaNb ^{COOMe} /COE	70:30	2300	Liquid	-37	-30	-	-
19	oxaNb ^{COOMe} /COE	50:50	3200	Liquid	-55	-46	-	-
20	oxaNb ^{COOMe} /COE	30:70	2700	Viscous	-75	-60	27	10
21	oxaNb ^{COOMe} /COE	10:90	2700	Solid	<i>n.o.</i>	-72	45	31
22	DCPD/COE	90:10	2000	Solid	104	109	-	-
23	DCPD/COE	70:30	1900	Solid	45	42	-	-
24	DCPD/COE	50:50	1600	Liquid	7	-5	-	-
25	DCPD/COE	30:70	2300	Viscous	-14	-40	37	-2
26	DCPD/COE	10:90	8200	Solid	<i>n.o.</i>	-67	53	39
27	DCPD/CDT	90:10	9600	Solid	47	-	-	-
28	DCPD/CDT	70:30	7100	Solid	31	-	-	-
29	DCPD/CDT	50:50	4800	Liquid	<i>n.o.</i>	-	14	-15
30	DCPD/CDT	30:70	5000	Liquid	<i>n.o.</i>	-	19	3
31	DCPD/CDT	10:90	4600	Viscous	<i>n.o.</i>	-	28	13
32	DCPD/COD	90:10	6900	Solid	50	-	-	-
33	DCPD/COD	70:30	6200	Viscous	28	-	-	-
34	DCPD/COD	50:50	4600	Liquid	-25	-	-	-
35	DCPD/COD	30:70	5600	Liquid	-42	-	-	-
36	DCPD/COD	10:90	3700	Viscous	<i>n.o.</i>	-	27	-7

^a ROMP in entries 1–21 were performed at 40 °C. ROMP using DCPD (entries 22–36) were performed at 25 °C ^b Full monomer and CTA conversions were observed by ¹H NMR analysis. Experimental molar mass value determined by ¹H NMR analysis (refer to the Experimental Section). ^c Glass transition, melting and crystallization temperatures as determined by DSC analyses according to the following cycles: -100 to +100 °C at 10 °C min⁻¹; +100 to -100 °C at 10 °C min⁻¹. *n.o.* = not observed. ^d Glass transition temperature values calculated using Flory-Fox equation.

The apparent physical state of the copolymers at room temperature changed from solid to liquid according to the ratio and the nature of the comonomers. Most often, copolymers prepared from [NB-OLF]₀/[mOLF]₀ ratios of 30:70, 50:50 and 70:30 were liquids at room temperature. Thermal analysis of the copolymers by DSC showed glass transition (T_g) and melting (T_m) temperatures in coherence with the apparent physical state of the copolymers at 23 °C (see the ESI, Fig. S42 for illustrative DSC traces). Generally, copolymers enriched in

mOLF featured some crystallinity, and the copolymers were usually amorphous below 50mol% of mOLF. The T_m values shifted to lower temperatures when the amount of NB-OLF increased. For instance, T_m of pure PCDT was observed at +32 °C (see the ESI, Table S1, entry 2), while it gradually decreased to a value ranging from +28 °C to +14°C upon copolymerization with NB or DCPD, and it eventually disappeared when more than 50mol% of NB or DCPD was used (Table 2, entries 4–8; 27–31). T_g values of random copolymers were recorded, as expected, between those of their corresponding homopolymers (see the ESI, Table S1), and systematically increased with larger amounts of NB-OLF. For instance, in the ROMP/CM of DCPD/COE, when the loading of DCPD increased from 30 to 90mol%, the T_g value of the copolymer increased from –14 °C to 104 °C (entries 22–26). For all copolymers, only one T_g was observed (when experimentally possible). The Flory–Fox equation which correlates the T_g value of homopolymers (see the ESI, Table S1) to that of their random copolymers ($1/T_g = w_1/T_{g1} + w_2/T_{g2}$, with T_g = glass transition temperature of the copolymer, w_1 and w_2 = weight fractions of the two comonomers, T_{g1} and $T_{g2} = T_g$ of each homopolymer of similar molar mass value)^{lxxxiii} enable the prediction of the T_g values of the P(NB-*co*-COE), P(NB^{COOMe}-*co*-COE), P(oxaNb^{COOMe}-*co*-COE) and P(DCPD-*co*-COE) copolymers (Table 2, Fig. 5). R^2 values > 0.9 indicated a linear relationship between experimental and calculated T_g values, thus highlighting their close match, and enabling to evaluate the T_g values which could not be determined experimentally (Fig. 5).

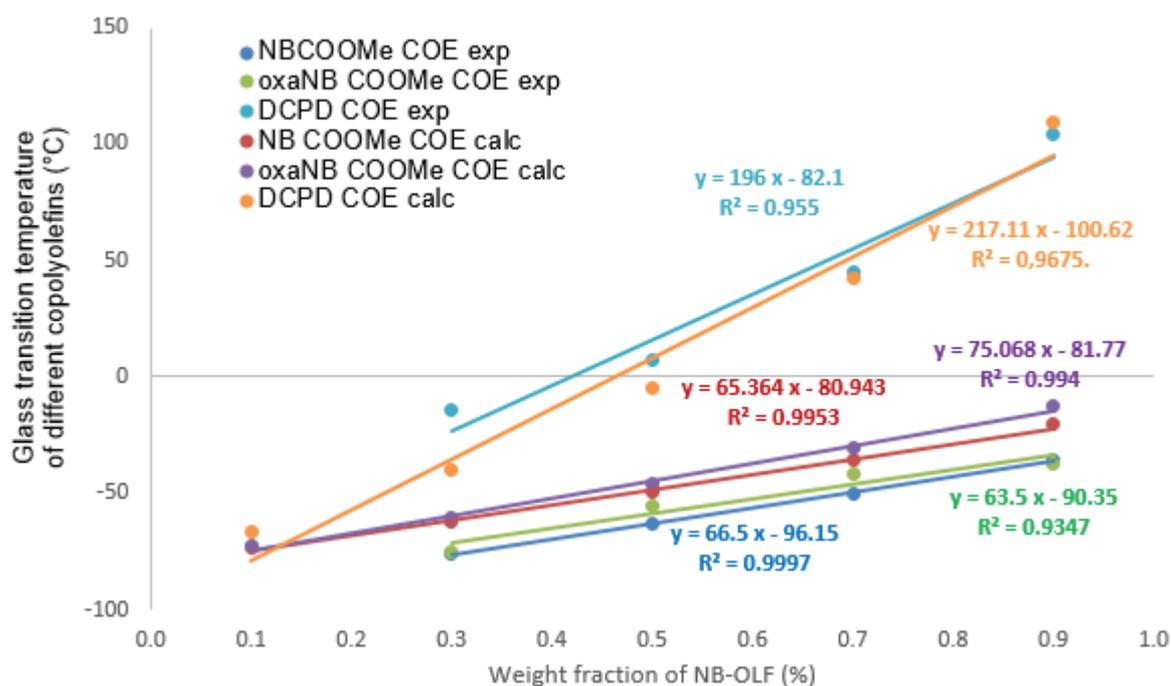


Fig.5. Comparison of experimental (DSC) and calculated (Flory-Fox) T_g values of P(NB^{COOMe}-*co*-COE), P(oxaNb^{COOMe}-*co*-COE) and P(DCPD-*co*-COE) copolymers as a function of NB-OLF weight fraction.

Rheological properties of bis(trialkoxysilyl) telechelic copolyolefins. Low viscosity liquid (at room temperature) copolymers were thus synthesized by adjusting the nature and the ratio of comonomers. Further insights into the rheological behavior of these copolymers were next gained through investigations of their viscous properties in simple shear flows. P(NB-*co*-COE) copolymers being visually more viscous at 23 °C than the other ones, viscosity measurements were performed at 55 °C, while other measurements were performed at 25 °C (Table 3).

For a given set of olefins, with the same molar mass and at the same temperature of analysis, copolymers made from equimolar mixtures of comonomers were always the most fluid (lowest viscosity value; Table 3, entries 2, 5, 8, 10). Among all copolymers synthesized at 23 °C from a 50:50 ratio of comonomers, P(NB^{COOMe}-*co*-COE) and P(oxaNb^{COOMe}-*co*-COE) exhibited the lowest viscosity, most likely as the result of the NB substituents (ester or cyclopentene) (see the ESI, Fig. S43–S46 for flow curves of all those liquid copolymers).

Table 3. Newtonian viscosity and rheological behavior of different α,ω -bis(trialkoxysilyl) telechelic copolyolefins synthesized by ROMP/CM using CTA **1** and **G2** in CH_2Cl_2 for 24 h. ^a

Entry	NB-OLF/mOLF	[NB-OLF] ₀ : [mOLF] ₀	$M_{n,\text{NMR}}^b$ (g.mol ⁻¹)	Temp. of analysis ^c (°C)	Newtonian viscosity ^c (Pa.s)	Rheological behavior ^c
1	NB/COE	70:30	2500	55	>400	Shear-thinning
2	NB/COE	50:50	2300	55	5	Newtonian
3	NB ^{COOMe} /COE	90:10	2200	25	28	Shear-thinning
4	NB ^{COOMe} /COE	70:30	2800	25	6.2	Newtonian
5	NB ^{COOMe} /COE	50:50	2100	25	2.4	Newtonian
6	NB ^{COOMe} /COE	30:70	2500	25	5	Newtonian
7	oxaNb ^{COOMe} /COE	70:30	3500	25	4.4	Newtonian
8	oxaNb ^{COOMe} /COE	50:50	3200	25	2.4	Newtonian
9	oxaNb ^{COOMe} /COE	30:70	2500	25	7.4	Newtonian
10	DCPD/COE	50:50	2700	25	4	Newtonian
11	DCPD/COE	30:70	2300	25	55	Shear-thinning
12	DCPD/COD	50:50	3000	25	> 30	Shear-thinning

^a ROMP in entries 1–9 was performed at 40 °C. ROMP of DCPD (entries 10–12) was performed at 25 °C; [Comonomers]₀/[CTA]₀/[**G2**]₀ = 2000:100:1. ^b Full monomer and CTA conversions were determined by ¹H NMR analysis. Experimental molar mass value determined by ¹H NMR analysis (refer to the Experimental Section). ^c Measured with a Contraves Low Shear 30 viscosimeter; uncertainty = ± 5%.

Conclusion

Copolymerization of a NB-based monomer (NB, NB^{COOMe}, oxaNB^{COOMe}, ENB or DCPD) with a monocycloolefin (COE, CDT or COD), using CTA **1-OMe**, **-OEt** in presence of **G2** catalyst, provides an effective access to low viscosity, liquid (at 23 °C) α,ω -bis(trialkoxysilyl) telechelic random copolyolefins (**DF**). The only side product, namely the cyclic nonfunctional copolyolefin (**CNF**), was always formed in minor amount (typically < 15wt%).

In the ROMP process, **G2** catalyst showed a remarkably high productivity with notable TONs up to 50 000 for NB/COE, NB/CDT, ENB/CDT, NB^{COOMe}/COE and oxaNB^{COOMe}/COE

at 40 °C, and up to 45 000 for DCPD/CDT and DCPD/COD at 23 °C. In the CM process using CTA **1**, a higher reactivity was observed towards COE, COD, CDT and oxaNB^{COOMe} rather than NB, NB^{COOMe} and ENB; we assume that this is most likely due to steric hindrance of the C=C double bond of NB units compared to that of COE or CDT units. The higher affinity towards oxaNB units rather than other NB-type monomers was noted, and possibly results from favorable electronic effects induced by the oxygen in NB units.

The thermal transition, physical state at room temperature and viscosity of the random copolymers could be tuned according to the nature and the ratio of olefins. In most cases, copolymers with 30–70mol% of NB-OLF were in a liquid state, while copolymers containing 50mol% of each comonomer exhibited the lowest viscosity at room temperature.

α,ω -Bis(trialkoxysilyl) end-capped liquid copolymers were thus successfully isolated. Such copolymers are thus valuable SMP prepolymers for adhesives application.^{lxxxiv}

Experimental Section

Materials. All catalytic experiments were performed under inert atmosphere (argon, < 3 ppm O₂) using standard Schlenk line and glove box techniques. Cyclooctene (COE), 1,5,9-cyclododecatriene (CDT), 1,5-cyclooctadiene (COD), norbornene (NB), dicyclopentadiene (DCPD) and CH₂Cl₂ (stabilized with amylene) were purchased from Sigma-Aldrich or ACROS, and dried and distilled over CaH₂ before use. Methyl 5-norbornene-2-carboxylate (NB^{COOMe}), ethylidene norbornene (ENB), and Grubbs' 2nd-generation catalyst (**G2**) were purchased from Sigma-Aldrich and used as received. Methyl 5-oxanorbornene-2-carboxylate (oxaNB^{COOMe}; see the ESI, Fig. S47–S48) was synthesized according to the reported literature procedure.⁷⁵ (MeO)₃Si(CH₂)₃NHC(O)OCH₂CH=CHCH₂OC(O)NH(CH₂)₃Si(OMe)₃ (CTA **1**) was synthesized as previously reported.⁵⁴

Instrumentation and measurements. ¹H (500, 400 MHz), ¹³C{¹H} (125, 100 MHz) HMBC, and DEPT NMR spectra were recorded on Bruker Avance AM 500 and AM 400 spectrometers

at 23 °C in CDCl₃. Chemical shifts (δ) are reported in ppm and were referenced internally relative to tetramethylsilane (δ 0 ppm) using the residual ¹H and ¹³C solvent resonances. A relaxation delay of 1 s and 1.5 s was used during the acquisition to afford “quantitative” ¹H and ¹³C{¹H} NMR spectra, respectively.

Monomer conversions were determined from ¹H NMR spectra of the crude polymer sample, from the integration (Int.) ratio $\text{Int.Polymer}/[\text{Int.Polymer} + \text{Int.monomer}]$, using the methine hydrogens ($-\text{CH}=\text{CH}-$; δ (ppm): 5.30 (PCOE), 5.66 (COE); 5.44 (PCDT), 5.09 (CDT), 5.54 (PCOD), 5.60 (COD), 5.31 (PNB), 6.04 (NB), 5.39 (PNB^{COOMe}), 6.22 (NB^{COOMe}), 5.30 (PoxaNb^{COOMe}), 6.28 (oxaNb^{COOMe}), 5.61 (PDCPD), and 6.00 (DCPD)).

Molar mass values of the polymers were determined by ¹H NMR analysis in CDCl₃ ($M_{n,\text{NMR}}$) from the integral ratio of the signals of end-groups' hydrogens (typically δ 0.65 (H³)) to internal olefin hydrogens (δ 5.41 (H¹² and H¹⁷)) (Figure 2).

Average molar mass ($M_{n,\text{SEC}}$) and dispersity ($D_M = M_w/M_n$) values were determined by size exclusion chromatography (SEC) in THF at 30 °C (flow rate = 1.0 mL.min⁻¹) on a Polymer Laboratories PL50 apparatus equipped with a refractive index detector and a set of two ResiPore Plgel 3 μm MIXED-E 300 \times 7.5 mm columns. Polymer samples were dissolved in THF (2 mg.mL⁻¹). All elution curves were calibrated with 12 monodisperse polystyrene standards (M_n range = 580–380 000 g.mol⁻¹). $M_{n,\text{SEC}}$ values of polymers were uncorrected for their possible difference in hydrodynamic volume vs. polystyrene. The SEC traces of the polymers all exhibited a monomodal and symmetrical peak (Figure S3).

FTIR spectra were recorded on an IR Affinity-1 SHIMADZU spectrometer equipped with a PIKE technologies GladiATR device for measurements.

Differential scanning calorimetry (DSC) analyses were performed on a Setaram DSC 131 apparatus calibrated with indium at a rate of 10 °C min⁻¹, under continuous flow of helium (25 mL.min⁻¹), using aluminum capsules (typically 10 mg of polymer). Thermograms were

recorded according to the following cycles: -100 to $+100$ °C at 10 °C min^{-1} ; $+100$ to -100 °C at 10 °C min^{-1} .

Apparent viscosity was measured with a Contraves Low Shear 30 viscosimeter, equipped with a Couette geometry, over a shear rate range from 0.23 s^{-1} to 9 s^{-1} . At each imposed shear rate, the apparent viscosity was determined in the steady state regime. Temperature was fixed at 25 ± 0.3 °C using a fluid bath. For each sample, the viscosimetric test duration lies between 45 and 90 min.

General ROMP Procedure. All polymerizations were performed according to the following typical procedure (Table 1, entry 1). The only differences lie in the nature of the monomers, CTA and initial monomer concentrations ($[\text{mOLF}]_0$, $[\text{NB-OLF}]_0$ and $[\text{CTA}]_0$). Under argon atmosphere, a Schlenk flask (20 mL) equipped with a magnetic stir bar, was charged sequentially with dry CH_2Cl_2 (5.0 mL), COE (0.76 mL, 0.65 g, 5.9 mmol), NB (0.55 g, 5.9 mmol), and CTA **1** (0.17 g, 0.29 mmol). The resulting solution was placed at 40 °C and the polymerization was started upon addition, *via* a cannula, of a dry, freshly prepared CH_2Cl_2 solution (2.0 mL) of **G2** (5.0 mg, 5.3 μmol). The reaction mixture turned highly viscous within 2 min. The viscosity then slowly decreased over the next 10 min. After the desired reaction time (not optimized, typically 24 h), volatiles were removed under vacuum. The copolymer was recovered without further purification, typically as a pale brown viscous liquid, readily soluble in chloroform and THF.

Separation of cyclic nonfunctionalized (CNF) copolymers from functionalized copolymers. CNF copolyolefins were separated from crude copolymers by column chromatography on silica gel 60 acidified with HCl (37%) until $\text{pH} < 2$, using CH_2Cl_2 as eluent. Functionalized copolymers (**DF**) thus remained grafted onto the acidified silica, while **CNF** copolymers were isolated from the eluted solution.

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