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Advances on the Synthesis of Silyl-Modified Polymers (SMPs)

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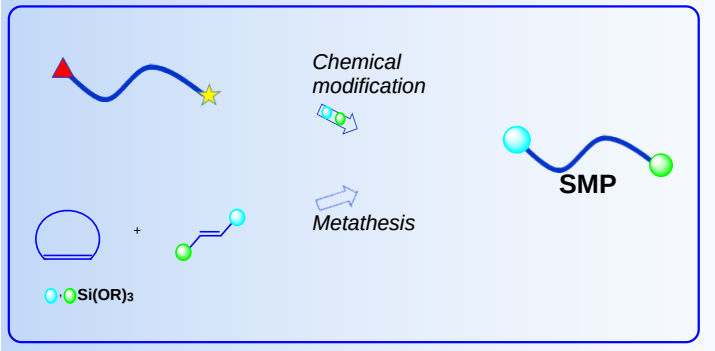
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Abstract

Silyl-modified polymers (SMPs) are alkoxysilyl functionalized polymers of high importance both academically and industrially. SMPs are being developed for coating, adhesive, sealant and elastomer applications. In this highlight, emphasis is placed first on the different chemical modification approaches available to tackle the synthesis of SMPs by in situ functionalization (ISF) and post-polymerization functionalization (PPF) routes, with their pros and cons being underlined. Recent progress and modern trends towards alkoxysilyl telechelic polyenes and polyolefins by olefin metathesis strategies is next discussed. The state of the art of alkoxysilyl functionalized polymers, especially of telechelic ones, delineated according to these latter two main synthetic pathways, is then covered along with their subsequent curing, and illustrated by selected examples including in particular polyenes, polyolefins and a some other selected relevant polymers.

TOC

Silyl-modified polymers (SMPs) are being synthesized from chemical modification and olefin metathesis strategies.



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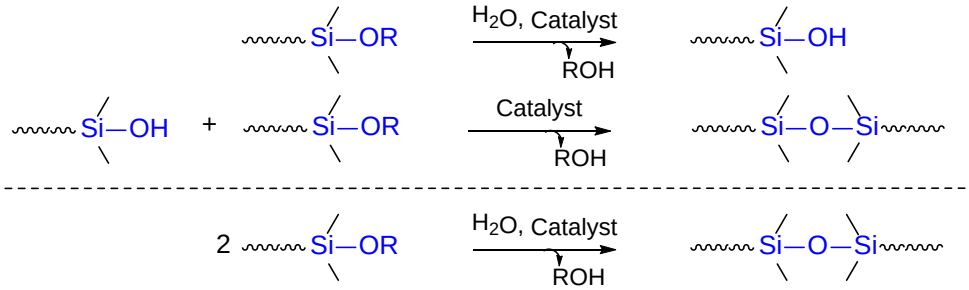
Introduction

Silyl-modified polymers (SMPs)

Silyl-modified polymers (SMPs), defined as polymers typically featuring alkoxysilyl functional groups (FGs),[1,2,3,4] have been known for more than 40 years, being essentially exploited over the past two decades in the coatings, adhesives, sealants and elastomers (CASE) industry. SMPs constitute the main components in solvent-free, poly(vinyl chloride)-free, and isocyanate-free sealants, adhesives and coating materials towards architectural, construction or industrial (aerospace, aeronautics) applications.[5,6,7,8,9,10,11] Their good adhesion to a wide range of substrates (*e.g.* metal, ceramic, plastics, glass…), their good temperature and UV (weather) resistance, and their excellent durability with limited surface treatment (absence of shrinkage or crack over time), are especially valued. In particular, SMPs are widely used to bond directly to glass with minimal surface preparation, and are suitable for large surface areas within adequate working times, efficient handling, while providing actual insulation. They thus represent the adhesives of choice for bonding glass in all types of vehicles and side panels in trailers/trucks, for door and window construction, fixing solar panels, assembly parts, interior elements, container construction, etc. Also, in the biomedical domain, a recent illustration of the potential of SMPs has been provided by the research group of David Haddleton who developed an ibuprofen transdermal skin patch as a novel drug delivery system, from the SMP adhesive produced without solvent by Bostik.[12]

SMPs are commercially available hybrid polymers which combine the environment- and user-friendly advantages of the silicon-cure chemistry of silicone sealants (no strong odor, fast and controlled curing process, no bubbling – i.e. no CO_2 emission and thus no foaming –, no staining of porous substrates) to the backbone of a polymer (typically polyurethane, polyether, polyisobutylene, polyacrylate), with bond strength, durability and elasticity over a wide range of temperatures and humidity ratios.[13,14,15] SMPs thus present the advantage of

being particularly environmentally and industrially attractive water-based and solvent-free adhesives for which shrinkage, typically encountered with solvent-based adhesives, hardly occurs upon curing.[16,17,18,19,20,21,22,23,24,25,26] The curing process of SMPs involves hydrolysis of the silyl alkoxide FG(s) which then results in the formation of cohesive siloxane (–Si–O–Si–) bonds, thus insuring the cross-linking of a liquid or gel pre-material into a 3D solid one, and assuring the cohesive adhesive joint providing the resistance of the assembly.[2,5,7,13–15,21] Curing is a two-step process involving first the conversion of the alkoxysilane to silanol followed by the condensation of –Si–OH and –Si–OR to form siloxane linkages upon elimination of ROH (or by condensation of two –Si–OH accompanied with H_2O abstraction) (Scheme 1). The condensation process is promoted by the surrounding moisture arising from the environment and/or the substrate onto which the SMP is applied, and also most often by the presence of an acid or base catalyst. Polysiloxane network formation may even take place at room temperature (RT) and the curing process is advantageously fast. Polymers with Si–OR bonds can also react with silanol groups or metal oxides present at the surface of inorganic materials, thus making them valuable in the preparation of organic-inorganic composite materials.[27] Given the renewed interest in the use of silica as a reinforcing filler for elastomers, trialkoxysilyl functionalized polymers have thus become attractive for their ability to facilitate the dispersion of silica and to promote the polymer interactions with the filler.



Scheme 1. Curing (hydrolysis and polycondensation) process of SMPs.

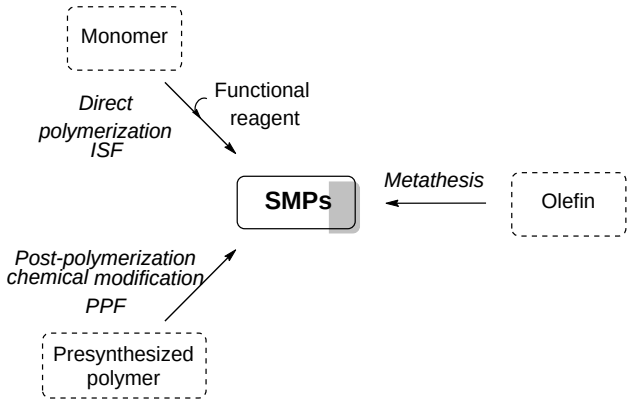
Finally, SMPs represent an alternative to polyurethanes used in the adhesives, sealants and paint industries. Indeed, one major drawback of uncured polyurethane-based sealants and adhesives is the presence of unreacted isocyanate groups which are very reactive and harmful to humans in various forms, and thus undesirable. In particular isocyanate groups react with H_2O thus forming CO_2 which induces the formation of voids within the material, thereby promoting cohesion failure. SMPs will also comparatively pick-up less air-borne dust particles due to their lower static charge, induce less streaking, prompt no shrinkage after curing due to the absence of solvent, be paintable, and enable damp substrate bonding. The major manufacturers of SMPs are Bostik, Evonik, Henkel, Kaneka and Wacker.

Within SMPs, the $-Si(OR)_x$ moiety may be either an end-capping or a side-chain function. Although commercially relevant SMPs with advanced performances are typically α,ω-di(alkoxysilyl) telechelic polymers, mono-$Si(OR)_3$ end-capped (i.e. semi telechelic) polymers have also been reported, with successful ensuing curing.

Synthetic routes to SMPs

While the successful end-capping of a polymer still remains somewhat synthetically challenging, the two most conventional synthetic approaches towards end-functionalized polymers include either i) the direct formation of the chain-end functionalized polymer by introduction of the reactive group during the polymerization (in situ functionalization (ISF)) either through the functional initiator (during the initiation), the functional chain-transfer agent (CTA; during the propagation), or the functional terminating agent (during termination) to end-cap the growing polymer chain, or ii) the post-polymerization chemical modification of a preformed polymer (post-polymerization functionalization (PPF)) (Scheme 2).[28,29,30,31,32,33,34] Another possible synthetic route towards SMPs, specific to polyenes and polyolefins (POs), is the metathesis of olefins (Scheme 2).[28,31, 35 , 36 , 37] Living and controlled/living polymerization methods now enable to access well-defined end-

functionalized polymers with a high degree of end-functionalization, featuring controlled and tunable molar mass, and controlled narrow dispersity, chain-end fidelity, functionality, microstructure and tacticity, resulting in polymer materials with various physical properties.[28-37]



Scheme 2. Synthetic strategies towards SMPs.

Scope of this highlight

It is the purpose of this highlight to summarize routes and modern trends in the special class of alkoxysilyl functionalized polymers, emphasizing on telechelic ones, and illustrating with selected studies and important milestones (Table 1). This highlight is subdivided in two main parts. The first part covers the state of the art of polymers bearing alkoxysilyl FGs delineated according to the more traditional ISF and PPF synthetic approaches. Examples of SMPs featuring alkoxysilyl end-capping groups or side-chain FGs are mentioned. The second part describes contemporary olefin metathesis strategies for the synthesis of α,ω-(alkoxysilyl) telechelic polyenes and POs. The chemistry employed to obtain SMPs, including polyenes and POs as well as various selected relevant alkoxysilyl functionalized polymers, is presented along with, when reported, their subsequent curing and the utility of the product materials. Focus is placed on the chemistry developed towards SMPs, on their macromolecular features (especially molar mass and dispersity) when available, and not on the spectroscopic characteristics nor on the materials themselves. Scientific articles which appeared in the

literature in the last decade and a half are the main focus of this highlight, although appropriate earlier examples are also mentioned so as to provide a complete overview.[38]

Table 1. SMPs obtained by chemical modification or metathesis routes.

Chain-end functionality	**Synthetic route**	**Polymer**	**Ref.**
Me —Si—OMe Me	ADMET[a]	Polycyclooctene	39
Me —Si—OiPr Me OMe —Si—OMe OMe OEt —Si—OEt OEt	Chemical modification - ISF[a]	Polyisoprene Polyisoprene-based triblock copolymer	40,41, 42,43
Me —Si—OMe OMe	ADMET	Polyether/carbosiloxane segments	44,45,46
$(CH_2)_3Cl$ —Si—OMe OMe OMe —Si—OMe OMe	Chemical modification - ISF	Polybutadiene	47
OMe —Si—OMe OMe	Chemical modification - ISF	Polystyrene Polystyrene-*b*-Polybutadiene	48,49
OMe —Si—OMe OMe	Chemical modification - PPF[a]	Polyethylene Polylactide Polythiophene	50,51,52 53 54,55
OEt —Si—OEt OEt	Chemical modification - PPF	Polybutadiene Hydrogenated Polybutadiene Poly(ethylene glycol) Polycaprolactone Polycaprolactone/Polydimethylsiloxane blend Polydimethylsiloxane Polybutylacrylate Polyaziridine	56,57,58,59 60,61 22,61,62,63,64 65,66 60 7 67
OMe —Si—OMe OMe OEt —Si—OEt OEt	Chemical modification - PPF	Poly(propylene glycol) Poly(tetramethylene oxide) Poly(ethylene glycol-*co*-propylene glycol)	7,22,23,25,68,69

OMe —Si—OMe OMe OEt —Si—OEt OEt	ROMP/CM[a]	Polycyclooctene Polycyclopentadiene Polynorbornene Poly((substituted)norbornene-*co*-cyclooctene) Poly(butadiene-*co*-isoprene) Poly(butadiene-*co*-norbornene) Poly(butadiene-*co*-cyclododecatriene)	70,71,72,73
[a] ADMET = acyclic diene metathesis; ISF = in situ functionalization; PPF = post-polymerization functionalization; ROMP = ring-opening metathesis polymerization; CM = cross metathesis.			

2. Synthesis of SMPs

2.1. Synthesis of SMPs by chemical modification

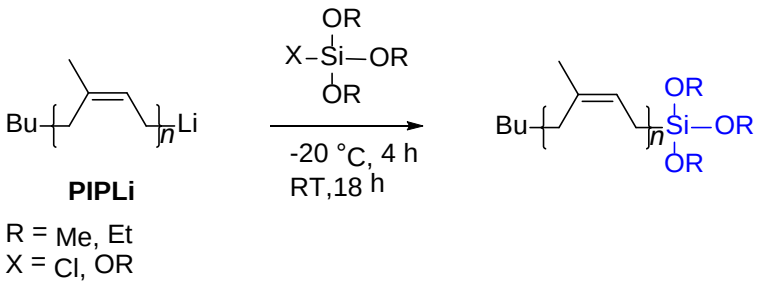
Tuning of a polymer end-capping group(s) can be achieved through either the use of a functional initiator used in the initiation step (A α-end-group), upon *in situ* termination of the growing polymer chain with a functional quenching reagent (B ω-end-group), or upon post-polymerization chemical modification of pre-existing A and/or B chain-end group(s), thus affording the desired parent end-functionalized polymer.[28–35,74,75,76,77] In the first functional initiator/in situ termination (in-situ functionalization (ISF)) routes, the functional initiator/termination agent should be compatible with the polymerization process and with the chemical composition of the polymer. These ISF methods may suffer from a poor control of the degree of end-functionalization with mixtures of incomplete mono- and/or di-functionalized polymers being possibly recovered. In the PPF approach, a single parent (synthetic and natural as well) polymer precursor can serve as a template towards the preparation, through chemical modification, of a whole and large family of chain-end functionalized polymers displaying identical molar mass, dispersity, tacticity, and yet different architectures and properties. Another advantage of the PPF towards end-functionalized analogues is to avoid any catalyst poisoning and any issues in catalyst FG-tolerance. Conversely, the limitation of the third PPF method remains the possibly unreactive nature of the polymer requiring sometimes harsh operating conditions and possibly accompanied with a lack of selectivity, which overall may compromise the end-

functionalization of the polymer. These latter two points are especially relevant for the synthesis of functionalized polyenes or POs.[75–77] Quantitative conversion of chemical moieties is also essential to avoid a time-consuming and costly purification of the polymer from the unreacted reagents. Advances in PPF over the last three decades, especially due to the progress in revisited coupling chemistries such as thiol-ene/yne processes, chemistries based on isocyanates, ketones, aldehydes, epoxides, anhydrides, activated esters, cycloaddition reactions, etc., nowadays afford a reliable strategy towards end-functionalized polymers.

2.1.1. Synthesis of SMPs through an in situ functionalization (ISF) approach

End-functionalization of a polymer upon termination of the polymerization using a functional reagent to react in situ with the growing polymer chain is an easy way to introduce chain-end functionality onto a polymer. Benefiting from earlier developments in anionic polymerization, several SMPs have thus been synthesized following this ISF approach. This method has indeed been more widely exploited than the ISF route using a functional initiator. However, it remains so far limited to access polybutadiene (PBD), polyisoprene (PIP) and polystyrene (PS) SMPs.

α-Trimethoxysilyl (or triethoxysilyl) end-capped 1,4-PIPs were synthesized upon deactivation (THF, –20 °C for 4 h then RT for 18 h) of poly(isoprene)-yl-lithium (PIPLi; M_n = 800 g.mol^{-1}, $Đ_M$ = 9.8) by using tetramethoxysilane, tetraethoxysilane, or 3-chloropropyltrimethoxysilane as reported by Derouet and coworkers (Scheme 3).[40,41,42] On the basis of ^{1}H and ^{29}Si 1D and 2D NMR investigations, the nucleophilic substitution reaction of alkoxy groups from the alkoxysilane CTA by the poly(isoprene)-yl ω-carbanions was shown to be effective, and to occur exclusively on the silicon atom and not on the carbon bearing the X substituent (evidenced with X = Cl).



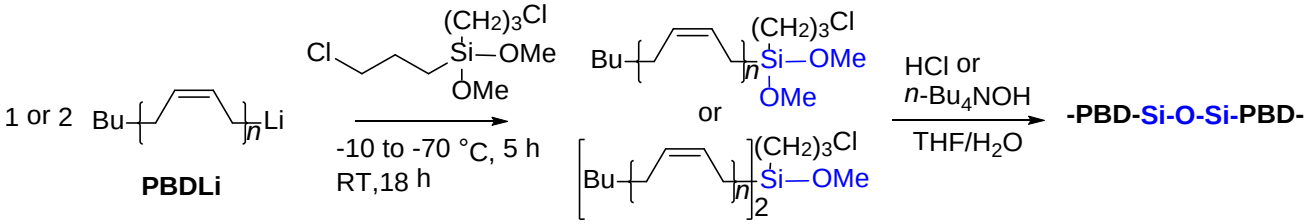
Scheme 3. Synthesis of α-alkoxysilyl end-capped PIP from PIPLi.[41]

A PIP-based block copolymer with alkoxysilyl pending groups was prepared towards the synthesis of microporous membranes featuring functional silyl groups, as reported by Nakahama and coworkers.[43] A one-pot addition of (4-vinylphenyl)dimethyl-(isopropoxy)silane (VP-$SiMe_2$(OiPr)) to an anionic living PIP (THF, −78 °C, 5 min), previously obtained from oligo(α-methylstyryl)dipotassium, afforded the triblock copolymer with a PIP central block flanked with two poly(VP-$SiMe_2$(OiPr)) outer segments ($M_{n,NMR}$ = 68,000 g.mol^{-1}, $Đ_M$ = 1.2). Cross-linking of the isopropoxysilyl groups was next achieved via hydrolysis in dilute aqueous HCl solution and subsequent condensation of the resulting silanol groups from poly(VP-$SiMe_2$(OiPr)) segments. The films therefrom were next investigated for their microstructure.

In a similar approach, a high (80–90%)-1,4-PBD end-capped with a (3-chloropropyl)(dimethoxy)silyl group was prepared by Soutar and coworkers in good yield (up to 85% functionalization) (Scheme 4).[47] A previously formed living poly(butadiene)-yl-lithium (prepared from the anionic polymerization of 1,3-butadiene initiated by *n*-butyllithium) was reacted with 3-chloropropyl(trimethoxy)silane (THF, −10 °C for > 5 h and RT for 18 h), with displacement of one or two methoxy groups ($M_{n,NMR}$ ca. 2100 g.mol^{-1}, $Đ_M$ = 1.2). Also, termination of poly(butadien)-yl-lithium with tetramethoxysilane afforded a mixture of silylated PBDs including polymers terminated by $-Si(OMe)_3$, among other polymer materials resulting from further coupling by elimination of methoxy groups such as

the coupling of two chains through $Si(OMe)_2$ linkages. Likewise, the anionic polymerization of 1,3-butadiene initiated by 3-dimethylaminopropyllithium gave the living α-dimethylaminopropyl poly(butadien)-yl-lithium, which was next reacted with 3-chloropropyl(trimethyoxy)silane

(> 80% termination). Subsequent quaternization of the terminal tertiary amino group of the resulting α,ω-heterofunctionalized polymer $(MeO)_2[(CH_2)_3Cl]Si\{C_4H_6\}_n(CH_2)_3NMe_2$ with methyl iodide next quantitatively produced the parent ionic difunctionalized polymer $(MeO)_2[(CH_2)_3Cl]Si\{C_4H_6\}_n(CH_2)_3NMe_3^+I^-$.[47] This work further showed that the two methoxy groups on the silicon of the α-monofunctionalized PBD $(MeO)_2[(CH_2)_3Cl]Si\{C_4H_6\}_nBu$ were not readily hydrolyzed by water, but that they could be removed in acidic (HCl) or basic (*n*-Bu_4NOH) conditions as evidenced by ^1H and ^{13}C NMR and FTIR spectroscopies (disappearance of Si–OMe bond). Interestingly, the terminal methoxysilyl group of this latter PBD coupled to the surface of silica gel (80 °C, 24 h) through Si–O–Si linkages.[47]



Scheme 4. Synthesis of α-methoxysilyl end-capped PBD from PBDLi, and subsequent hydrolysis.[47]

The alkyl lithium-initiated anionic polymerization of styrene afforded living poly(styryl)lithium anions which could be similarly end-capped with a variety of FGs. PS with an α $-Si(OMe)_3$ end-capping group was thus synthesized by Ward and coworkers from the anionic polymerization of styrene initiated by *sec*-butyllithium, and subsequent quantitative end-capping of the living chain ends with *p*-chloromethylphenyl trimethoxysilane

(in excess) ($M_{n,NMR}$ = 2900–11,000 g.mol^{-1}, $Đ_M$ = 1.05–1.3).[48] Subsequent acid catalyzed hydrolysis and condensation (upon heating) of the trimethoxysilane end-groups (THF, HCl, 36 h, 25 °C, quantitative) resulted in star-branched PS, as evidenced by NMR spectroscopy and SEC analysis. This represented the first report of core-functionalized star-shaped polymers as silicon (Si) surface modifiers. Similarly, using butadiene (5 equiv.) or 1,1-diphenylethylene (DPE, stoichiometric amount) as end-capping reagent, PS-*b*-PBDLi or PS-DPELi, respectively, were thus obtained from PSLi, as reported by Quirk and coworkers.[49] Subsequent functionalization upon termination with glycidoxypropyltrimethoxysilane generated the corresponding mono(trimethoxysilyl) functionalized polymers, as evidenced by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopies. These latter trimethoxysilyl chain-end functionalized PS were hydrolyzed (THF, aqueous HCl, 115 °C) into four-armed star-branched polymers.

Also, note that some mono-, di-, tri-alkoxy-substituted styrene monomers were successfully anionically polymerized to provide PS with pendant alkoxysilyl functions. Likewise, mono- di- and tri-alkoxysilyl side-chain functionalized PBDs were prepared by Nakahama and coworkers from the anionic polymerization of 2-mono-(di-, tri-)alkoxysilyl-1,3-butadienes using oligo(α-methylstyryl)dipotassium. Similarly, PBD/PIP block copolymers featuring pendant Si(OR)$_{1-3}$ groups, were also prepared upon addition of 2-mono-(di-,

tri-)alkoxysilyl-1,3-butadienes to anionic living PIP. Subsequent hydrogenation of the resulting poly(2-silyl-substituted-1,3-butadiene)s and corresponding PIP copolyolefins using Pd/C catalyst led to the quantitative saturation of the double bonds regardless of the substituent on silicon atom. Also, Teyssié and coworkers, and Nakahama and coworkers, reported the anionic polymerization of 3-trialkoxysilylpropyl methacrylates using 1,1-diphenylhexyllithium in the presence of LiCl, affording polymethacrylates with pendant C_3H_6–Si–$(OR)_3$ groups on each repeating unit (OR = OMe, OEt, $OCHMe_2$). Similarly, the

anionic polymerization of N-propyl-N-(3-triisopropoxysilylpropyl)acrylamide gave polyacrylamide chain laterally functionalized with alkoxysilyl groups. In these latter series of works, bulky alkoxide Si-substituent(s) prevented the nucleophilic attack of the Si–O bond during the polymerization.[27 and references therein]

2.1.2. Synthesis of SMPs through a post-polymerization functionalization (PPF) approach

More recently, thiol-ene chemistry was used by Boisson, D'Agosto and coworkers to access to a large range of homotelechelic PEs (Scheme 5).[50,51] α,ω-Divinyl telechelic PEs were first synthesized from PE by a catalyzed chain growth in the presence of $[(C_5Me_5)_2NdCl_2Li(OEt_2)_2]$ catalyst in combination with di(10-undecenyl)magnesium as a functional CTA, after a simple and efficient treatment with iodine and *t*BuOK (toluene, 95 °C). The resulting vinyl end-groups of the PE oligomers ($M_{n,NMR}$ up to 2500 g.mol^{-1}, $Đ_M$ = 1.22) were next readily transformed into a variety of reactive functionalities upon reaction with functional reactive thiols in the presence of azobisisobutyronitrile (AIBN). Thus, bis(trimethoxysilyl) telechelic PE was quantitatively obtained upon reaction of α,ω-divinyl telechelic PE with (3-mercaptopropyl)trimethoxysilane following a PPF approach, as characterized by ^{1}H and ^{13}C NMR analyses. This represents, to my knowledge, the only example of alkoxysilyl telechelic PO prepared form PPF or ISF.[50,51]

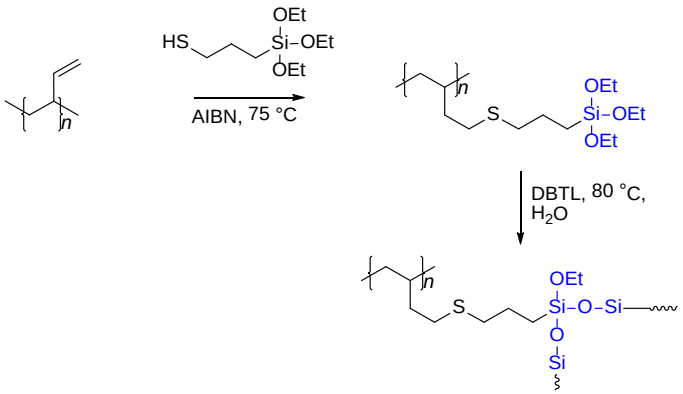


Scheme 5. Synthesis of bis(trimethoxysilyl) telechelic PE by thiol-ene chemistry.[50]

In another study, commercially available high-density cross-linkable vinyl trialkoxysilane PE (POLIDAN, Padanaplast) was successfully cross-linked in water or air to induce hydrolysis of Si–OR groups and formation of Si–O–Si cross-links by condensation,

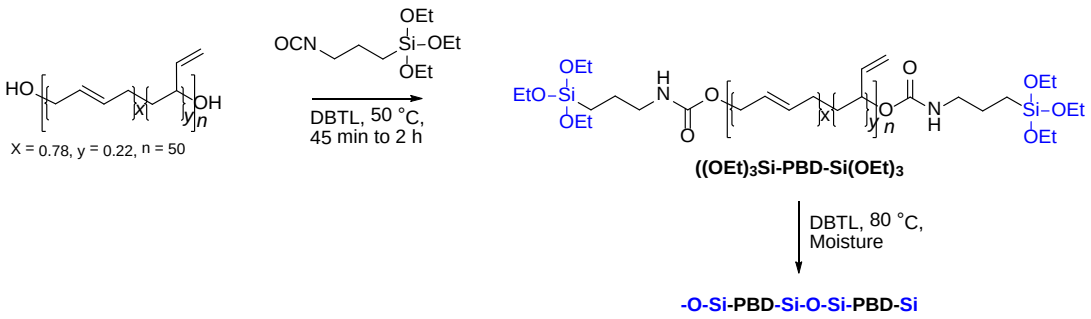
using different temperatures, humidities, and reaction times in the presence of dibutyl tin dilaurate (DBTL).[52:]

Similarly, the radical addition under moisture of 3-mercaptopropyl(triethoxy)silane to the C=C double bonds of a low molar mass dihydroxy telechelic PBD (AIBN, 75 °C) quantitatively afforded the analogous PBD with 1.05 to 7.9 $-[S(CH_2)_3Si(OEt)_3]_2$ pendant moieties per chain, as reported by Bunel and coworkers (Scheme 6).[57] The influence of the catalyst (CF_3SO_3H, acetic acid, or best: DBTL), temperature (best: 80 °C), moisture and curing time (5–24 h) were next evaluated by swelling measurements and determination of the mechanical properties (storage modulus *E'* at the rubbery plateau, maximum of tan δ) of the cross-linked materials.[56]



Scheme 6. Synthesis of triethoxysilyl functionalized PBD and subsequent cross-linking.[56,57]

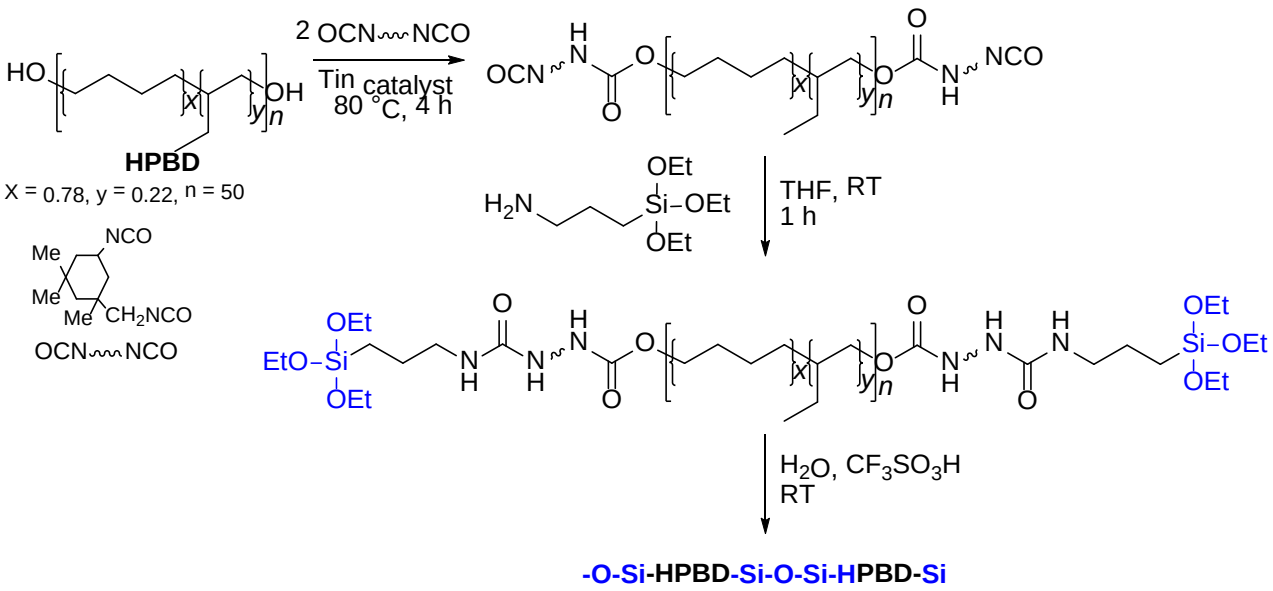
Bunel and coworkers have also prepared low molar mass bis(triethoxysilyl) telechelic PBD from the PPF of the corresponding α,ω-dihydroxy functionalized PBD using 3-isocyanatopropyl(triethoxy)silane, a quasi-quantitative reaction catalyzed by DBTL (50 °C, 45 min–2 h) (Scheme 7).[58] Subsequent cross-linking was carried out under moisture with DBTL at 80 °C, and the swelling and mechanical properties of the resulting materials were modulated according to the number of alkoxysilyl groups per polymer chains (1.2 to 2.4), whereas the glass transition temperature remained constant.[59]



Scheme 7. Synthesis of bis(triethoxysilyl) telechelic PBD from dihydroxy telechelic PBD, and subsequent cross-linking.[58,59]

Hydrosilylation also provides another efficient entry towards polymers flanked with an alkoxysilyl group pending on each repeating unit. Thus, as reported by Chauhan and coworkers, the highly selective, mild and clean hydrosilylation of 1,2-PBD with hydromono-(di-)alkoxysilanes ($HR'_{2or1}Si(OR)_{1or2}$ = $HSiMe_2(OEt)$, $HSiMe(OSiMe_3)_2$) catalyzed by recyclable Pt nanoclusters afforded the parent internally alkoxysilyl functionalized PBDs.[78] Similarly, Rempel and coworkers reported the reaction of PBD with $HSi(OEt)_3$ in the presence of $Rh(Cl)(PPh_3)_3$ (toluene, 110 °C, 10–20 h), thereby providing internally triethoxysilyl functionalized PBD.[79] Also, the gas solubility and permeability of various cured (saturated water vapor, ca. 100 °C) poly(alkoxysilylbutadiene) films were studied in relation to the bulkiness of the alkoxy groups and cross-linking density.[80]

In another work, Lam and coworkers prepared α,ω-triethoxysilyl telechelic polymers through a two-step PPF approach from hydrogenated PBD (HPBD) diols upon reaction with isophorone diisocyanate (stoichiometric ratio NCO/OH = 2, bulk, 80 °C, 4 h, vacuum) followed by the addition of aminosilane (stoichiometric ratio NCO/NH_2 = 1, THF, RT, 1 h) ($M_{n,SEC}$ = 8200–14,000 $g.mol^{-1}$, $Đ_M$ = 2.2–2.7). Hydrolysis and condensation reactions (H_2O, triflic acid, RT, bulk or THF) gave different micro-phase separated network materials (Scheme 8).[60,61]



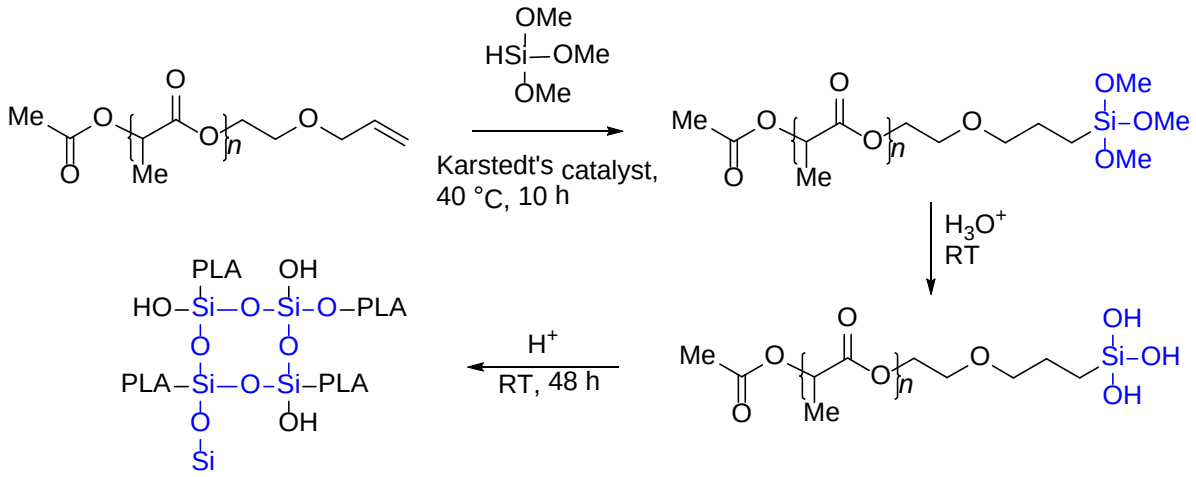
Scheme 8. Synthesis of bis(triethoxysilyl) telechelic HPBD from dihydroxy telechelic HPBD, and subsequent cross-linking.[60,61]

This latter strategy was also applied to the PPF preparation of trialkoxysilyl terminated poly(ethylene glycol) (PEG) ($M_{n,SEC}$ = 1000–1500 g.mol^{-1}, $Đ_M$ = 1.1–1.7; gel time),[61,62] poly(proylene glycol) (PPG) ($M_{n,SEC}$ = 16,200 g.mol^{-1}, $Đ_M$ = 1.41),[7,22,23] PEG-*co*-PPG,[22] poly(tetramethylene oxide) ($M_{n,SEC}$ = 9600 g.mol^{-1}; mechanical properties),[7,25,68,69] polybutylacrylate ($M_{n,SEC}$ = 9900 g.mol^{-1}),[7] and poly(dimethylsiloxane) (PDMS) ($M_{n,SEC}$ = 4100–12,500 g.mol^{-1}, $Đ_M$ = 2.1; T_g = –113 to –123 °C; mechanical properties),[60] which were subsequently hydrolyzed and polycondensed. In particular, moisture-curable polyurethanes end-capped with trialkoxysilane were thus obtained as precursors to one-component and solvent-free adhesives matrials.[7,22,23,25]

Following again the same approach, triethoxysilyl telechelic polycaprolactone (PCL) was prepared by Liu and coworkers from a PCL diol (M_n = 1000–2000 g.mol^{-1}) and the –NCO groups of isocyanatopropyltriethoxysilane, in the presence of DBTL (65 °C).[65] Similarly, a blend of triethoxysilyl end-capped PCL and PDMS oligomers was prepared from a mixture of the corresponding polydiols.[66] The resulting PCL elastomer or PCL/PDMS blend were then combined under humidity with a commercial epoxy resin (diglycidyl ether of

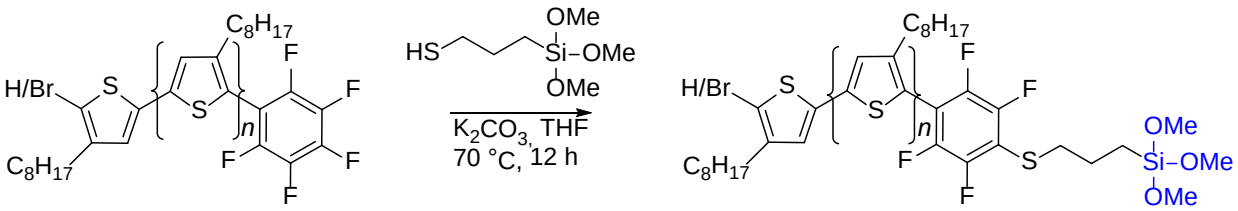
bisphenol A, DGEBA) to form ternary composites which were ultimately cured using an amine-based curing agent and a sol–gel process (DBTL, RT, 3 weeks, under ca. 60% relative humidity), respectively.[65,66]

Silyl-terminated oligomers of poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) were synthesized by hydrosilylation of allyl-terminated pre-synthesized polyesters as reported by Kimura and coworkers (Scheme 9).[53] The previously prepared acetylated PLAs were chemically end-modified upon reaction with trimethoxysilane in the presence of Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane; 40 °C, 10 h; 75% hydrosilylation). The resulting α-alkoxysilyl functionalized PLAs were characterized by ^{1}H NMR ($M_{n,NMR}$ ca. 2800 g.mol^{-1}), SEC ($M_{n,SEC}$ = 3900 g.mol^{-1}, $Đ_M$ ca. 1.37), differential scanning calorimetry (DSC, T_g ca. 32 °C, T_c ca. 84 °C, T_m ca. 127 °C), and thermal gravimetric analysis ((MeO)$_3$Si–PLAs showed a higher thermal stability than the parent acetylated PLA). These polyesters were next readily hydrolyzed (aqueous HCl, 48 h) into hyper-branched polymers ($M_{n,SEC}$ (bimodal) ca. 17,300, 5200 g.mol^{-1}, $Đ_M$ ca. 1.14–1.20; T_g = 47 °C, T_c = 105 °C, T_m ca. 125–130 °C; the higher T_g and T_c values compared to the parent (MeO)$_3$Si–PLA were attributed to the cross-linking structure that made the chain mobility significantly lower) with particulate morphology.



Scheme 9. Synthesis of α-trimethoxysilyl PLA, and subsequent hydrolysis.[53]

Introduction of pentafluorobenzene (PFB) as a single end-group in polythiophene (PTP) derivatives was reported by Heeney and coworkers via in situ quenching of the polymerization.[54] PFB is a versatile "click" handle due to its stability towards basic conditions thus avoiding the need for protecting groups, and due to its ability to undergo fast nucleophilic aromatic substitutions without required modification, thereby enabling to quantitatively tether a variety of common thiol, amine, and alcohol nucleophiles to the PTP backbone under mild conditions. PTP end-capped with a single cross-linkable trimethoxysilyl ω-FG was thus obtained via the quantitative reaction of a preformed PTP–PFB with the commercially available reagent (3-mercaptopropyl)trimethoxysilane via the nucleophilic attack at the *para*-position, as assessed by matrix-assisted laser desorption–ionization time-of-fight (MALDI-ToF) mass spectrometry (MS) and ^{19}F NMR analyses (Scheme 10).[54] The resulting –Si(OMe)$_3$ end-groups were next utilized to form, by spin-coating followed by annealing, a partially retractable thin film on the surface of glass substrates. Note also, that hybrids between conjugated poly(3-hexylthiophene), a benchmark material for organic electronics, and inorganic materials made of silica-core organosilica-shell particles, thus featuring particle–O–Si(OR)$_2$–PTP bonds, have also been reported by Kiriy and coworkers upon growing the polymer from the particle.[55]



Scheme 10. Post-polymerization α-functionalization of PTP with an α-trimethoxy functional thiol.[54]

Also, the solvolysis and condensation reactions of PEG diol with tetraethoxy- or tetramethoxy-silane (H^+ catalyst, MeOH or THF, 50 °C, 30 min) provided the corresponding trialkoxysilyl end-capped PEG oligomers, ultimately affording gels, as reported by Vincens

and coworkers.[63] Reaction of the hydroxyl end groups of three PEG moieties bound to a molybdenum center with $Cl(CH_2)_3Si(OEt)_3$ afforded the corresponding tris[(triethoxy)silyl] functionalized organometallic complex. This latter was subsequently co-condensed with tetraethoxysilane thus providing by sol-gel technique, organic–inorganic hybrid polymers with different properties.[64]

Finally, reaction of a bifunctionalized living poly(*N*-*tert*-butylaziridine), prepared by Goethals and coworker by cationic ring-opening polymerization of the *N*-*tert*-butylaziridine using triflic anhydride, with 3-aminopropyltriethoxysilane afforded the bis(triethoxysilyl) telechelic polyaziridine. Subsequent hydrolysis (THF, $CHCl_3$ or MeOH, HCl, 25 °C) induced the formation of polyaziridine networks (M_w = 2000–9000 g.mol^{-1}) displaying a swelling behavior.[67]

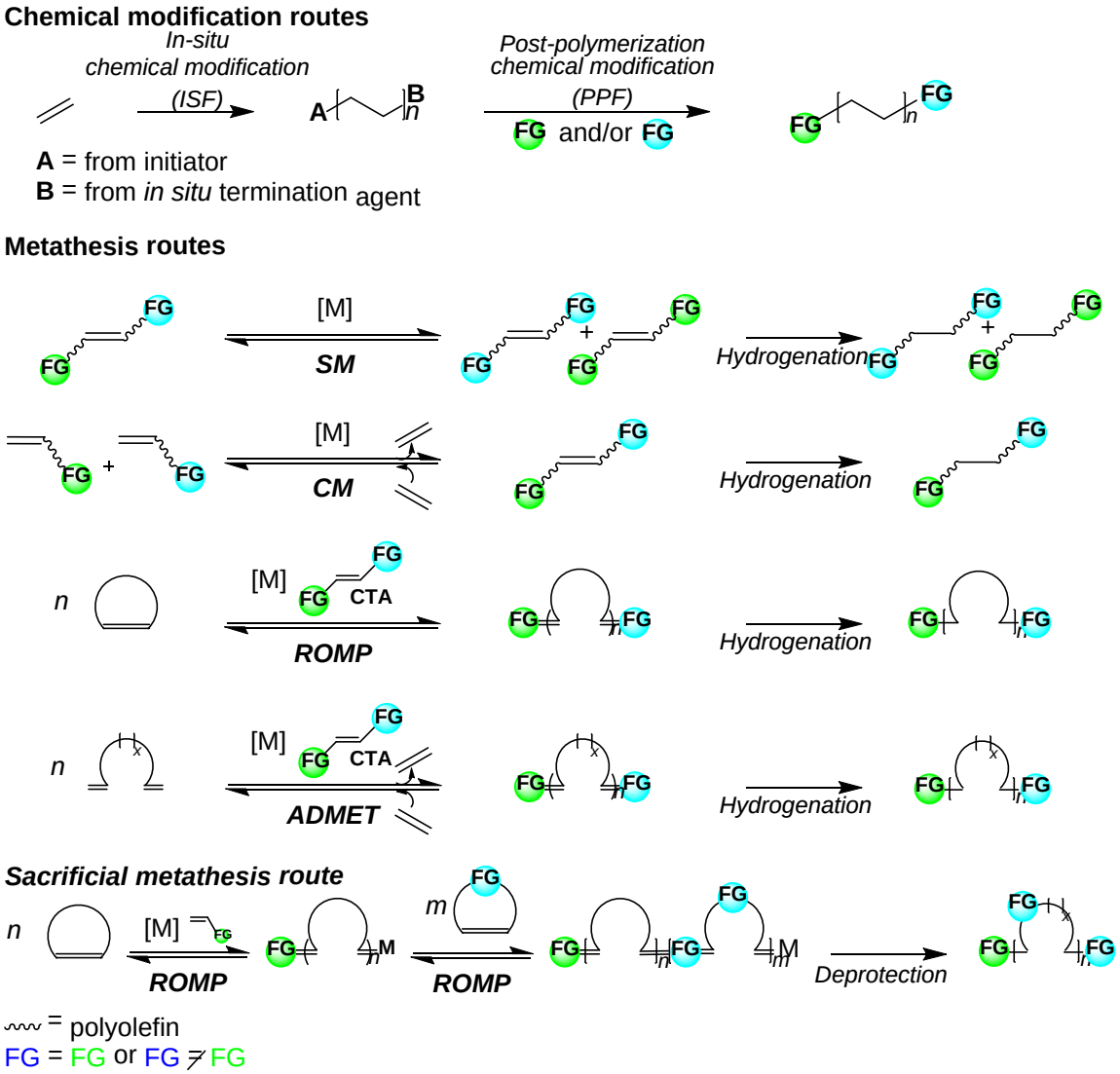
2.2. Synthesis of alkoxysilyl telechelic polyenes and polyolefins by olefin metathesis

Telechelic polyenes and POs, as functionalized polymers, are valuable materials with respect (but not limited) to, adhesion, toughness, print/paintability, compatibility with diverse more polar materials and rheological properties.[36,37,77,81,82] Introduction of reactive groups into these non-polar materials, thereby providing access to functionalized polymers, is highly industrially desirable so as to enlarge their field of applications, but yet remains rather synthetically challenging. Silyl-modified polyenes and polyolefins are a special type of SMPs which are desirable to enable adhesion to olefinic substrates, which is typically difficult due to their non-polar and non-porous surface. Current academic and industrial efforts are thus dedicated to develop such polymers. Although sily-modified POs flanked with alkoxysilyl pendant groups may also be cured, α,ω-di(alkoxysilyl) telechelic polyenes and POs remain the industrially targeted materials.

2.2.1. Strategies for the synthesis of telechelic polyenes and polyolefins

Common strategies for the synthesis of telechelic polyenes and POs basically involve the functional tuning/chemical modification of polymers (ISF and PPF as described above),[28–35] and the more topical metathesis polymerization approaches (Schemes 1, 11).[28,31,75–77,81,83] As presented above, the preparation of alkoxysilyl functionalized PE upon PPF of α,ω-divinyl telechelic PE remains the sole example of such chemical modification routes towards alkoxysilyl telechelic polyenes/POs.[50,51] On the other hand, the synthesis of telechelic polyenes/POs through the selective catalytic introduction of the functional end-group following living olefin metathesis polymerization processes valuably provides popular *in situ* methods applicable to a large array of monomers and carried out under extremely mild and user-friendly conditions. The olefin metathesis polymerization toolbox of mechanistically related techniques include ring-opening metathesis polymerization (ROMP) of cyclic olefins, and acyclic diene metathesis (ADMET) polymerization, while other related process including ring-opening metathesis (ROM), ring-closing metathesis (RCM), self-metathesis which refers to olefin homodimerization (SM), and cross metathesis (CM) of olefins, may also take place (Scheme 11).[84,85,86,87]

SM and CM of chain-end functional internal or terminal (poly)enes and (poly)olefins can give telechelic polymers with identical or distinct (heterotelechelic) end-capping FGs. However, these routes require to adequately select the olefinic substrate so as to optimize the (stereo)selectivity in the reaction, thus limiting their use.[88,89,90,91,92]



Scheme 11. General synthetic routes towards telechelic polyenes and POs.

ROMP and ADMET are the two most common and versatile routes to telechelic polyenes/POs. ADMET, as well as CM, are olefin metathesis polycondensation reactions involving linear symmetrically functional α,ω-diene or alkene monomers, respectively, which are thus driven by the removal of the small byproduct (usually ethylene gas) typically by an argon/nitrogen flow. ADMET is actually the most widely used olefin CM polymerization technique.[93, 94, 95] These latter step-growth polymerizations only give high molar mass polymers at high degrees of monomer conversion, consistent with Carothers equation. ROMP of cyclic alkene is a chain-growth polymerization thermodynamically driven by the release of the cycloalkene monomer ring-strain.[36, 96, 97, 98] The major shortcoming of such metathesis

approaches is however the required chemical tolerance of the metal alkylidene catalyst towards FGs to be introduced at the chain ends. Developments over the last decades to overcome these synthetic challenges now offer FG-tolerant commercially available catalysts, and robust and reliable metathesis techniques. The nature of the catalyst being of foremost importance in metathesis, latest advances have established ruthenium-based catalysts (in particular, the commercially available Grubbs ruthenium carbenes are the most widely used) as the most competitive in terms of activity and FG tolerance.[85] When performed in the presence of a difunctional acyclic symmetric internal alkene CTA, ADMET and ROMP/CM straightforwardly provide access to the desired telechelic polyenes/POs (Scheme 11). Note that these metathesis reactions towards telechelic polyenes/POs require the prior synthesis of a library of CTAs. Given that metathesis polymerization preserves carbon double bonds along the backbone during the polymerization, an ultimate hydrogenation of the resulting polyalkenamers (polyenes) is required to get the corresponding POs without any double bonds in the backbone (Scheme 11). Indeed, post-metathesis polymerization hydrogenation has been successfully reported.[29,37,75,88,99,100,101,102,103,104,105,106,107,108] One can thus prepare telechelic polyenes/POs with finely controlled molar mass and dispersity, and a high degree of selective end-functionalization by ADMET and ROMP.

Thus, ADMET polymerization and depolymerization methods have been used for the synthesis of telechelic polyenes/POs oligomers. Metathesis depolymerization and degradation of 1,4-PBD, *cis*-1,4-PIP, their copolymers or other polyenes, carried out in the presence of various difunctional monoene CTAs, gave the corresponding telechelic polymers, such as borane, diester, diimide, epoxy, or trithiocarbonyl end-capped polyenes/POs.[104,105,106, 109 , 110 , 111 , 112] Alcohol or amine groups being detrimental to the metathesis catalysts, polyenes/POs chain-end functionalized with such groups were prepared

by ADMET using FGs (such as acetoxy or phtalimide)-protected α-olefin CTAs, followed by a post-polymerization deprotection step.[107,108]

Also, in a ROMP process, end-capping polyenes/POs with FGs can be implemented in three different ways. First, a functional initiator can be used in the initiation step. Even though each initiated chain is then ensured to bear the FG, this necessitates the prior synthesis of the organometallic complex bearing the suitable functional carbene, thereby requiring some expertise and skills in this field, and thus limiting the scope of this pathway. Besides, only semitelechelic polymers are thus formed. Functionalities such acetate, hydroxyl, halide have been reported from this approach.[113,114] Secondly, introduction of the desired functionality through the use of a functional quenching reagent during the termination step requires a long life-time and stable living species. Within this pathway, functional vinyl ethers such as azide, fluorescein, biotin derivatives, have been most commonly used.[115,116] Termination upon addition of carbonyl groups (especially aldehydes), lactones, oxygen, or a functional acyclic olefin such as acrylates (by CM), provide aldehyde, carboxylic acid, or acrylate chain-end functionalized polyenes/POs.[117,118] Finally, addition of a functional acyclic alkene as CTA has become by far the most simple, effective and largely applied (metathesis) approach towards the preparation of telechelic polyenes/POs.[28,31,36,96] The process involves the CM of the acyclic olefin CTA with the active chain-end. This route is metal-efficient since each catalytically active species generates multiple polymer chains, all end-capped by the desired FG. Adjusting the monomer and CTA stoichiometry nicely enables to control and tune the molar mass of the resulting end-functionalized polymer. *Cis*-alkenes are generally preferred CTAs because of their higher reactivity, while activated double bonds usually favor the CM. Thus, both protected and unprotected reactive FGs successfully gave acetoxy, amino, borane, (thio)carbonate, carboxylate, halide, pseudo-halide, hydroxyl, and cross-linkable epoxide or methacrylate telechelic polyenes/POs. In particular, commercially valuable hydroxyl

telechelic polyenes/POs were largely synthesized from acetoxy protected CTAs followed by a post-polymerization deprotection step.[31,36,119,120,121,122,123,124,125,126,127,128,129,130]

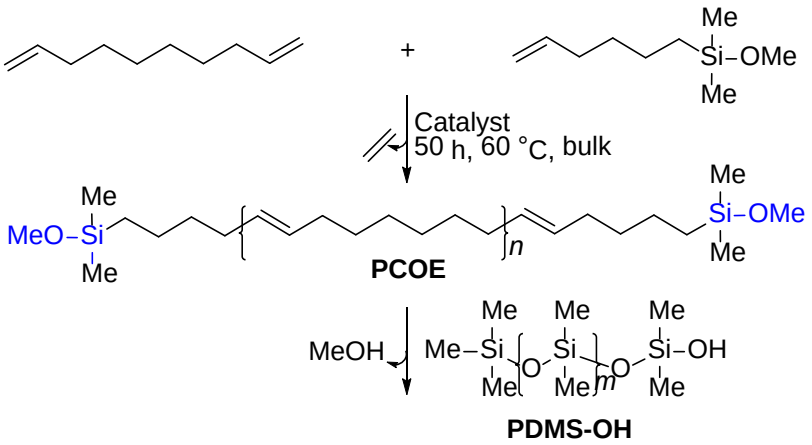
Sacrificial synthesis of telechelic polyenes/POs, a more recently established approach, involves the ROMP formation of a block copolymer composed by a first segment made of the desired monomer units end-capped by a first FG, and by an additional cleavable block issued from the polymerization of a readily degradable co-monomer bearing a protected FG. Subsequent deprotection then liberates this latter chain-end FG (Scheme 11). Hydroxyl-, carboxyl-, thiol-, amine functionalized ROMP polymers have thus been successfully prepared.[28,31,36,85,96,131,132,133,134,135] Besides from not being atom-economic, this method is limited to a few FGs and more suitable for short telechelic polymers, and it has thus not been extensively developed. To the best of my knowledge, no example of SMP has been reported from this approach.

Nowadays, chemical modification techniques and metathesis pathways have thus become equally viable routes towards the preparation of well-defined and finely tuned telechelic polyenes/POs. However, contemporary metathesis pathways remain more straightforward and convenient, and subsequently more explored. The most relevant alkoxysilyl telechelic polyenes/POs synthesized from olefin metathesis strategies are gathered in Table 1.

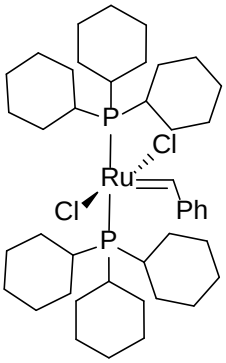
2.2.2. Synthesis of alkoxysilyl telechelic polyenes and polyolefins by ADMET

ADMET chemistry has been not so often used towards the preparation of alkoxysilyl telechelic polyenes/POs. A first example involved the synthesis of di(methoxydimethylsilane) telechelic polycyclooctene (PCOE) oligomers using Grubbs' ruthenium $Ru(Cl_2)(CH{=}Ph)(PCy_3)_2$ (**G1**, Figure 1) or Schrock's molybdenum $Mo(=CHCMe_2Ph)(N\text{-}2,6\text{-}iPr_2C_6H_3)(OCMe(CF_3)_2)_2$ catalysts in the ADMET polymerization of 1,9-decadiene, as reported by Wagener and coworkers (Scheme 12).[39] Having first evidenced that the $Si–OCH_3$

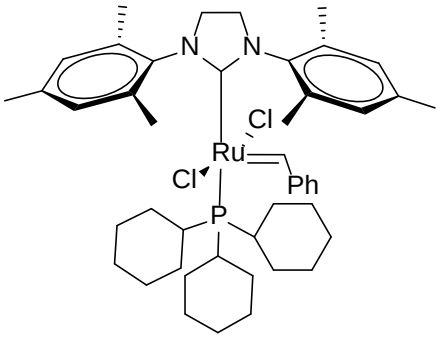
bond remained stable under typical ADMET conditions in the presence of the Ru or Mo catalyst, the 5-hexenylmethoxydimethylsilane monofunctional reagent was then used to terminate the propagation reaction (in bulk, 50 h, 60 °C), thus affording $(MeO)Si(Me)_2(CH_2)_4\{CH=CH(CH_2)_6\}_n(CH_2)_4Si(Me)_2(OMe)$ oligomers, as characterized by FTIR, ^1H, ^{13}C, and ^{29}Si NMR spectroscopies. The initial monomer-to-chain limiter ratio was shown to control the molar mass of the polymer as determined by NMR and SEC analyses ($1200 < M_{n,NMR} < 3500$ g.mol^{-1}, $Đ_M$ = 1.6–2.0). Subsequent condensation of these methoxysilyl terminated PCOEs with hydroxyl end-capped PDMS, $HOSiMe_2O\{SiMe_2O\}_nSiMe_3$, gave ABA triblock copolymers, thus demonstrating the difunctionality of these SMP oligomers.



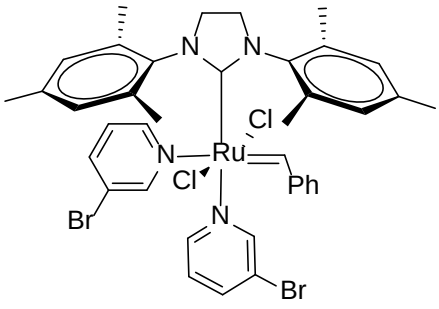
Scheme 12. ADMET synthesis of di(methoxysilyl) telechelic PCOE, and subsequent copolymerization with PDMS-OH.[39]



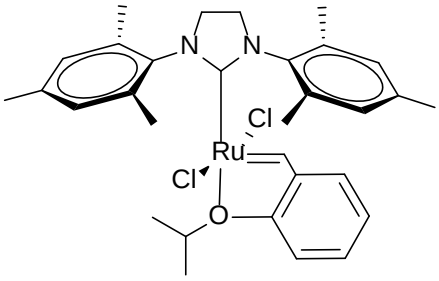
Grubbs' 1st generation catalyst
(G1)



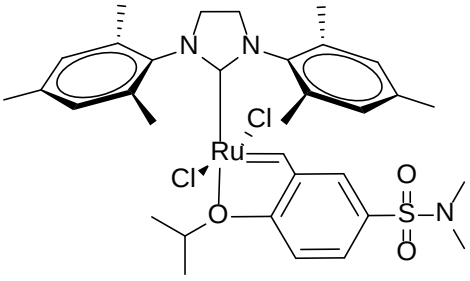
Grubbs' 2nd generation catalyst
(G2)



Grubbs' 3rd generation catalyst
(G3)



Hoveyda-Grubbs' 2nd generation catalyst
(HG2)

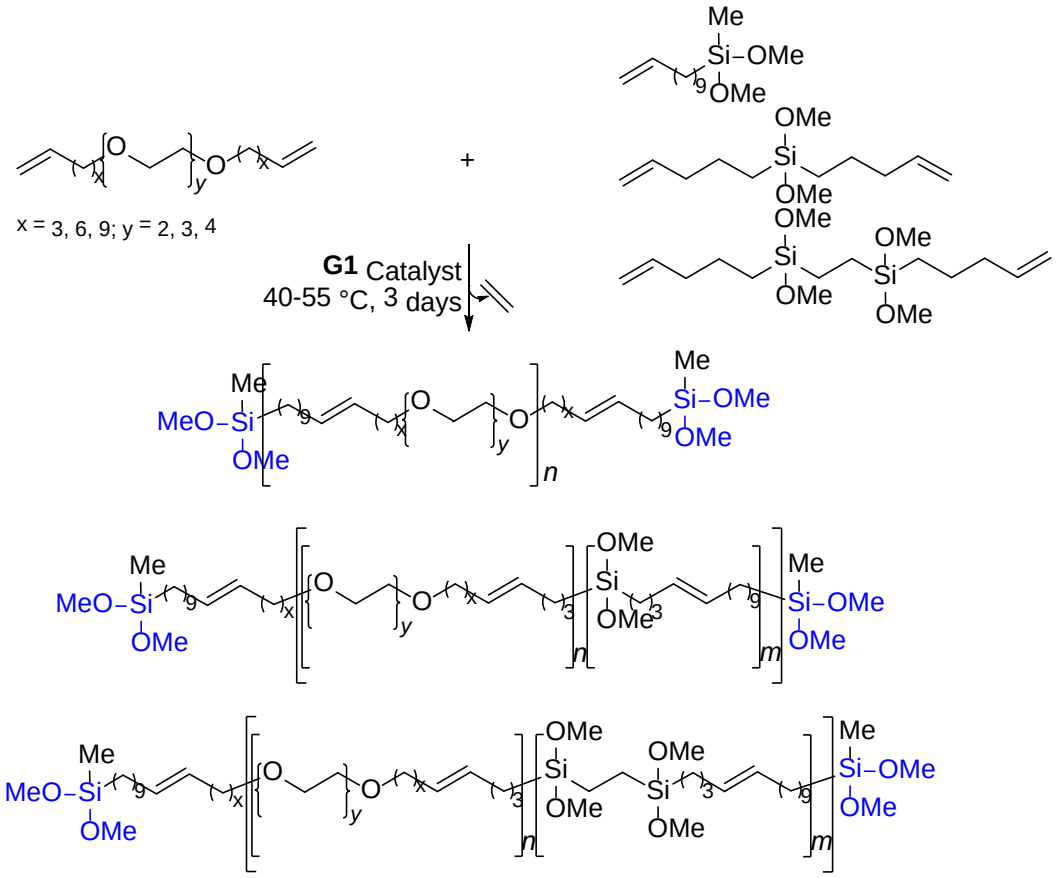


Zhan's catalyst
Zhan

Figure 1. Common Ru-catalysts used in olefin metathesis reactions.

Wagener and coworkers have described the synthesis, characterization, and thermal analysis of unsaturated ‘‘latent reactive’’ oligoether/carbosiloxane copolymers prepared via ADMET polymerization (Scheme 13).[44,45,46] Dimethoxymethylsilyl end-capped linear unsaturated polymers described as alternating $(AB)_n$ microblock copolymers of oligo(oxyethylene) and oligo(methylene), were prepared using Grubbs’ 1st generation catalyst (**G1**) under mild conditions (40–55 °C, 3 days). This involved a series of oligo(oxyethylene) α,ω-dienes monomers with different lengths of oligo(oxyethylene) and methylene spacers between the carbon–carbon double bond and the oligo(oxyethylene) unit, along with either the latent monofunctional reactive ‘‘chain-end’’ cross-linker 10-undecenyldimethoxymethylsilane, or one symmetrical ‘‘chain-internal’’ cross-linker, di(4-pentenyl)dimethoxysilane or 6,6,9,9-tetramethoxy-6,9-disilatetradeca-1,13-diene. Characterization of the resulting random copolymers ($30{,}700 < M_{n,SEC} < 51{,}750$ g.mol^{-1}, $Đ_M$ =

1.6–2.1) revealed a wide spectrum of properties (e.g.: T_g = –79.0 to –50.4 °C; T_m = –35.4 to 57.1 °C; T_d^5 (degradation temperature at 5% weight loss) = 227 to 314 °C)[44] dependent on both the length of oxyethylene segments and also on the length of carbon chains in between them. Exposure to moisture triggered the hydrolysis of methoxy groups, which underwent condensation reaction to provide chemically cross-linked materials that led to the formation of thermosets. The thermoset's mechanical response was varied from flexible plastic to purely elastic behavior, depending on the ratio of oligooxyethylene and carbosiloxane monomers within the different compositions.[44,45,46]



Scheme 13. ADMET synthesis of bis(dimethoxysilyl) telechelic polyether/carbosiloxane copolymers.[44,45]

These chain-end functionalized copolymers just described offered "latent reactive" methoxy-substituted carbosiloxane moieties randomly incorporated throughout the polycarbosiloxane backbone.[136,137,138] Hydrolysis of the chain internal methoxysilyl FGs in

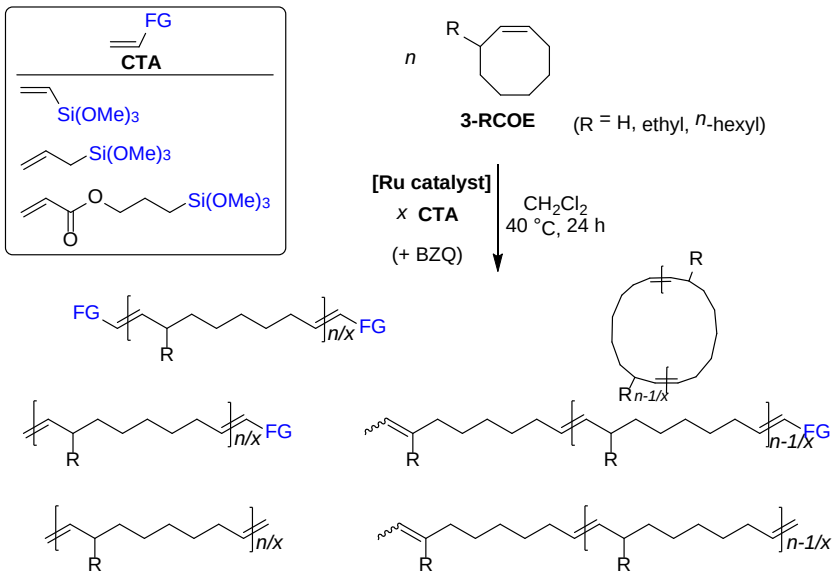
the presence of moisture and condensation led, in the absence of a curing catalyst, to the formation of stable siloxane linkages affording hybrid silicone thermoset materials.[46,139,140]

2.2.3. Synthesis of alkoxysilyl telechelic polyenes and polyolefins by ROMP/CM

Using the ROMP/CM synthetic routes, the straightforward introduction of reactive alkoxysilyl FGs towards the preparation of alkoxysilyl end-functionalized polyenes/POs was effectively achieved through direct metathesis using alkoxysilylalkene CTAs. The approach is quite versatile, provided the metal catalyst remains stable in the presence of the alkoxysilylalkene CTA, affording a series of alkoxysilyl telechelic (co)polymers.[27,28,36,141,142,143,144]

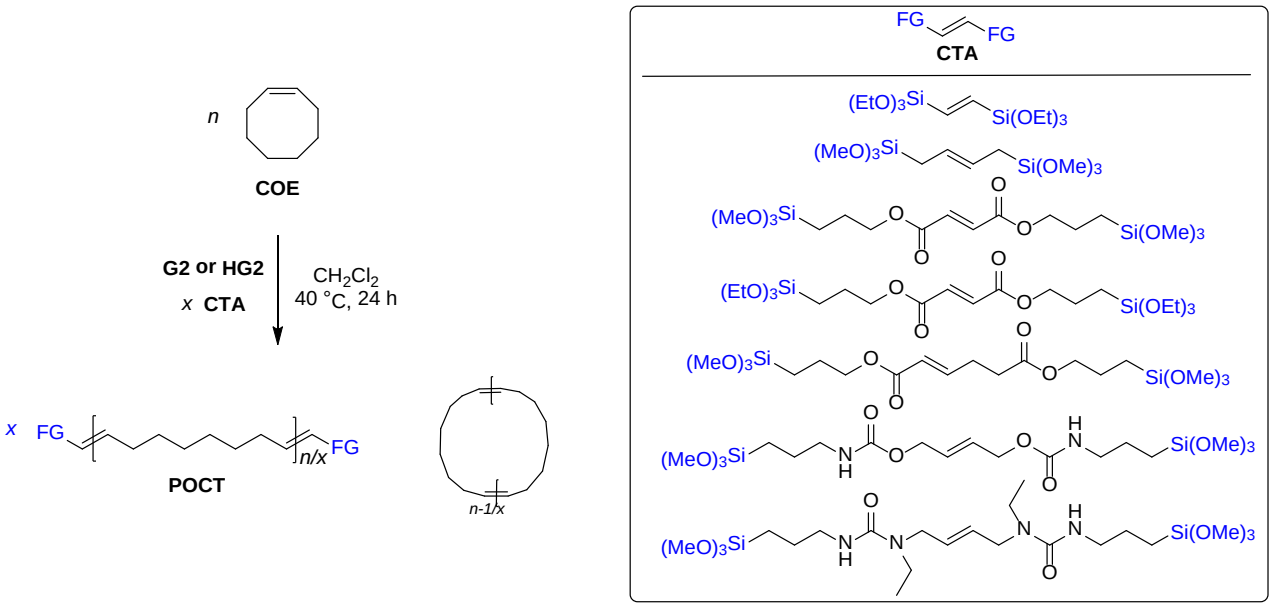
Using a set of mono(trimethoxysilylalkene) functional CTAs (vinyl trimethoxysilane, allyl trimethoxysilane, and 3-(trimethoxysilyl)propyl acrylate), the Ru-catalyzed ROMP/CM of cyclooctene (COE) and other 3-alkyl-substituted COEs (3-RCOEs, R = ethyl, *n*-hexyl) gave a statistical distribution of end-capped polymers ($M_{n,NMR}$ = 1300–39,000 g.mol^{-1}, $Đ_M$ = 1.25–1.85), including linear nonfunctionalized, isomerized linear nonfunctionalized, cyclic nonfunctionalized, α-monofunctionalized, isomerized α-monofunctionalized, and/or α,ω-difunctionalized PCOE, as reported by Guillaume and Carpentier and coworkers (Scheme 14).[70] A two-stage mechanism was proposed to involve first, the formation of alkoxysilyl monofunctionalized and non-functionalized (linear and cyclic) macromolecules through ROMP/CM and RCM processes. Next, the C=C isomerization combined with a second CM process would form the isomerized (linear non-functionalized and monofunctionalized) and difunctionalized macromolecules. The trimethoxysilyl chain-end functionalized polymers (mono-, isomerized mono-, di-functionalized) were recovered in larger amounts than the non-functionalized polymers (linear, isomerized linear, and cyclic), while the bis(trimethoxysilyl) functionalized PCOE remained a minor component, as demonstrated by ^{1}H, ^{13}C NMR, SEC and MALDI-ToF MS analyses and fractionation experiments. The influence of several

parameters (nature of the CTA, substituent on COE, catalyst, and to a lesser extent of the solvent) on the rate and selectivity of the reaction was studied. As anticipated, addition of 1,4-benzoquinone (BZQ) completely inhibited the isomerization process upon involving the Ru-hydride species (arising from the degradation of the Ru-alkylidene catalyst) accountable of this side reaction, in its reduction into 1,4-hydroquinone. Also, bulkier substituents on 3-RCOE monomers promoted the selective formation of monofunctionalized polymers, and Grubbs' 2nd-generation catalyst (**G2**) afforded the best compromise in terms of productivity (turnover numbers (TONs) up to 2,000 mol(COE).mol(Ru)$^{-1}$ and 200 mol(CTA).mol(Ru)$^{-1}$), reactivity and selectivity (in the presence of BZQ, CH_2Cl_2 at 40 °C, 24 h) in comparison to Hoveyda-Grubbs 2nd-generation catalyst (**HG2**), Zhan's catalyst (**Zhan**) (Figure 1), or some other specific Ru-carbene-alkylidene catalysts from Omega Cat Systems Company (Rennes, France).



Scheme 14. Ruthenium catalyzed tandem ROMP/CM of 3-RCOEs using monofunctional trimethoxysilyl-alkene CTAs, showing the structural diversity of the PCOEs.[70] Note that the degree of polymerization of each PCOE is only indicative, given the possible formation of side macromolecular species.

The similar ROMP/CM of COE using symmetrical bis(trialkoxysilyl)alkenes as CTAs then selectively (> 90wt%) provided α,ω-bis(trialkoxysilyl) telechelic PCOE along with a minor amount of cyclic non-functionalized PCOE ($M_{n,NMR}$ = 2100–16,400 g.mol^{-1}, $Đ_M$ = 1.4–1.9), as evidenced by NMR, MALDI-ToF MS, SEC analyses and fractionation experiments (Scheme 15).[71] Two methoxysilyl functional CTAs (namely $[(MeO)_3SiCH_2CH=]_2$ and $[(MeO)_3Si(CH_2)_3NHC(O)OCH_2CH=]_2$) were identified as the most efficient in terms of reactivity, catalyst productivity and selectivity (ca. 93%) towards the formation of the bis(trialkoxysilyl)telechelic PCOE, with **G2** and **HG2** catalysts giving the best compromise (vs. Grubb's third generation catalyst (**G3**), **Zhan** and Omega Cat System Company's catalysts) in terms of selectivity and productivity (TONs up to 95,000 mol(COE).mol(Ru)$^{-1}$ and 5000 mol(CTA).mol(Ru)$^{-1}$).



Scheme 15. Ruthenium catalyzed tandem ROMP/CM of COEs using difunctional trialkoxysilyl-alkene CTAs towards the formation of bis(trialkoxysilyl) telechelic PCOE.[71] Note that the degree of polymerization of each PCOE is only indicative, given the possible formation of side macromolecular species.

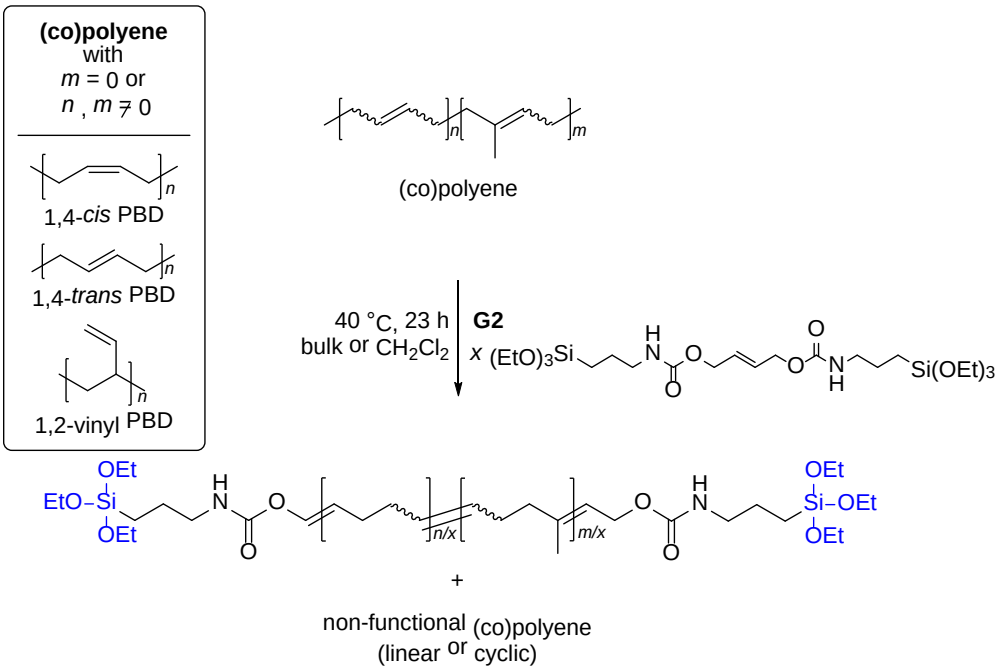
The same ROMP/CM/alkoxysilyl alkene CTA strategy was applied by the same authors to the preparation of α,ω-bis(trialkoxysilyl) telechelic copolyenes towards low

viscosity liquid polymer materials aimed at one-component adhesive applications.[72] 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)) was copolymerized (CH_2Cl_2, 40 °C -except for DCPD at 23 °C, 24 h) with a monocycloolefin (mOLF = COE, 1,5-cyclooctadiene (COD), or 1,5,9-cyclododecatriene (CDT)) using **G2** catalyst in the presence of bis(trialkoxysilyl)-functional symmetric acyclic alkenes $[(RO)_3Si(CH_2)_3NHC(O)OCH_2CH=]_2$ (OR = OMe or OEt) as CTA. A high selectivity toward the formation of the corresponding bis(trialkoxysilyl) telechelic copolyolefins (> 85wt%; only minor amounts of cyclic non-functionalized copolyolefins formed), and a high catalytic productivity (TONs up to 50,000 mol(comonomers).mol(Ru)$^{-1}$ and 1250 mol(CTA).mol(Ru)$^{-1}$) were established, as evidenced by fractionation experiments and detailed 1D and 2D ^{1}H and ^{13}C NMR spectroscopy and SEC analyses. The nature and the ratio of comonomers was shown to enable the tuning of thermal and rheological properties of the random copolymers, as evaluated by DSC and viscosimetric analyses. 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 (2.4 Pa.s), while copolymers with a 30–70mol% of NB-OLF were in a liquid state.

Finally, α,ω-bis(triethoxysilyl) telechelic PBD and poly(butadiene-*co*-isoprene) (P(BD-*co*-IP)) were also prepared from the functional CM degradation of commercial low molar mass (co)polydienes (PBDs or P(BD-*co*-IP)s with different chain-end FGs and amount of

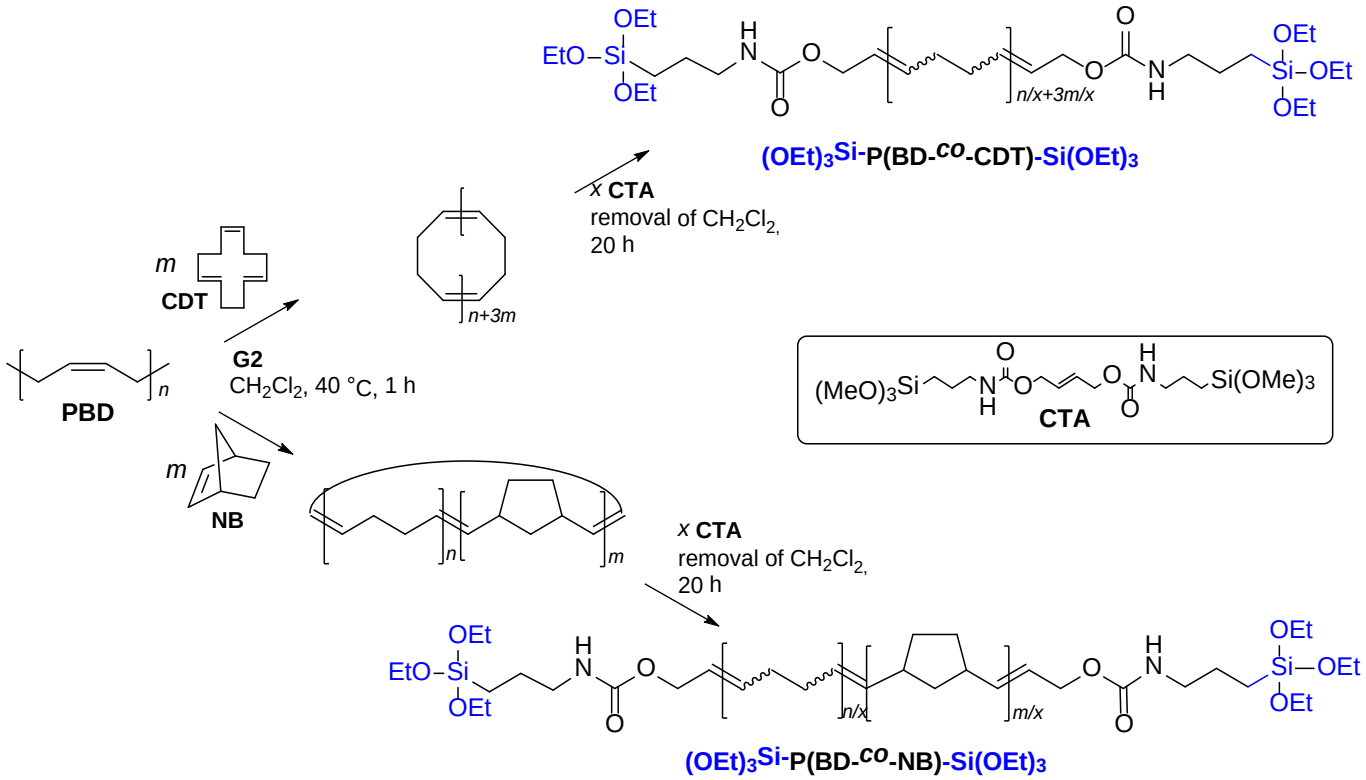
1,2-vinyl units) using **G2** catalyst in the presence of the acyclic symmetrical $[(EtO)_3Si(CH_2)_3NHC(O)OCH_2CH=]_2$ CTA, as reported by Guillaume and Carpentier and coworkers (M_n = 1500–24,000 g.mol^{-1}, $Đ_M$ = 1.6–2.8) (Scheme 16).[73] A high chemoselectivity (80–90wt% of the difunctionalized copolyenes as assessed by 2D NMR

analyses) and a high catalytic productivity (non-optimized TON up to 24,000 mol(P(BD-*co*-IP)).mol(Ru)$^{-1}$) were established. Interestingly, combination of the CM degradation of PBD with the ROMP of NB or CDT using **G2** catalyst in the presence of this same bis(triethoxysilyl)diurethane based CTA, successfully afforded the corresponding low viscosity liquid α,ω-bis(triethoxysilyl) telechelic copolyenes (658–29,000 Pa.s as evidenced by rheological analyses), poly(BD-*co*-NB) and poly(BD-*co*-CDT), respectively (M_n = 2400–14,700 g.mol^{-1}, $Đ_M$ = 1.5–3.0) (Scheme 17). In this case, the reaction was shown to proceed through the formation of cyclic polydiene intermediates, and the selectivity towards the ultimate difunctionalized copolyenes ranged from 41 to 97wt%. The low cost and easy handling of the PBDs and P(BD-*co*-IP)s, and the high productivity reached suggested possible industrial outcomes from such liquid α,ω-bis(trialkoxysilyl) (co)polyenes materials.



Scheme 16. Functional metathesis degradation reactions of PBDs (*m* = 0) or P(BD-*co*-IP) (*n* and *m* ≠ 0) (co)polymers using **G2** catalyst in the presence of a bis(triethoxysilyl)diurethane-based CTA towards the formation of bis(triethoxysilyl) telechelic polyenes.[73] Note that the

degree of polymerization of each PCOE is only indicative, given the possible formation of side macromolecular species.



Scheme 17. Functional PBD CM degradation via ROMP of CDT or NB using **G2** catalyst in the presence of a bis(triethoxysilyl)diurethane-based CTA towards the formation of bis(triethoxysilyl) telechelic copolyenes.[73] Note that the degree of polymerization of each PCOE is only indicative, given the possible formation of side macromolecular species.

Conclusion

Well-defined end-functionalized polymers are of major relevance for applied research. Whereas the modern metathesis approaches enable to straightforwardly access to alkoxysilyl telechelic polyenes/POs, SMPs have been traditionally synthesized from chemical modification routes (either ISF or PPF pathways). In this highlight we have provided an overview of the various strategies available to access to SMPs, emphasizing on the

opportunities provided by both ISF/PPF and metathesis reactions. Each of these general pathways described herein has its own advantages and limitations.

While PPF of already isolated/purified and well-defined polymers enables a good/easy control of the macromolecular structure, metathesis functionalization routes also allow to achieve a good control over the microstructure of the polyenes/POs. Besides, metathesis as well as ISF are beneficial one-pot methodologies easy to implement. The selectivity of the reactions is a key parameter to assess the formation of only alkoxysilyl telechelic polymers. Whereas, the quantitative conversion of chemical end-moieties through ISF or PPF procedures is essential to avoid the formation of a mixture of various alkoxysilyl end-functionalized polymers, the use of a difunctional alkene CTA in a tandem ROMP/CM appears as a valuable, mild and rather highly selective route to alkoxysilyl telechelic polyenes/POs. However, regardless of the approach, the stability of the polymer backbone and/or of its pending moieties (and of the catalyst as well in metathesis approaches) towards the FG to be introduced, is a major (if not the most prevalent) factor for the success of the alkoxysilyl end-functionalization. Relatively few scientific papers mention the hydrolysis/polycondensation of the alkoxysilyl end-groups of polymers. Yet this ultimate curing step from such alkoxysilyl functionalized pre-polymers towards CASE applications still remains to be more largely considered. In spite of the recent advances in the field of SMPs, investigations of their thermo-mechanical properties and their cured analogues, still remains to be further developed.

Conflicts of interest

There are no conflicts to declare.

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