Catalytic synthesis of functionalized (polar and non-polar) polyolefin block copolymers†

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Herein, we report a methodology for the synthesis of polyolefin containing block-copolymers using a catalytic postpolymerization modification strategy. The most common polyolefin grades are converted into macroinitiators using a cross-metathesis reaction. These functionalized polyolefins are then used to initiate living: coordinative ring opening polymerization of lactide, anionic ring opening polymerization of epoxide, and radical polymerization of styrene to yield the corresponding block copolymers. The high activity of the catalysts employed in the different steps offers improved practicality for scalable synthesis.

Introduction

Over the past few decades, block copolymers have emerged as a class of soft materials with a wide range of technological applications.1–3 Due to the high tunability of their chemical structure (morphology, architecture, and domain size), block copolymers have been utilized as surfactants, thermoplastic elastomers, nano-templates, membranes, etc.4 Controlled polymerizations such as ionic, controlled radical (ATRP, NMP, RAFT), and ring opening polymerizations have been the standard means for producing block copolymers.5 While these methods have proven successful, they lack the ability to homopolymerize the world’s two most produced and inexpensive monomers: ethylene and propylene.5,6

Polyolefins today are produced industrially via catalytic insertion (co)polymerization of ethylene, propylene, and linear α-olefins on the scale of 70 × 106 metric tons per year.5,7 The tunability of the polymer’s crystallinity offers a mixture of properties such as toughness, elasticity, solvent resistance, etc. which are difficult to reproduce economically by other monomers.6,8 Therefore, the incorporation of polyolefins into block copolymers is of great value, as it would further expand the usefulness of the largest family of polymers in our society. However, due to the high oxophilicity of the insertion metal catalysts used in industry, commercial polyolefin block copolymers have been limited to non-polar monomers, which also limits applications.6,7,9 Hence, the synthesis of functionalized block copolymers containing polyolefins remains a modern challenge for synthetic chemists.

Over the years, alternative approaches have been developed to synthesize functionalized polyolefin block copolymers.

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metathesis reaction between olefins and acrylates quantitatively converts the polyolefins into macroinitiators. In step 3, the living coordinative Ring Opening Polymerization (cROP) of lactide,24 anionic Ring Opening Polymerization (aROP) of epoxide,25 and Atom Transfer Radical Polymerization (ATRP) of styrene26 are employed to quantitatively synthesize the block copolymers from the polyolefin macroinitiators (Scheme 1). Finally, we also demonstrate the advantage of using exclusively catalytic reactions to synthesize olefin containing block copolymers by comparing the overall productivity of our process to previously reported strategies.

Prior to our work, other groups have employed post-polymerization modification techniques to convert vinylic terminated polyolefins into macrorinitiators. Hydrosilation,23 thiol-ene,24 hydroalumination25,26 and esterification27 reactions have been applied with moderate to high conversions. It is worth noting that these reactions were only performed on low molecular weight vinylic terminated polyolefins ($M_n < 5$ kg mol$^{-1}$). The non-quantitative conversion of most of these reactions and the exclusive reactivity toward the vinyl terminated polymers (which is catalyst dependent and often not the most common end-group) drastically restricts the impact of these previous methods. Additionally, in situ cross coupling compatibilization has been attempted by Duchateau et al. resulting in a process with less than 50% efficiency for producing the desired block copolymer.28 The approach reported here, aims to address these limitations by quantitatively converting mono and di-substituted alkene terminated polyolefins, of any molecular weight into block copolymers.

**Results and discussion**

A series of single site homogenous insertion catalysts were used to produce a polyolefin library containing HDPE, PP, LLDPE and HBPE (Chart 1).29–32 Two grades of linear polyethylene were synthesized. Low molecular weight linear polyethylene (l-HDPE) with an $M_n = 800$ g mol$^{-1}$ was produced from a phosphinosulfonate nickel catalyst,30 and serves as a model system since there is a high concentration of end-groups which eases the characterization of the product by NMR spectroscopy. While a higher molecular weight semi-crystalline HDPE (h-HDPE), $M_n = 18$ 000 g mol$^{-1}$, with an industrially relevant melting temperature ($T_m = 132$ °C) was produced from a phosphinosulfonate palladium complex.39 h-HDPE was implemented to show that the methodology is quantitative for various molecular weights and for a variety of polymerization catalysts. A bis(phenoxymine)titanium dichloride catalyst34 was implemented to synthesize the stereoselective synPP and LLDPE. Finally, a Pd-diimine catalyst32 was used to produce an amorphous polyethylene that we refer to as HBPE, with a comparatively higher molecular weight of $M_n = 89$ 000 g mol$^{-1}$. The molecular structure of this polymer makes it soluble at room temperature in most organic solvents which is advantageous for the characterization of the material as the low concentration of end-group makes it otherwise challenging to quantify conversion.

![Scheme 1](image) **Scheme 1** Generalized route for block copolymer synthesis.

As recently illustrated by Mecking et al., implementing a ruthenium catalyzed cross coupling metathesis represents an efficient approach to functionalizing amorphous polyolefins.34 However, in order to implement cross coupling metathesis for the functionalization of the full library of polyolefins, it was necessary to identify reaction conditions compatible with the elevated temperature (120 °C) necessary to solubilize semi-crystalline polyolefins. We found that by adding 1 mol% of Hoveyda–Grubbs II catalyst34 (HG-catalyst) simultaneously with a cross coupling partner, 2-hydroxyethyl acrylate (HEA) or 2-(2-bromoisobutyryloxy) ethyl acrylate (BIEA), over 30 minutes was highly effective for converting l-HDPE end groups. Slow feeding of the olefin metathesis catalyst was necessary to thwart its thermal deactivation. Fig. 1 presents the $^1$H NMR for l-HDPE, illustrating quantitative conversion (see ESI‡ Section 9 for sensitivity experiments) of both terminal (5.9 ppm and 5.0 ppm) and internal olefins (5.5 ppm).33

Next, we applied similar reaction conditions to the full library of polyolefins with only minor adjustments to HEA feed procedure depending on the ratio of internal to terminal double bonds present. Quantitative conversions of the polyolefin double bonds were achieved for all cross coupling reactions for all polyolefins as determined by $^1$H NMR (Table 1). Stacked spectrums for the different polymers can be found in the ESI‡ (S1–S8). The absence of internal olefinic double bonds in the $^1$H

![Chart 1](image) **Chart 1** Polyolefin library.
Acrylates are ideal coupling partners because electron de-coupling, but the homo-coupling product will be easily re-acted. Evidence of complete conversion of the macroinitiator was demonstrated by the total disappearance of the methylene protons adjacent to the hydroxyl group (3.8 ppm) in $^1$H NMR, was determined from GPC or HT-GPC. Determined from 1H NMR of precipitated polymer. Molecular weight too low for GPC analysis.

Table 1 Cross metathesis reactions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Polyolefin</th>
<th>Acrylate</th>
<th>Conv. (%)</th>
<th>$M_n$ (kg mol$^{-1}$)</th>
<th>$D^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>l-HDPE</td>
<td>HEA</td>
<td>Quant</td>
<td>0.9$^d$</td>
<td>—$^e$</td>
</tr>
<tr>
<td>1-2</td>
<td>h-HDPE</td>
<td>Quant</td>
<td>19</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>synPP</td>
<td>Quant</td>
<td>5.5</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>1-4</td>
<td>LLDPE</td>
<td>Quant</td>
<td>17</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>1-5</td>
<td>HBPE</td>
<td>Quant</td>
<td>95</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>1-6</td>
<td>l-HDPE</td>
<td>BIEA</td>
<td>Quant</td>
<td>1.1$^d$</td>
<td>—$^e$</td>
</tr>
</tbody>
</table>

$^a$ See ESI for conditions. $^b$ Determined from $^1$H NMR of precipitated product. $^c$ Mole fraction of polyolefin. $^d$ Determined from GPC or HT-GPC. $^e$ Unable to determine due to overlapping signals in the $^1$H NMR.

NMR spectrum at 5.5 ppm confirms that no polyolefin homopolymer remained (see ESI† Section 8 for homopolymer $^1$H NMR). The original polyolefins may participate in homocoupling, but the homo-coupling product will be easily re-activated and will eventually be paired with HEA. Moreover, acrylates are ideal coupling partners because electron deficient olefins are known to be slow at homodimerization. This is confirmed by our own experiments when we subjected only HEA to our reaction conditions and did not observe any homo-coupling product formation.

HEA-functionalized polyolefins were used as macroinitiators for cROP of lactide and aROP of tert-butyl glycidyl ether (tBuGE), while BIEA functionalized HDPE was used to initiate the ATRP of styrene (Table 2). The implementation of controlled polymerizations ensures that all polyolefin chains are converted into block copolymers and that no homopolymer is formed. We performed the immortal cROP of lactide on l-HDPE, h-HDPE, synPP, LLPDE, and HBPE (Table 2 entry 2-1 to 2-5). Sub-stoichiometric loadings of Sn(Oct)$_2$ were used to catalyze the cROP. Evidence of complete conversion of the macroinitiator was demonstrated by the total disappearance of the methylene protons adjacent to the hydroxyl group (3.8 ppm) in $^1$H NMR, Fig. 1.

To further showcase the versatility of our approach, we performed ATRP of styrene resulting in quantitative conversion of BIEA functionalized l-HDPE to yield l-HDPE-PS block copolymer (entry 2-6). Additionally, we carried out the immortal aROP of an epoxide monomer by using sub-stoichiometric amounts of KN(TMS)$_2$ (entry 2-7). However, to perform the acrylate polymerization, it was necessary to reduce the acrylate linker of l-HDPE-HEA into a primary alcohol to avoid side reactions. More advanced architectures can be achieved beyond simple diblock copolymers with this methodology. An example of this is a 3-miktoarm star. Star polymers have gained much attention in literature recently for their unique ability to yield highly asymmetric lamellae domains, which are not accessible by linear diblock copolymers. By cross coupling a polyolefin to a dual initiating coupling partner, one that contains an alcohol and 2-bromoisobutyrate functionality, both cROP of lactide and ATRP of styrene can be done resulting in a l-HDPE-PLA-PS 3-miktoarm star (Fig. 2). Efficient synthesis of the 3 arm star is demonstrated by the increase in molecular weight (GPC chromatograms in ESI Fig. 57†) after each step.

In addition to chemical versatility, our approach offers another significant benefit, productivity. The scalability of any material synthesis is a key consideration when thinking about applications. In which, one of the main limitations preventing the broader application of block copolymers comes from the overall low productivity of the living polymerization methods. They require using stoichiometric amounts of initiator per polymer chain and/or the use of expensive monomers/initiator. Our system addresses this limitation by implementing catalytic reactions and using industrially relevant monomers. We compared the productivity of our methodology to other...
and controlled radical polymerization\textsuperscript{43} make this system a powerful platform to generate a wide range of polyolefin containing materials. The use of highly active catalysts in each step of the process results in an overall process with unprecedented productivity lending itself to potential industrial applications.

Conflicts of interest
There are no conflicts to declare.

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Notes and references