Cross metathesis functionalization of polyolefins†

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A cross metathesis strategy is reported for the post-polymerization functionalization of the pendant vinyl groups present in a range of polyolefin architectures. This represents a general strategy for the synthesis of tailored random and block copolymers as well as homopolymers.
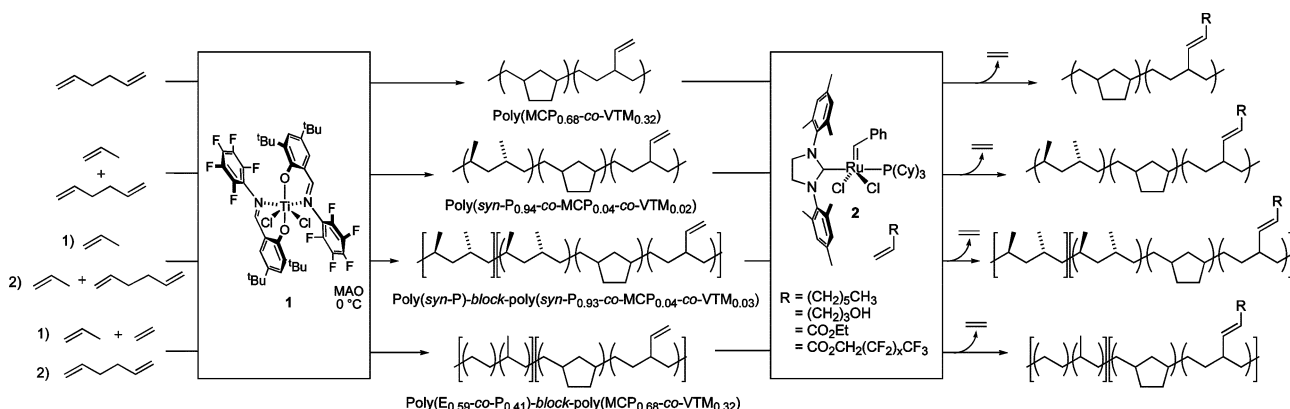
Over the last two decades, homogeneous polymerization catalysts have been used to produce polyolefins with unprecedented structural control. Advances in stereochemical control offer routes to polymers with precise organization of tacticity,[1,2] while the development of living catalysts has provided the means to synthesize polyolefins of defined sequence and molecular weight.[3] An inherent liability of most olefin polymerization catalysts is their inability to incorporate functionality that is often desired to modify polarity, dielectric properties, or chemical reactivity of a polymer. Functional polyolefins have been made by direct copolymerization of functional monomers with olefins,[4,5] and by post-polymerization reactions[6] of latent functional groups, such as vinyl groups or boranes, which do not react with the catalyst during polymerization.[7] Herein we report the post-polymerization modification of alkene-containing polyolefin architectures using cross metathesis (CM) functionalization.

The alkene is perhaps the most versatile latent functional group to allow post-polymerization modification. We recently reported that bis(phenoxyimine) titanium catalysts[8] incorporate 1,5-hexadiene with a secondary insertion/isomerization mechanism that leads to the incorporation of 3-vinyl tetramethylene (VTM) as well as methylenecyclopentane (MCP) units in the polymer (Scheme 1).[9] Using living titanium catalyst **1**,[10] well-defined random copolymers and block copolymers with propylene and 1,5-hexadiene were synthesized. The VTM units of these materials are readily functionalizable alpha-olefin structures that do not participate in crosslinking during polymerization. Unlike unsaturated polymers derived from butadiene, all of the unsaturation is pendant to the main-chain which can be essential for post-polymerization without chain degradation (*vide infra*). Small amounts of MCP and VTM units can be incorporated into copolymers while maintaining

the physical properties of the base polymer. For applications which require amorphous, low T_g functional polymers, poly(ethylene-*co*-propylene)-*block*-poly(MCP-*co*-VTM) diblock copolymers were synthesized to extend the range of available architectures (Scheme 1).‡

VTM units offer the opportunity to investigate various chemical methods for covalently attaching specific functionalities to polyolefin materials. As part of our functionalization studies we explored cross metathesis reactions of a range of commercially available alkenes with random copolymers (Table 1, entries 1–5) and block copolymers (Table 1, entries 6–8) with VTM units catalyzed by Grubbs' ruthenium carbene complex (**2**).[11] This catalyst system is remarkably tolerant of functional groups and is efficient for a variety of CM reactions. In our initial work we decided to focus our efforts on CM functionalization involving alkenes and acrylates (Table 1). 1-Octene provides a suitable model for introducing long-chain branching in the polymers (entry 1), while 4-penten-1-ol (entries 5 and 6) introduces polar functionality to the otherwise non-polar polymer. Ethyl acrylate (entries 2 and 3) was chosen as a way to add non-protic polarity. Fluorinated acrylates (entries 4, 7 and 8) were explored since fluorine facilitates phase separation from hydrocarbon polymers and decreases the index of refraction of the polymer.[12] The yields for the CM reactions of VTM containing polymers were determined based on the VTM vinyl ^{1}H NMR resonance at $\delta = 4.9$ ppm ($H_2C =$) relative to the product alkene resonances (Table 1). The yields were found to be strongly dependent upon the method used to remove ethylene from the reaction as well as the reaction time.§ At longer CM reaction times (> 12 h), cross-product yields were moderate ($\sim 50\%$) when ethylene was not removed from the solution, as expected. To drive the reaction towards the cross product, a 10-fold excess of alkene was used. Figure 1 shows the GPC traces before and after a CM reaction of 4-penten-1-ol with 2 mol% VTM units in a *syndio*-polypropylene copolymer (entry 5); no significant cross-linking or chain-degradation reactions occurred in this or other CM reactions. GPC chromatographs of functionalized poly(MCP-*co*-VTM)s (entries 1–4) showed changes in M_n but constant molecular weight distributions *versus* their unfunctionalized precursors, reflecting a change in hydrodynamic volume but no chain-degradation or cross-linking of the functionalized poly(α-

† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b3/b313954a/

Poly($MCP_{0.68}$-*co*-$VTM_{0.32}$)

Poly(*syn*-$P_{0.94}$-*co*-$MCP_{0.04}$-*co*-$VTM_{0.02}$)

Poly(*syn*-P)-*block*-poly(*syn*-$P_{0.93}$-*co*-$MCP_{0.04}$-*co*-$VTM_{0.03}$)

Poly($E_{0.59}$-*co*-$P_{0.41}$)-*block*-poly($MCP_{0.68}$-*co*-$VTM_{0.32}$)

R = $(CH_2)_5CH_3$
= $(CH_2)_3OH$
= CO_2Et
= $CO_2CH_2(CF_2)_xCF_3$

Scheme 1 Synthesis of various polymer architectures and cross metathesis functionalization reactions.

Table 1 Results for the CM reactions of VTM containing polymers with various olefins[a]

Entry	Polymer substrate	VTM/ mol%[b]	M_n (M_w/M_n)[c]	T_g/°C[d]	Alkene (equiv.)	Time/h	VTM conv./ mol%[b]	M_n (M_w/M_n) product	T_g/°C[d] product
1	poly(MCP-co-VTM)	32	191 000 (1.24)	−19.3	1-octene (10)	2.5	91	222 700 (1.24)[c]	−16.5
2	poly(MCP-co-VTM)	32	191 000 (1.24)	−19.3	ethyl acrylate (2)	2	50	138 300 (1.27)[e]	0.7
3	poly(MCP-co-VTM)	32	191 000 (1.24)	−19.3	ethyl acrylate (10)	7	90	143 200 (1.27)[e]	5.3
4	poly(MCP-co-VTM)	32	191 000 (1.24)	−19.3	2,2,2-trifluoroethyl acrylate (2)	2	45	234 000 (1.28)[c]	32.9
5	poly(syn-P-co-MCP-co-VTM)	2	267 700 (1.07)	0.4[f]	4-penten-1-ol (10)	2	45	267 900 (1.07)[c]	−0.5[f]
6	poly(syn-P)-block-poly(P-co-MCP-co-VTM)	0/3[g]	50 500 (1.12)/123 400 (1.12)[g]	−1.7[h]	4-penten-1-ol (10)	1	70	120 700 (1.12)[c]	−1.8[h]
7	poly(E-co-P)-block-poly(MCP-co-VTM)	0/32[g]	208 300 (1.12)/524 700 (1.13)[i]	−55.4/−19.8[g]	2,2,3,3,4,4,4-heptafluoro-butyl acrylate (2)	2	51	551 500 (1.15)[c]	−56.7/ 63.4[g]
8	poly(E-co-P)-block-poly(MCP-co-VTM)	0/32[g]	208 300 (1.12)/524 700 (1.13)[i]	−55.4/−19.8[g]	2,2,3,3,4,4,4-heptafluoro-butyl acrylate (10)	4	79	580 800 (1.14)[c]	−58.1/77.9[g]

[a] All reactions were run with 2 mol% of **2** at 55 °C. [b] Determined using ^{1}H NMR spectroscopy (vinyl *versus* alkane region). [c] GPC values (g mol^{-1}) are relative to polystyrene standards in 1,2,4-trichlorobenzene at 140 °C. [d] Determined by differential scanning calorimetry (DSC) (10 °C min^{-1}). [e] GPC values (g mol^{-1}) are relative to polystyrene standards in THF at 30 °C. [f] T_m = 120 °C. [g] Data for the first/second block of the copolymer. [h] T_m = 138 °C. [i] Data for the first block/entire diblock copolymer.
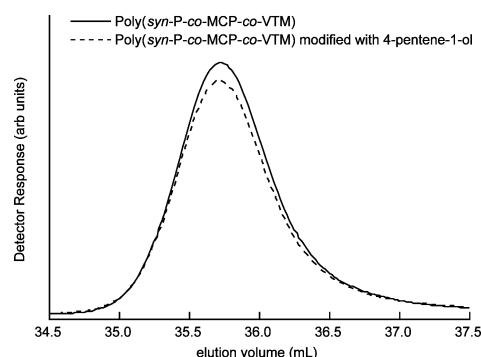
Fig. 1 GPC chromatographs (RI detector) for *syndio*-polypropylene (2 mol% VTM) and the product of the CM reaction with 10 equivalents of 4-penten-1-ol (entry 5).

olefin). From ^{13}C NMR data of poly(MCP-co-VTM),[9] adjacent as well as isolated VTM units are available to **2**. Since the adjacent 1,2 vinyl units of polybutadiene form cyclopentene units[13] in the presence of a ruthenium carbene complex, it is reasonable to expect the formation of cycloheptene units from adjacent VTM units in the poly(MCP-co-VTM) copolymer.¶ Clearly, the advantage of polymers containing VTM units over polymers where the unsaturation is derived from butadiene is the absence of main-chain alkene groups which results in cleavage of the polymer backbone.[13–15]

1-Octene is a model compound for the introduction of long chain branching onto the polymer backbone (entry 1). Similar CM reactions were successfully run with 1-hexene and 1-octadecene; other alkenes are under further investigation. In the case of these simple olefins as well as fluorinated acrylates (entries 4 and 7), the conversion increased as the boiling point of the alkene increased since it allowed the more efficient removal of ethylene.§ However, when the perfluoroalkyl chain on the acrylate was increased from trifluoroethyl to heptafluorobutyl, α,α,α-trifluorotoluene or 1,1,2-trichloro-1,2,2-trifluoroethane was required as a solvent to avoid polymer precipitation. In contrast, poly(MCP-co-VTM) became increasingly soluble in tetrahydrofuran after CM with ethyl acrylate (entries 2 and 3). CM reactions of the polymers containing crystalline *syndio*-polypropylene blocks generally proceeded in lower yield than amorphous polymers; we attribute this to partial crystallization in solution which impedes functionalization. Interestingly, the addition of fluorinated acrylates to the VTM units resulted in a significant increase in T_g for that block; trifluoroethyl acrylate gave a 52 °C increase in T_g, while the T_g increased 98 °C using heptafluorobutyl acrylate. Notably, Hillmyer and coworkers have reported that polydienes chemically modified with CF$_2$ groups gave a comparable increase in T_g.[12]

In summary, we propose the CM functionalization of alkene-containing polyolefins is a general strategy for the synthesis of functional polyolefin architectures. Our future work will explore the development of new alkene-containing polymers suitable for CM functionalization, as well as the modification of polyolefins with other functional groups.

Notes and references

‡ See Electronic Supplementary Information (ESI). T_m and T_g values were measured by DSC (10 °C min^{-1}).

§ A slight dynamic vacuum with periodic backfilling of N$_2$ afforded better removal of ethylene than a N$_2$ purge or a partial pressure of N$_2$.

¶ In the absence of a CM partner alkene, poly(MCP-co-VTM) crosslinked in the presence of **2**. In CM reactions, acrylates primarily gave *trans* CM products while α-olefins gave a mixture (~1 : 1) of *cis* and *trans* alkenes.[11]

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