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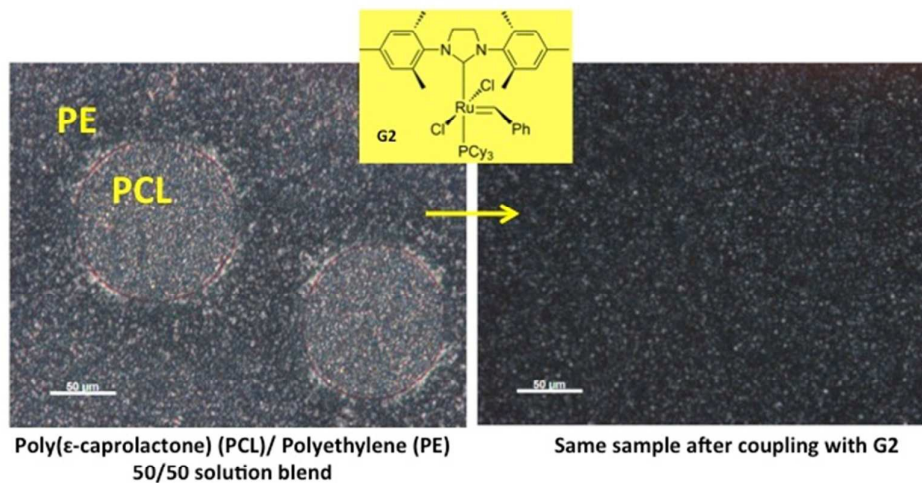
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**A whiff of diblocks is enough!** Straightforward coupling of two vinyl-terminated macromolecules was achieved by cross metathesis (CM) using Grubbs' second-generation catalyst (G2) giving access to a diversity of "self-compatible" polymer blends. Solution blends, in the absence of G2, showed clear macrophase separation while metathesized samples did not anymore. A small fraction of diblocks only proved to act as an excellent compatibilizer.



## *In-situ* compatibilisation of alkenyl-terminated polymer blends using cross metathesis

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Several compatibilised polyolefin-based blends have been obtained via rather simple and robust chemistry: olefin cross metathesis using Grubbs' second-generation catalyst (G2) of alkenyl-terminated macromolecules of different nature. The viability of the concept was first demonstrated for low molecular weight polyolefin macromolecules before being extended to higher molecular weight polymers, including polar ones such as poly( $\epsilon$ -caprolactone) (PCL), poly(pentadecalactone) (PPDL) and poly(methylmethacrylate) (PMMA). When taking all the possible cross metathesis reactions into account, a statistical distribution of homopolymers and diblock copolymers is likely to be formed. While clear macrophase separation is visible in the uncompatibilised blends of macromolecules, it is absent for the *in-situ* compatibilised products, as was confirmed by optical microscopy. It was demonstrated that even small amounts of diblock copolymers can effectively compatibilise the two phases. All materials were analysed by HT SEC, DSC, HT HPLC and optical microscopy. Such a proof of principle indicates that using cross metathesis on a large library of macromolecules might be a versatile "synthetic handle" to reach a variety of *in-situ* compatibilised blends.

### Introduction

From a practical point of view, straightforward blending of polymers allows tuning of material properties without resorting to building complex polymeric architectures. A wide variety of physical properties such as stiffness and toughness can in principle be realised by choosing the right composition of polymers. However, it is not only a matter of composition. The morphology of the polymer blend and how the material is processed is also of paramount importance. Mixtures of different types of polymers tend to macrophase separate, which leads to delamination and poor mechanical properties. In a two-phase morphology, the sizes, shapes, continuity of, and adhesion between the phases determine the properties. Therefore, control of morphology means control of properties. Diblock copolymers would be the ideal compatibilisers for these heterogeneous blends, since their presence would reduce the interfacial tension between the two phases and suppress coalescence. These compatibilised polymer blends are potentially at reach when diblock copolymers are produced *in-situ* by coupling unsaturated macromolecules using cross metathesis (CM). This approach therefore presents two major assets: 1) a broad variety of diblock copolymers can be synthesized given that a library of alkenyl-terminated polymers is available; 2) the tolerance of the metathesis catalysts to polar groups allows us to efficiently couple not only apolar polymers (*i.e.* polyolefins) but also polar ones.

Polyolefins containing unsaturated chain-ends are readily accessible since  $\beta$ -H or  $\beta$ -Me transfer to monomer is a common chain termination process for olefin polymerisation catalysts. Typical examples are: polyethylenes (HDPE, LLDPE),<sup>1,2</sup> ethylene/propylene copolymers (EP),<sup>3</sup> atactic polypropylene (*a*PP),<sup>4</sup> isotactic polypropylene (*i*PP),<sup>4a,5</sup> syndiotactic polypropylene (*s*PP),<sup>6</sup> but also isotactic polystyrene (*i*PS)<sup>7</sup> and others. Typically, the main use of these unsaturated macromolecules is as comonomers to be incorporated as medium and long chain branches by means of the "grafting through" approach, affording so-called *branch-block* copolymers.<sup>8</sup> These alkenyl-terminated macromolecules can also be used for further functionalisation.<sup>9</sup> Finally, they can be used to be coupled with other alkenyl-terminated polymers affording the corresponding block copolymers by cross metathesis, which is the topic of this paper. Alkenyl-terminated polar polymers are generally prepared using an unsaturated initiator and the appropriate polymerisation process.

To successfully couple alkenyl-terminated macromolecules, one has to rely on robust chemistry such as olefin metathesis. The success story of the development of  $L_2X_2Ru=CHR$ <sup>10</sup> has led to the high popularity for the very versatile, yet simple to carry out, metathesis reaction: a metal-catalysed redistribution of carbon-carbon double bonds. Thanks to the considerable increase in catalyst performance, the applications range from ring-closing metathesis (RCM), ring-opening metathesis polymerisation (ROMP) and acyclic diene metathesis

polymerisation (ADMET) to cross metathesis (CM). For example, olefin metathesis is increasingly being used as a tool to functionalise and polymerise plant oils to develop more sustainable polymers.<sup>11</sup> Although the extended use of metathesis in polymer chemistry has been reviewed,<sup>12</sup> some literature examples relevant to the framework of this study are summarized. These focus on ROMP's, ADMET's and CM's recent applications in the field of (functional) polyolefins. In this context, it is worth noting that various precision polyolefins have been successfully synthesised via step-growth ADMET, followed by extensive hydrogenation.<sup>13</sup> By carefully perturbing the size and the position of regularly spaced branches, they can serve as models for copolymers of ethylene with various  $\alpha$ -olefins. One can therefore isolate the effect of specific structural features and perform careful structural analysis. Random multi-block copolymers have been produced via segment interchange olefin metathesis.<sup>5</sup> It makes use of unsaturated polymers produced by ADMET on which subsequently CM is performed. The various segments of the two polymers, when treated with a compatible olefin metathesis catalyst, will interchange and eventually yield a random distribution of segments coming from both base polymers.<sup>14</sup> As a final example, it is now possible to conduct ADMET on diene monomers containing rigid cyclic structures, imparting good thermal stability.<sup>15</sup> When considering ROMP, beyond the synthesis of end-functionalised polynorbornenes,<sup>16</sup> highly branched graft copolymers were achieved via norbornene-terminated polymers.<sup>17</sup> Linear polyethylene (HDPE) block copolymers were also obtained by sequential ROMP of cyclooctenes<sup>18</sup> and functional LLDPEs (with functional groups along the polymer backbone) were accessed by copolymerisation of cyclooctene and substituted cyclooctene (followed by deprotection).<sup>19</sup> Recently, isotactic precision polyolefins by ROMP of an enantiomerically pure functional cyclooctene have even been reported.<sup>20</sup>

Here, we aim to evaluate qualitatively whether a variety of *in-situ* compatibilised polymer blends is accessible by coupling a fraction of the alkenyl-chain end groups of the polymers forming the blend using cross metathesis. To get insight into the effectiveness of the coupling reaction, this strategy was first applied as a proof of principle to low molecular weight polyolefins and was subsequently applied to higher molecular weight polymers. The morphology of the polymer blends was used as a tool to evaluate the efficiency of the block copolymers to function as compatibilizers.

## Experimental

### General considerations

All syntheses and manipulations of air and moisture sensitive compounds were carried out in an oven-dried Schlenk-type glassware on a dual manifold Schlenk line, a vacuum line (typically 1 mbar), or in a nitrogen-filled glovebox (typically <1.0 ppm of oxygen and moisture).

### Materials

All solvents and reagents were purchased from commercial sources (Sigma-Aldrich, BioSolve) unless stated otherwise. Toluene (Merck) was purified by passing over beds with BTS catalyst followed by molecular sieves (3 Å) and Selexsorb CD (BASF). The 2<sup>nd</sup> generation Grubbs catalyst, C<sub>46</sub>H<sub>65</sub>Cl<sub>2</sub>N<sub>2</sub>PRu (**G2**) was retrieved from Aldrich and was used without further purification. Pentadecalactone (PDL), and  $\epsilon$ -caprolactone ( $\epsilon$ CL) were freshly distilled from CaH<sub>2</sub> under nitrogen prior to use. 3-Buten-1-ol was degassed before use. N,N'-bis(salicylaldimine)-1,2-ethylenediamine aluminium ethyl ([Salen]AlEt) was synthesized using the procedure reported in the literature.<sup>21</sup> Methylmethacrylate (MMA, 99%) was passed over a column of activated basic alumina to remove the inhibitor. Azobis(isobutyronitrile) (AIBN) was recrystallised twice from methanol. The bis(methanol) complex of COBF, COBF(MeOH)<sub>2</sub> was prepared as described in the literature.<sup>22</sup>

### Synthesis of macromolecules

**HDPE 750 (1) and HDPE 1500 (2).** HDPE 750 (**1**) and HDPE 1500 (**2**) have been synthesized according to literature procedures.<sup>23</sup>

**aPP 1500 (3), aPP 5500 (4) and HDPE 18000 (5).** The polymerisations have been carried out in stainless steel PREMEX autoclaves, mounted on a semi-automated homemade polymerisation platform. The autoclaves with an internal volume of 125 mL were equipped with a mechanical stirrer (impeller), operated at 250 rpm. The reactors were dried by 4 cycles of nitrogen (10 min) and vacuum (5 min) with a jacket temperature of 130 °C. Toluene was dosed into the autoclaves. The temperature was then set to the desired value and after stabilisation of the system; ethylene was dosed into the reactors via Bronkhorst mass flow controllers. The pressure was set at 2 bar partial monomer pressure. After stirring the contents of the reactors for 30 min, 250 eq. of MAO (10 wt% Al, 0.25 mmol) were introduced via an automated injection unit. 30 min later, a 5 mL toluene solutions of Cp<sub>2</sub>ZrCl<sub>2</sub> (for **3** and **4**) or Cp\*<sub>2</sub>ZrCl<sub>2</sub> (for **5**) was injected into the reactor using the same injection unit. The pressure of the reactor was automatically kept at the selected partial monomer pressure. The reactor temperature was kept at the set point to within 1 °C by electrical heating and cooling with process water. After 1 h, the reactor was vented and the mixture was poured into a large volume of acidified ethanol, filtered and dried to constant weight at 70 °C under vacuum.

**PP 8000 (6).** PP 8000 (**6**) was synthesized according to the procedure reported in the literature.<sup>24</sup>

**PCL 9000 (7) and PPDL 15000 (8).** The vinyl end-capped poly( $\epsilon$ -caprolactone) (PCL) and poly(pentadecalactone) (PPDL) were synthesized by the addition of 3 g of  $\epsilon$ CL (26.5 mmol) or PDL (12.5 mmol), respectively, [Salen]AlEt (43 mg, 0.13 mmol), buten-1-ol (8.8 mg, 0.12 mmol) to toluene (3 g) in a 20 mL glass crimp cap vial under nitrogen, which was allowed to react overnight at 100 °C, after which full conversion (> 95 %) was confirmed by <sup>1</sup>H NMR analysis of the crude reaction mixture. Subsequently, the reaction mixture was dissolved in chloroform, precipitated in methanol, the precipitate was washed three times with methanol, and dried at 40 °C under vacuum.

**PMMA 11000 (9).** Methyl methacrylate was polymerised with AIBN in a round-bottom flask at 60 °C. MMA (50 g) in a flask sealed with a septum was deoxygenated in an ice bath by purging with nitrogen for 30 minutes. To a separate flask

provided with a stirring bar, 100 mg AIBN and 50 mg COBF were added. The flask was consecutively evacuated and purged with nitrogen three times. The monomer was added to the flask with AIBN and COBF. The solution was heated to 60 °C and the reaction was left with continuous stirring for 24 h. The PMMA **9** was isolated by pumping off the toluene. The macromonomer was dried in a vacuum oven at 60 °C for 24 h.

### Coupling reactions with G2

In the glovebox, a 50/50 mixture of the two macromolecules was added to a 20 mL crimp cap vial equipped with a magnetic stirrer bar and dissolved in toluene to make a ~3 % (in g polymer·mL<sup>-1</sup> toluene) solution. Typically, 200 mg scale reactions were conducted in 6 mL of toluene. The vials were sealed and subsequently placed in a temperature controlled carousel set at 100 °C. Once the polymers were dissolved, the required amount of **G2** catalyst stock solution was added (~1 mol %). All reactions were vigorously stirred under a flow of nitrogen for the whole duration of the reaction. After 12 h, the content of the vials was added to a large volume of acidified methanol, filtered on a Büchner funnel and dried in a vacuum oven overnight.

### Solution blending

The desired amounts of both samples were dissolved in 150 mL toluene at 110 °C in a round bottom flask equipped with a reflux condenser, under a nitrogen atmosphere. After complete dissolution, the mixture was precipitated in a large amount of cold methanol, filtered and dried to constant weight at 70 °C under vacuum.

### Characterisation

**High temperature SEC.** HT SEC was used to determine molecular weights. Analyses were performed on a Waters Alliance GPCV 2000 chromatograph equipped with three columns (three PL Olexis, 250 × 8.5 mm, Polymer Laboratories Ltd). Samples of 1 mg·mL<sup>-1</sup> were eluted with trichlorobenzene at a flow rate of 1 mL·min<sup>-1</sup> at 160 °C. Linear HDPE standards (PSS GmbH, Mainz, Germany) with an average molecular weight in the range of 5-1.500 kg·mol<sup>-1</sup> were used for calibration of the SEC columns.

**Thermal analysis.** Thermal analysis was conducted using a TA Instruments DSC Q1000. Approximately 4-5 mg of polymer were encapsulated in hermetically sealed aluminium pans and measured at a standard heating and cooling rate of 10 °C·min<sup>-1</sup> in a nitrogen atmosphere. Prior to recording the cooling and heating runs, the samples were held at 185 °C for 5 min to erase thermal history, then cooled at 10 °C·min<sup>-1</sup> to -20 °C. The sample was held at this temperature for 2 min and reheated from up to 180 °C at 10 °C·min<sup>-1</sup>. The reported melting temperatures are those obtained from the second heating.

**High temperature HPLC.** HT-HPLC was used to investigate the chemical composition distribution of the polymers. Samples were dissolved in 2-ethyl-1-hexanol for between 2-3 h and injected onto a Hypercarb column (100 × 4.6 mm, particle diameter 5 μm, Thermo Scientific) flushed with 2-ethyl-1-hexanol at 160 °C at a flow velocity 0.8 mL·min<sup>-1</sup> (98 μL sample loop). For all HPLC measurements a Polymer Laboratories Chromatograph PL GPC 210 system using a quaternary pump (Agilent Technologies) and a Polymer Laboratories PL-ELS 1000 evaporative light scattering detector

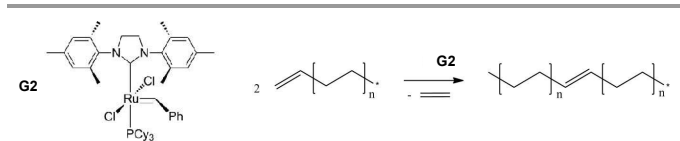
(ELSD). Three minutes after starting to pump, a linear gradient of 1-decanol and 1,2,4-trichlorobenzene was generated starting with 1-decanol and ending with pure 1,2,4-trichlorobenzene after 10 minutes. After pumping with pure TCB for 2 minutes, a further linear gradient from pure TCB to pure 2-ethyl-1-hexanol was undertaken over 2 minutes. Finally, the adsorption equilibrium of the column was re-established by pumping with pure 1-decanol for 20 minutes.

**Polarised optical microscopy.** POM was used to study the morphology. Samples were prepared by compression moulding a small amount of each material between two glass slides at 180 °C for 30 s and subsequent quenching in air. Optical micrographs were taken in polarised transmission mode with a Zeiss LM Axioplan optical microscope equipped with a Zeiss Axiocam camera and Linkam THMS 600 hot stage at a magnification of 20 × or 40 ×. Optical micrographs were obtained on samples with different thermal histories.

## Results and discussion

### Model studies: coupling of low molecular weight polyolefins

The schematics of the cross metathesis reaction performed as well as the structure of the catalyst used in this study are drawn below (Scheme 1). Two alkenyl-terminated polyolefins are coupled to each other under concomitant formation of ethylene (the condensate), which drives this dimerisation to completion.



**Scheme 1.** Cross metathesis reaction and structure of the 2<sup>nd</sup> generation Grubbs catalyst (**G2**) used in this study.

Grubbs' catalysts are transition metal alkylidene complexes that have the considerable advantage of tolerating functional groups. This is attractive to our purpose since it not only allows us to react alkenyl-terminated polyolefins with one another, but also with basically any other type of alkenyl-terminated polymer.

**Table 1.** Summary of molecular characteristics of the vinyl-terminated polyolefins used in the model studies

Sample	Macromolecule (MM)	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
1	HDPE 750	750	1,100	1.4
2	HDPE 1500	1,600	2,700	1.7
3	<i>a</i> PP 1500 <sup>a</sup>	1,500	2,600	1.7
4	<i>a</i> PP 5500 <sup>b</sup>	5,500	13,800	2.5

<sup>a</sup> <sup>1</sup>H NMR analysis revealed > 91.8 % vinyl end-groups, <sup>b</sup> <sup>1</sup>H NMR analysis revealed > 93.6 % vinyl end-groups.

The synthesis of diblock polymers by coupling of different vinyl-terminated macromolecules actually results in a statistical mixture of products. Basically, the two "homo-coupled" diblocks will also be formed, together with the desired "hetero-coupled" diblock. However, if the solubility (crystallisability) of the different blocks is contrasting enough, like it is the case

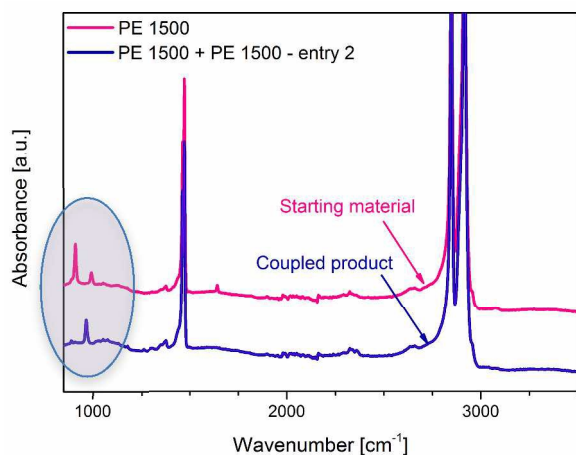
for a soft/hard diblock, one can in principle separate the products by solvent extraction leading to the isolation of the pure diblocks. First of all, low molecular weight alkenyl-terminated polyolefins have been used in the model studies to demonstrate the viability of the approach. The molecular characteristics of these macromolecules are listed in Table 1.

**Table 2.** Summary of molecular characteristics of the coupled products

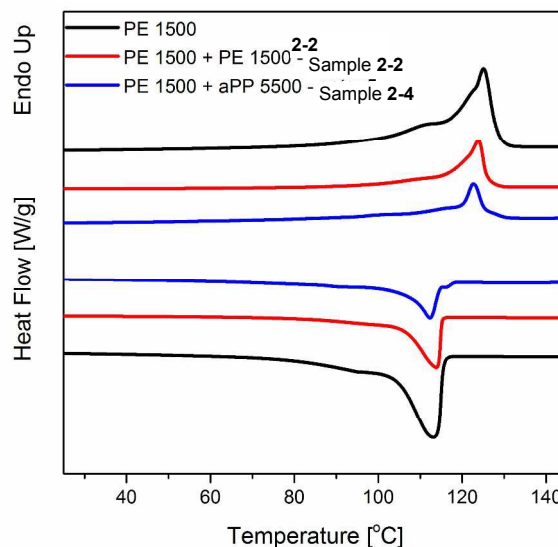
Sample <sup>a</sup>	MM1	MM2	$M_n$ ( $\text{g}\cdot\text{mol}^{-1}$ )	$M_w$ ( $\text{g}\cdot\text{mol}^{-1}$ )	PDI
1-1	HDPE 750	HDPE 750	1,400	2,400	1.7
2-2	HDPE 1500	HDPE 1500	2,300	3,900	1.7
4-4	aPP 5500	aPP 5500	6,800	15,000	2.2
2-3	HDPE 1500	aPP 1500	2,500	3,800	1.5
2-4	HDPE 1500	aPP 5500	4,600	8,700	1.9

Conditions: 6 mL toluene, 200 mg polymer, 1 mol% **G2**, 100 °C, 12 h.  
<sup>a</sup> Block copolymer names are composed of labels of macromolecules from Table 1.

First, three compositionally identical unsaturated model polymers were coupled (1-1, 2-2 and 4-4 in Table 2). Then, the CM on macromolecules that differ in molecular weight and nature was performed (2-3 and 2-4 in Table 2). Both the homo- and the hetero-coupling worked successfully. As shown above, when the two polymers were coupled, the molecular weights increased and the PDIs remained around or below 2. The high temperature SEC plots show in all cases a unimodal distribution. For block copolymers 1-2, 2-2 and 2-3, the molecular weight was almost double compared to the starting materials, which indicates a high conversion. At such a low molecular weight ( $M_n < 2,000$  g/mol) the concentration of the C=C double bonds is high enough to qualitatively follow the completion of the reaction by IR. An example of such an IR spectrum is shown in Figure 1.



**Figure 1.** IR spectra of starting material **2** in Table 1 and coupled product **2-2** in Table 2.



**Figure 2.** DSC thermograms of the starting material (HDPE 1500, **2**), the homo-coupled product **2-2** and the hetero-coupled to HDPE 1500 (**2**)/aPP 5.500 (**4**) product **2-4**. The reported curves are the second heating and cooling runs at 10 °C/min.

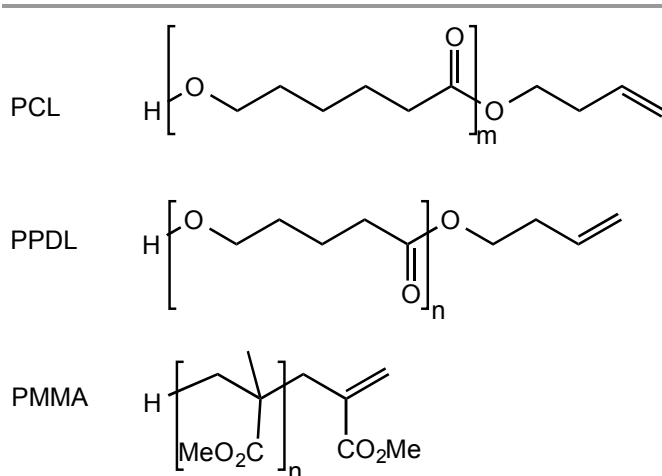
The starting monosubstituted alkene has characteristic bending vibration bands around 900 and 990  $\text{cm}^{-1}$ , whereas the disubstituted (trans) alkenes can be identified by a strong bending vibration band around 965  $\text{cm}^{-1}$ . The vibration around 1650  $\text{cm}^{-1}$  is a typical C=C stretching vibration which is much more pronounced vinylic groups than for internal olefins. Besides, the mixture of different coupled products (homo-/hetero-coupled) give a combined low intensity broad band. As for **4-4** and **2-4** in Table 2 though, the molecular weights of the coupled products were by far not as high as expected for full conversion. For example, consider the sample **2-4**, which is prepared by CM of **2** and **4**: one would expect **2-4**, **2-2** and **4-4** to be formed roughly in a 2:1:1 ratio leading approximately to an  $M_n$  of  $\sim 7,000$  g/mol, instead of the 4,600 g/mol obtained. This already gives a hint of the complex phase behaviour and therefore expected morphology of such blends, since they do not only consist of **2-4**, **2-2** and **4-4** block copolymers, but also non-reacted (short) **2** and **4** polymers. But since **2** and **2-2** as well as **4** and **4-4** will be miscible with the matrix material and are present in low concentrations compared to the matrix material, this does not have to be a problem for compatibilisation of **2** – **4** polymer blends.

A typical DSC plot is displayed in Figure 2. The melting temperatures ( $T_m$ ) as well as the crystallisation temperatures ( $T_c$ ) were unaffected by the coupling of two identical macromolecules (**2-2** in Table 2). The same is true for the melting enthalpy ( $\Delta H$ ), which remained constant when two crystalline HDPE 1500 (**2**) macromolecules were coupled to each other. Noticeably, the second endotherm around 111 °C present in the starting material was still observed for the homo-coupled product (**2-2** in Table 2). On the other hand, for the coupling of two different macromolecules (hard and soft, **2-4** in

Table 2), the  $\Delta H$  was dramatically depressed from 255 J/g in the pure HDPE (**2**) building block to 40 J/g when the same HDPE was coupled to the amorphous *a*PP 5500 (**4**). This can be correlated to the presence of a significant amount of amorphous (non crystallisable) fraction in the sample, part of which is tethered to the crystalline block and thus restricts the formation of crystalline domains. Besides, a decrease in  $\Delta H$  (thus crystallinity) could be the sign of block copolymers that undergo microphase separation in the melt (*vide infra*).  $T_m$  and  $T_c$  were significantly less affected though, keeping values around 125 °C and 113 °C, respectively, comparable to the values of the initial hard block. A scale up to 5 g of **2-2** proved successful and identical results were obtained. Still, there are still several questions concerning the melting behavior of the cross-metathesis product mixtures but these are out of the scope of this preliminary “proof of principle” study.

### Applicability to higher molecular weight macromolecules

In the previous section, it was demonstrated that coupling of alkenyl-terminated polyolefins of  $M_n < 5,000$  g/mol, can be achieved using **G2** catalyst in solution in toluene. Such block copolymers might function as compatibilisers of polymer blends by reducing the interfacial tension and suppressing coalescence, thereby giving rise to a finer morphology. However, in order to achieve interesting mechanical properties, the target molecular weight of the block copolymers has to be increased to a multitude of the entanglement density of the polymer (Table 3). In principle, altering the reaction temperature and catalyst concentration can regulate the molecular weight of the polyolefins. However, we did not intend to conduct such an extensive study, so only one macromolecule of each type was prepared, *i.e.*, an HDPE (**5**) and a poorly isotactic PP (**6**). Performing CM on a mixture of apolar and polar macromolecules containing alkenyl end groups gives rise to amphiphilic block copolymers with both hydrophilic and hydrophobic properties next to the corresponding homopolymers (both homo-coupled and unreacted ones), thus creating a “self-compatibilising” polymer blend. The more polar alkenyl-terminated macromolecules that were included in this investigation are poly( $\epsilon$ -caprolactone) (PCL, **7**, Scheme 2), poly(pentadecalactone) (PPDL, **8**, Scheme



**Scheme 2.** Structure of the PCL, PPDL and PMMA used in this section.

2) and poly(methylmethacrylate) (PMMA, **9**, Scheme 2). Since they are synthesized by ring-opening polymerisation (PCL, PPDL) and CCTP-radical polymerisation (PMMA), almost 100 % alkenyl-terminated chains can be obtained by choosing the right initiator. In these cases, the chain length can be regulated by simply adjusting the ratio of initiator to monomer. PCL is desirable because it is biodegradable, biocompatible and widely used in the biomedical field. Its low  $T_g$  and  $T_m$  are expected to improve the toughness and processing properties of the polyolefins in PCL – polyolefin blends. Some examples of polyolefin-PCL block copolymer synthesis have been reported in the literature.<sup>25-27</sup> PPDL, on the other hand, based on an eco-friendly monomer available in large quantities,<sup>28</sup> displays a crystallisation behaviour and crystal structure that reveals large similarities with HDPE.<sup>29</sup> Finally, PMMA is interesting because it is a widely used transparent engineering thermoplastic; a light weight and shatter-resistant alternative to glass that can replace polycarbonate when no extreme strength and toughness are necessary. PMMA-polyolefin block copolymers are interesting compatibilisers for PMMA – polyolefin blends, which for example would significantly improve the scratch resistance of polyolefins and the chemical resistance of PMMA. Several studies can be found in the literature as well.<sup>30-32</sup> The results of the coupling reactions with **G2** in toluene are presented in Table 4. Toluene was used as the common solvent to keep both vinyl-terminated macromolecules in solution, without poisoning the catalyst. Corresponding uncompatibilised blends, produced in solution in the absence of **G2**, were prepared for comparison purposes. The PDI values of the starting macromolecules were already higher than in the previous section and logically resulted in higher PDI values for the coupled materials. Besides, the increase in molecular weight of the coupled materials, compared to the starting materials, was not as significant as above (Table 3 vs. Table 4), indicating that the efficiency of the coupling reaction was far from optimal.

**Table 3.** Set of macromonomers used in this section

Sample	Macromolecule (MM)	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
<b>5</b>	HDPE 18000	18,300	45,800	2.5
<b>6</b>	PP 8000	7,600	17,500	2.3
<b>7</b>	PCL 9000	8,500 <sup>a</sup>	18,700	2.2
<b>8</b>	PPDL 15000	15,300 <sup>a</sup>	38,300	2.5
<b>9</b>	PMMA 11000	11,000 <sup>b</sup>	36,300	3.3

a) Those values were determined excluding the low molecular weight tail in the SEC trace, attributed to the presence of cyclics, b) Values reported against polystyrene standards.

**Table 4.** Characteristics of coupling reactions and solution blends

Sample	MM1	MM2	$M_n$ (g/mol)	$M_w$ (g/mol)	PDI
5-5 <sup>a</sup>	HDPE 18000	HDPE 18000	31,100	59,100	1.9
6-6 <sup>a</sup>	PP 8000	PP 8000	11,900	23,800	2.0
5-6 <sup>a</sup>	HDPE 18000	PP 8000	16,600	49,900	3.0
5-7 <sup>a</sup>	HDPE 18000	PCL 9000	16,100	39,300	2.4
5-8 <sup>a</sup>	HDPE 18000	PPDL 15000	25,600	51,200	2.0
5-9 <sup>a</sup>	HDPE 18000	PMMA 11000	24,700	61,800	2.5
5+6 <sup>b</sup>	HDPE 18000	PP 8000	11,800	40,100	3.4
5+7 <sup>b</sup>	HDPE 18000	PCL 9000	11,300	38,100	3.4
5+8 <sup>b</sup>	HDPE 18000	PPDL 15000	25,300	53,100	2.1
5+9 <sup>b</sup>	HDPE 18000	PMMA 11000	26,400	60,700	2.3

Conditions: 6 mL toluene, 200 mg polymer, 1 mol% **G2**, 100 °C, 12 h.

<sup>a</sup> Block copolymer names are composed of labels of macromolecules from Table 3. <sup>b</sup> Blend names are composed of labels of macromolecules from Table 3.

It is worth noting that HDPE 18000 (**5**) is highly crystalline, with a relatively high  $T_m$  and  $\Delta H$  whereas the poorly isotactic PP 8000 (**6**) did not display any endotherm in DSC at 10 °C·min<sup>-1</sup>. This is also true for the amorphous PMMA 11000 (**9**). For this reason, their coupling serves as crystalline/amorphous example, as opposed to the HDPE/PCL (**5-7**) and HDPE/PPDL (**5-8**) systems that both consist of two crystallisable blocks. Hence, the HDPE/PP (**5-6**) and HDPE/PMMA (**5-9**) coupling products showed only one endotherm during the second heating scan, whereas two endothermic peaks were observed for the HDPE/PCL (**5-7**) and HDPE/PPDL (**5-8**) systems. Similarly as in the previous section, the  $T_m$  as well as the  $T_c$  values were in most cases unaffected by the coupling reactions (Table 5). The parameter that varied the most, compared to the common HDPE block (**5**), was the crystallinity. The decrease in  $\Delta H$  was more pronounced for the blends than for the coupling reactions (not valid for the HDPE/PMMA combination). This observation might seem counter-intuitive since bigger microphase separation in the melt for the blends could provide more freedom for crystallisation to take place within the domains. However, a finer morphology for the coupled materials leads to more interface on which heterogeneous nucleation can occur.

Before proceeding to study the blend morphologies by optical microscopy to evaluate whether or not CM afforded well-compatible blends, HT-HPLC analyses at 160 °C were performed. This technique has only relatively recently been applied at high temperature for the microstructural analysis of polyolefins.<sup>33</sup> The separation is based on the interactions of the polymer samples with a stationary phase (Hypercarb column). The macromolecules can be selectively adsorbed and desorbed by the application of a gradient of solvent (from 100% 1-decanol to 100% trichlorobenzene (TCB)). This analysis technique was performed for the first time on PCL and PPDL and it was found that both polymers adsorbed from 1-decanol

**Table 5.** Thermal properties of the higher molecular weight materials, their combinations and blends as obtained from DSC (2<sup>nd</sup> heating and cooling scans at 10 °C/min)

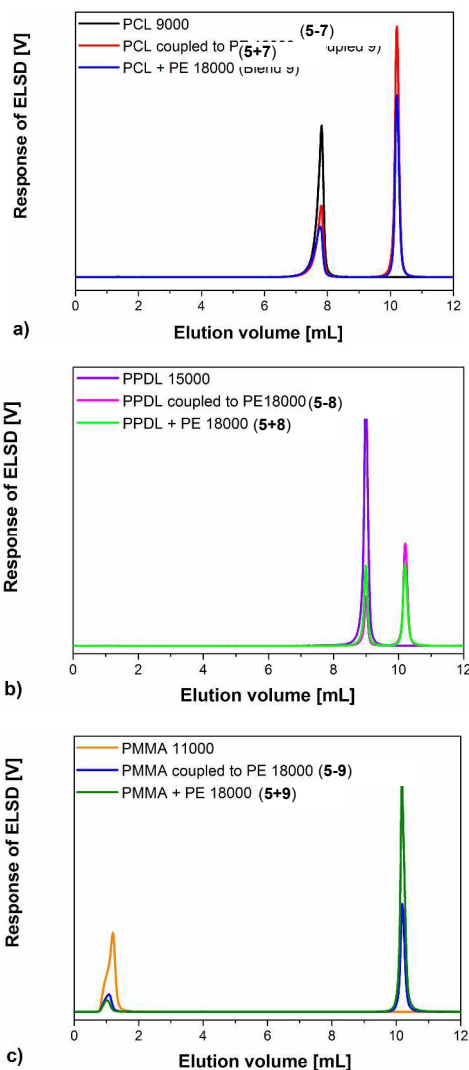
Sample	MM1	MM2	$T_m$ (°C)	$T_c$ (°C)	$\Delta H$ (J/g)
5	HDPE 18000	-	130.8	115.2	216.8
6	PP 8000	-	-	-	-
7	PCL 9000	-	57.2	34.0	65.4
8	PPDL 15000	-	95.8	77.9	113.2
9	PMMA 11000	-	-	-	-
5-6	HDPE 18000	PP 8000	129.5	115.9	144.7
5-7	HDPE 18000	PCL 9000	58.5	41.5	36.6
			129.9	116.2	123.9
5-8	HDPE 18000	PPDL 15000	95.0	82.8	64.4
			129.0	115.8	82.5
5-9	HDPE 18000	PMMA 11000	129.3	116.2	138.8
5+6	HDPE 18000	PP 8000	130.2	116.8	104.4
5+7	HDPE 18000	PCL 9000	56.7	37.3	38.5
			130.0	116.8	84.4
5+8	HDPE 18000	PPDL 15000	94.3	80.2	58.5
			129.4	115.8	78.2
5+9	HDPE 18000	PMMA 11000	129.2	115.8	161.5

and were eluted only after the addition of TCB into the mobile phase (Figure 3). PMMA, on the other hand, was not adsorbed at all and eluted immediately from the column. PMMA-based systems were explored before but at lower temperature.<sup>34</sup> PE 18000 (**5**), as demonstrated in the literature, adsorbed on the column and eluted in the gradient of 1-decanol–TCB. One would expect that the diblock copolymers would elute between the peaks of the polar blocks (PCL, PPCL and PMMA) and HDPE. However, according to the chromatograms, the peaks that would correspond to the diblock copolymers are not present in detectable amounts. The reason for not detecting the diblock copolymers will deserve further investigations, however, the first explanation that comes to mind is that the diblock copolymers are basically formed in too low quantities to be detected by this technique. Another possible explanation could be that the adsorption behaviour is strongly dominated by one of the blocks, although this seems less plausible since both blocks have an  $M_n$  of around 10,000 g·mol<sup>-1</sup>. In fact, in HPLC the adsorption is very dependent on the sorbent/solvent selection and tuning these parameters could certainly optimise these HT-HPLC results. Subsequently, investigations by polarised optical microscopy (POM) were conducted and proved to be particularly informative in terms of morphology of the different combinations. The images of uncompatibilised blends and the corresponding samples where **G2** was added to *in-situ* compatibilise the blends are shown in Figures 4 to 7.

For most of the systems (except HDPE/PMMA **5-9**), the uncompatibilised blends were macrophase separated with a domain size between 50 and 100 μm. Strikingly, however, this phase separation was absent for the metathesised samples. This observation confirms that, although the block copolymer

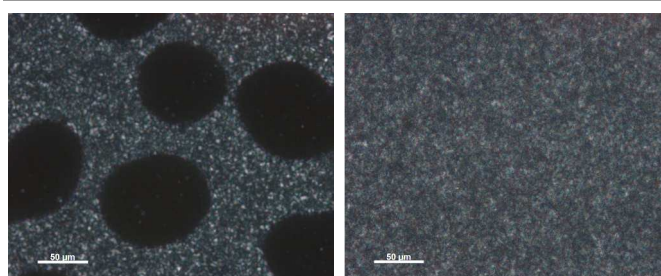


concentrations were too low to be detected by HT HPLC and SEC, CM allows the preparation of sufficient amounts of high molecular weight block copolymers to efficiently overcome the strong segregation strength between the constituting phases resulting in an *in-situ* compatibilised blend.

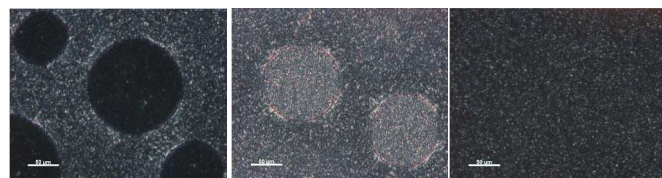


**Figure 3.** HT HPLC profiles of the combinations of a) HDPE/PCL, b) HDPE/PPDL and c) HDPE/PMMA.

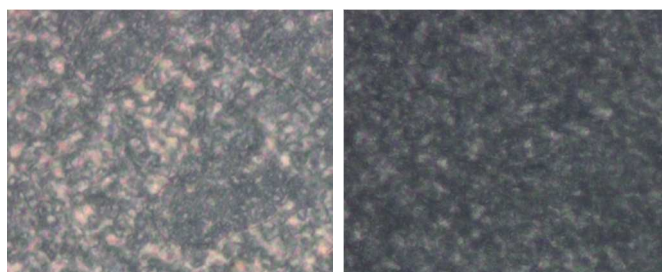
Going into more details, the first example corresponds to the HDPE/PP combination (5-6 in Table 4), where the hard HDPE 18000 and the soft PP 8000 were blended and coupled. The blend resulted in clearly separated crystalline and amorphous domains, whereas no segregation was observed in the *in-situ* compatibilised blend. The second example deals with the combination of HDPE 18000 and PCL 9000 (5-7 in Table 4), which both are crystalline. Again, the blend displayed macrophase separated domains. In this case, the HDPE crystallises first (Figure 5, left), followed by the PCL that in turn crystallised upon cooling below  $\sim 40$  °C (Figure 5, middle). This segregation was not observed for the sample



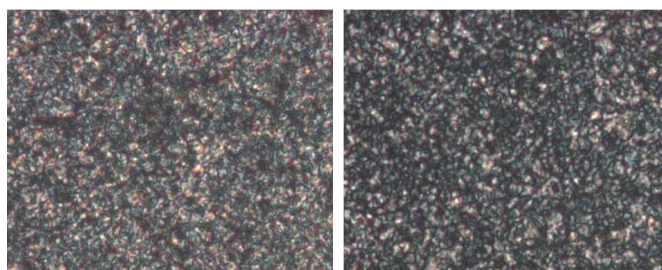
**Figure 4.** Optical micrographs of the HDPE/PP system: [left] uncompatibilised blend of 5+6 vs. [right] compatibilised blend 5-6, obtained after the following thermal history: heated to 160 °C (at 50 °C·min<sup>-1</sup>, held for 5 min) then cooled to RT at 10 °C·min<sup>-1</sup>. Black spheres is aPP.



**Figure 5.** Optical micrographs of the HDPE/PCL system: [left and middle] uncompatibilised blends of 5+7 vs. [right] compatibilised blend 5-7, obtained after the following thermal history: heated to 160 °C (at 50 °C·min<sup>-1</sup>, held for 5 min) then cooled to RT at 10 °C·min<sup>-1</sup>. Spheres are PCL.



**Figure 6.** Optical micrographs of the HDPE/PPDL system: [left] uncompatibilised blend of 5+8 vs. [right] compatibilised blend 5-8, obtained after the following thermal history: heated to 160 °C (at 50 °C·min<sup>-1</sup>, held for 5 min) then cooled to RT at 10 °C·min<sup>-1</sup>.



**Figure 7.** Optical micrographs of the HDPE/PMMA system: [left] uncompatibilised blend of 5+9 vs. [right] compatibilised blend 5-9, obtained after the following thermal history: heated to 160 °C (at 50 °C·min<sup>-1</sup>, held for 5 min) then cooled to RT at 10 °C·min<sup>-1</sup>.

made in the presence of **G2** (Figure 5, right), again demonstrating the effective *in-situ* compatibilisation of a blend of immiscible alkenyl-terminated polymers using **G2** as CM catalyst. Next, the case of HDPE/PPDL (**5-8**) was studied (Figure 6). Besides their resembling low polarity, these two polymers are very similar in terms of chain arrangements in the crystal structure (this is also true for PCL).<sup>35</sup> The pseudo-orthorhombic monoclinic unit cell of PPDL resembles that of HDPE albeit that its dimensions are slightly larger than for HDPE (and similar to PCL). In fact, the physical properties of PPDL, a polyester that contains 14 methylene units between each ester group, are somehow intermediate between those of PCL and HDPE.<sup>36</sup> This notwithstanding, macrophase separation was still observed in the uncompatibilised blend. Whether this is the result of the chemical difference or a difference in viscosity of the two polymers is not clear. Conversely, the *in-situ* compatibilised, partly coupled, mixture showed a much more homogeneous morphology with much smaller phases. Unexpectedly, despite their significant difference in terms of polarity, the uncompatibilised HDPE/PMMA blend (**5-9**) portrayed no obvious macrophase separation when observed in POM (Figure 7). What is observed does not depend on sample location as it was all checked and homogeneous. Actually, no distinction could be made between the solution blend and the coupled material on a 50-100  $\mu\text{m}$  scale. Taken into account the results for the other combinations above, it seems unlikely that this would be due to the too low molecular weight of the macromolecules used. Possible explanations could be that the vitrification of PMMA suppresses the phase separation because the sample was heated above the  $T_g$  of PMMA ( $\sim 100$  °C) or that the phase separation occurs at lower length scale (nanoscale), as reported for some HDPE-PMMA block copolymer in the literature.<sup>37</sup> SEM and TEM analysis should give a better picture of the macro- and microphase separation in the uncompatibilised polymer blends. Nevertheless, the POM measurements reported here give qualitative proof of principle of *in-situ* compatibilisation of blends consisting of non-miscible alkenyl-terminated polymers by means of cross metathesis.

## Conclusions

The present study intended to provide prove of principle of using CM to access a diversity of *in-situ* compatibilised polymer blends. This was achieved by coupling of two alkenyl-terminated macromolecules. The cross metathesis is a random coupling process. Assuming that during the coupling reaction at elevated temperatures a homogeneous melt or solution of the olefin-chain end-functionalized polymers is achieved, statistically 50% of the product will be the desired compatibilizer. Although this is a limited amount, the facile process and good miscibility of unreacted and homo-coupled products in either of the two phases makes this approach a very simple and effective one. Separation of one of the homopolymers by extraction with a proper solvent would in principle be possible, but for the application as compatibilizers, this is not necessary at all: each of the homopolymers

(unreacted and homo-coupled product) will dissolve in either the matrix or the dispersed phase of the polymer blend. Only the hetero-coupled product will be located at the interface of the two phases and will function as a compatibilizer for the two polymers forming the blend.

Model studies on low molecular weight polyolefins provided the ground for further experiments using higher molecular weight. However, the high molecular weight, *i.e.* low concentration of reactive groups and increased mass transfer limitation and phase separation, dramatically hampers the coupling reaction rate. For the low molecular weight macromolecules, a significant increase in  $M_n$  after coupling was detected by HT SEC. At higher molecular weight though, the HT SEC, DSC and HT HPLC results revealed only small dissimilarities between the metathesised samples and their solution blends. However, striking differences arose from optical microscopy. Although the effectiveness of the coupling reaction was maybe not as high as hoped for, the small fraction of diblock copolymers formed proved to act as an excellent compatibiliser. In the hypothesis that one manages to obtain a rather large library of vinyl-terminated macromolecules (in terms of block length and properties, *e.g.* polarity,  $T_g$ ,  $T_m$ ), this strategy to produce compatibilised blends of immiscible polymers can be extremely versatile.

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## Notes and references

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