Hypovalent substrates in transition metal catalysis: C-H bond functionalisation, ring-closing reactions & polymer synthesis
Olivos Suarez, A.I.

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Chapter 6

Rh-Mediated C1-Polymerisation: Copolymers from Diazoesters and Sulfoxonium Ylides.

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Abstract

In this chapter, we present our investigations of Rh-catalysed C1 (co)polymerisation reactions using carbene units as monomers. We demonstrate here, for the first time, the use of transition metal catalysts in carbene polymerisation using sulfur ylides as the carbene monomer precursors. Furthermore, we show that it is possible to generate unique diblock copolymers from sulfoxonium ylides and diazoesters as the respective carbene monomer precursors. This constitutes an entirely new approach to the synthesis of functional copolymers. The copolymerisation reactions were successful, and high $M_w$ poly(methylene)-poly(ester)-carbene copolymers were obtained with a diblock-syndiotactic microstructure in decent yields. These copolymers can be used as blending agents to mix polyethylene (PE) or polymethylene (PM) with poly(ethyl 2-ylidene-acetate) (PEA). The copolymer properties are highly dependent on the functional-group content. Model studies and investigations on the influence of the catalyst structure on the obtained polymer yields provide insights into the catalyst activation and deactivation processes operative under the applied reaction conditions.
6.1 Introduction.

Polymers bearing polar functionalities are an important class of materials due to their beneficial properties with respect to adhesion, paint/printability and miscibility. Industrial attention on the production of such polymers is almost entirely focused on polymerisation of vinylic monomers (C2 monomers). However, despite the obvious advantages in terms of availability and cost aspects of vinylic monomers, these C2 polymerisation techniques also have some important limitations. Examples are the poor stereocontrol of radical polymerisation reactions, the generally low reactivity of alkenes (especially ethylene) towards radical polymerisation (hampering copolymerisation reactions), and difficulties in preparing stereoregular (co)polymers from coordination-insertion polymerisation of functionalised olefins with (late) transition metals. Synthesis of (highly) syndiotactic and isotactic (rich) homopolymers of a variety of polar vinyl monomers is possible via living coordination-addition polymerisation (metal-controlled anionic polymerisation or ‘group-transfer’ polymerisation). However, these systems also have limitations, among which are the ‘stoichiometric’ living character of these reactions (instead of true a catalytic turnover) and limitations in polymerisation of 1,2-bis-functionalised C2 monomers.

C1 polymerisation (carbene polymerisation) offers an interesting alternative synthetic approach to polymers that are currently not available via more traditional C2 polymerisation, especially if densely functionalised stereoregular (co)polymers are desired. Polymerisation of functionalised C1 monomers is a powerful tool to obtain functionalised polymers with a large structural diversity. Up to now, only a few reports (including diazo compounds and ylides) have shown the ability of achieving such polymerisation reactions. The most important examples report the use of carbenes from either diazo compounds or sulf(oxo)nium ylides as the C1 monomer precursors (Scheme 1). The recently reported rhodium-mediated carbene polymerisation reaction developed in our group allow the formation of high $M_w$ and highly stereoregular polymers.
that are functionalised with ester moieties at every carbon atom of the polymer backbone in good yields.\textsuperscript{7} Other interesting examples are the boron-mediated polyhomologation techniques developed by Shea and co-workers, using sulphur ylides as monomers, which makes possible to prepare polymers with precise control over the nature of the end-group functionalities.\textsuperscript{9} To the best of our knowledge, transition metal-catalysed C1 polymerisation reactions using sulfoxonium ylides as monomers were thus far unknown.

A common feature of these reactions is that the applied C1 monomers, diazo compounds and sulfoxonium ylides, can be both considered as carbene precursors (Scheme 2). Hence, a combination of these reagents with a suitable C1 polymerisation catalyst may allow preparation of co-polymers having both polar functionalised (:CHR) and non-functionalised (:CH\textsubscript{2}) C1 monomers incorporated in the polymer carbon-chain. Such reactions would provide an interesting alternative to the use of diazomethane in carbene copolymerisation reactions.\textsuperscript{10}

The boron homologation reactions reported by Shea and coworkers are not compatible with the use of polar functionalised reagents. Attempts to (co)-polymerise sulfoxonium ylides and ethyl diazoacetate (EDA) with a boron catalyst leads to catalyst deactivation already after the second ‘functionalised carbene’ insertion step.\textsuperscript{9e} Transition metal catalysts, especially Rh\textsuperscript{i}(diene) complexes, perform well in EDA polymerisation to prepare highly syndiotactic poly(ethyl 2-ylidene-acetate) (st–PEA). Therefore, we decided to investigate the activity of Rh-catalyst in C1 polymerisation employing sulfoxonium ylides as the carbene monomer source, aiming at desirable copolymerisation reactions of functionalised and non-functionalised ‘carbenes’. In principle, such copolymerisation can also be achieved using diazomethane as the C1 co-monomer instead of a sulfoxonium ylide,\textsuperscript{10} but diazomethane is highly toxic, inherently unstable, and explosive at higher temperatures and concentrations (in marked contrast to the much safer and rather stable diazo esters and diazo ketones\textsuperscript{11}). Sulfoxonium ylides are quite stable, non-explosive, less toxic and thereby much safer methylene carbene (:CH\textsubscript{2}) precursors than diazomethane, which makes them much more interesting from a synthetic point of view.
We therefore decided to study a series of Rh\(^{I}\)(diene), active in C1 homopolymerisation of diazo compounds, to extend the scope of substrates towards other carbene sources, such as sulfoxonium ylides. Furthermore, we look into the compatibility of these catalysts towards different carbene precursors as alternatives to diazo compounds in carbene copolymerisation reactions. We were particularly interested in the use of new carbene precursors capable of introducing non-functionalised methylene units that allow us to avoid the use of the well-known explosive carbene precursor diazomethane. Herein, we describe the preparation and characterisation of new homopolymers and copolymers using diazo esters and methylene sulfoxonium ylides as monomers in Rh\(^{I}\)(diene)-mediated reactions. In addition, catalyst (de)activation pathways are disclosed.

6.2 Results and discussion.

6.2.1 Rh-mediated homo-polymerisation of ‘carbenes’ from EDA.

We previously reported that \([\text{N,O–ligand})\text{Rh}^{I}(\text{diene})]\) complexes are catalyst precursors for the polymerisation of carbenes from alkyl diazoacetates.\(^7\) For all catalysts tested thus far, it was demonstrated that the polymeric material PEA has the same well-defined stereoregular properties with comparable chain length, albeit produced in different yields.\(^7d\) Rh(diene) catalysts also polymerise acetylenes efficiently, and in these reactions the \(\pi\)-acidity of the diene ligand proved to have a clear influence on the overall electron density at the metal, thus favouring the coordination of the substrate and increasing the activity.\(^12\) The following section will show experiments that were aimed at the understanding of the role of diene ligands during the activation of the catalyst in EDA carbene polymerisation. After this section, we will present our studies on extending the substrate scope for C1 homo- and co-polymerisation using sulfoxonium ylides as monomers.

**Carbene polymerisation reactions with different dienes.** Pre-catalysts shown in Figure 1 were evaluated in carbene polymerisation with ethyl-diazoacetate (EDA) under the same reaction conditions for \([\text{N,O–ligand})\text{Rh}^{I}(\text{diene})]\) complexes already reported.\(^7\) In all reactions, well-defined \(st\)-PEA polymer was isolated by precipitation with methanol followed by centrifugation of the reaction mixture. Additionally, some ill-defined oligomer and some carbene dimerisation products (diethyl maleate and diethyl fumarate) were obtained as a separate fraction after evaporation of the methanol used to precipitate the syndiotactic polymer. In some cases, the conversion of EDA was not complete after 16 hours and some ‘methanol insertion product’ MeOCH\(_2\)COOEt and remaining EDA were detected (Table 1).
We examined a series of [Rh(diene)Cl]$_2$ complexes in order to get a better insight in the influence of the $\pi$-acidity of the olefin on the performance of the catalysts in carbene polymerisation. When the performance of catalysts 1–7 is compared, it seems that the electron-deficient olefins have a negative effect on both the total PEA yield and the length of polymer. For some of the complexes containing more $\pi$-acidic ligands, incomplete conversion of EDA was observed. Notably, while the presence of electron-deficient diene tfb in Rh$^I$(tfb) (tfb=tetrafluorobenzobarrelene) catalysts 6 and 7 and the electron-rich Rh$^I$ center in catalyst 5 results in a remarkably enhanced activity in acetylene polymerisation compared to other dienes, these catalysts perform poorly in carbene polymerisation. Catalysts 4–7 rapidly convert EDA, but produce mostly ill-defined oligomers and dimers rather than $st$-PEA polymer. In contrast to phenyl acetylene polymerisation, complexes with less $\pi$-acidic diene complexes (catalyst 8–13) perform better in carbene polymerisation. Thus, phenyl acetylene polymerisation and C1 carbene polymerisation clearly follow entirely different pathways, and the diene ligand apparently plays a different role.

Other experiments performed in our group revealed that pre-activation of the catalyst by exposure to an O$_2$ atmosphere leads to an increase in the initiation efficiency. Incorporation of one oxygen-atom in the polymer-forming active species formed during polymerisation was further demonstrated by ESI-MS experiments. This demonstrates that oxidation of the
Rh-mediated C1-polymerisation: copolymers from diazoesters and sulfoxonium ylides.

precatalyst is one method to activate the pre-catalyst for carbene polymerisation. Interestingly, the mono-oxygenated species formed by aerobic oxidation of pre-catalyst 12 are isomers of the rhodaoxoethane \([(R_2’C_8H_{10}O)Rh^{III}]\) type species that rearrange to hydroxo \([(R_2C_8H_9)Rh^{III}–OH]^+\) allyl-isomers (Scheme 3).

Additionally, DFT studies showed that the unmodified Rh\(^{I}(\text{diene})\) complex can be activated by oxidative addition of an allylic C–H bond to initiate chain propagation, while the unmodified (diene)Rh\(^{I}(\text{alkyl})\) species should (according to DFT) produce mostly dimers or at most very short oligomers due to rapid β–H elimination.\(^{7i-j,13}\) Hence, the performance of every

Table 1. Polymerisation of EDA with Rh\(^{I}(\text{diene})\) catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion(^b)</th>
<th>Yield PEA (%(^c))</th>
<th>(M_w) (kDa)(^d)</th>
<th>PDI ((M_w/M_n)(^d))</th>
<th>Yield Oligomer</th>
<th>Dimers</th>
<th>st-PEA</th>
<th>Oligomers-EA</th>
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<tr>
<td>2</td>
<td>2</td>
<td>85</td>
<td>3</td>
<td>74</td>
<td>1.7</td>
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<td>&lt;5</td>
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<td>100</td>
<td>20</td>
<td>135</td>
<td>2.2</td>
<td>57</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>11(^{f})</td>
<td>100</td>
<td>50</td>
<td>150</td>
<td>3.6</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>10</td>
<td>12(^{g})</td>
<td>100</td>
<td>30</td>
<td>760</td>
<td>3.6</td>
<td>35</td>
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<tr>
<td>11</td>
<td>14</td>
<td>100</td>
<td>21</td>
<td>527</td>
<td>9.8(^{h})</td>
<td>57</td>
<td></td>
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<tr>
<td>12</td>
<td>15</td>
<td>100</td>
<td>47</td>
<td>626</td>
<td>10.4(^{h})</td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)General reaction conditions: 2 mmol EDA, and 2 or 1 mol% Rh, 5 mL dichloromethane. \(^b\)Calculated from the \(^1\)H NMR spectra in chloroform-\(d_3\) at r.t. by integration of remaining EDA and the methanol insertion product MeOCH\(_2\)COOEt (conversion can be somewhat overestimated due to the volatile character of these compounds). \(^c\)Isolated yield relative to the total amount of EDA added. \(^d\)Data collected from soluble fraction at room temperature. \(^e\)Isolated yield calculated from the fraction collected after methanol evaporation and integration by \(^1\)H NMR. \(^f\)Data taken from ref 7k,l. \(^g\)Data taken from ref 16. \(^h\)Multimodal distribution.
complex must be directly related to its ability to rearrange to an (allyl)Rh\textsuperscript{III}–Y type species (Y = -H, -alkyl, -OH, -OEt) through activation of an allylic C–H bond as the key to achieve carbene polymerisation (Scheme 3, anaerobic activation), while the remaining non-modified (diene)Rh\textsuperscript{I} species should be responsible for formation of the dimers and the ill-defined atactic oligomers. The (diene)Rh\textsuperscript{I} complexes 1–7 either do not have allylic C–H bonds to generate the required (allyl)Rh\textsuperscript{III}–Y species, or are expected to have a much higher energy barrier for allylic activation than complexes 8, 9, 10, and 14 (due to enhanced $\pi$-back donation from the metal centre to the electron deficient diene). This explains, in a general form, the poor activity of complexes 1–7 in carbene polymerisation.

Additionally, the molecular weight of the polymer is clearly dependent on the applied diene ligand, and the steric bulk around the olefin is shown to have a positive influence on the polymer yield.\textsuperscript{16} Increasing the steric bulk around the olefin should prevent or slow down the termination pathways. Thus, we also prepared the new complex 14 that contains a more sterically hindered diene ligand. This compound was obtained according to the reaction route depicted in Scheme 4.

Indeed, complex 14 produced $st$-PEA in comparable polymer yield and with increased chain length compared to 8. In fact, complexes 2 and 4–7 produce considerably shorter polymer chains as compared to catalysts 14 and 8, again reflecting the negative effect of the

\textbf{Scheme 3.} Chain propagation mechanism of $st$-PEA via Rh\textsuperscript{III}-allyl species vs. ill-defined oligomer formation via $\beta$–H elimination/reinsertion with Rh\textsuperscript{I}(diene) complexes.
Rh-mediated C1-polymerisation: copolymers from diazoesters and sulfoxonium ylides.

The diene is not the only factor that plays a role in the activation of the catalyst, and also the N,O– ligand has an influence on the polymer yield produced in these reactions. It has been shown that the use of prolinate as a ligand has a positive effect on the yield of the polymer compared to other ligands, while variation of the N,O– ligand hardly influences the length of the polymer chain.\textsuperscript{7d} Additionally, [(N,O–ligand)RhI(diene)] complexes are shown to be more active in carbene polymerisation compared to [RhI(diene)Cl]₂. These ligands seem to participate in, or facilitate the catalyst activation process in some manner. This clearly demonstrates that the N,O– ligand must be involved in the initiation stage (i.e. formation of the active species from the precatalyst) and likely does not bind to rhodium anymore during chain propagation. Hence, the ancillary ligand that remains attached to the metal centre during catalysis is derived from the diene, and this ligand influences the reaction sequence during chain propagation (Scheme 3). Indeed, the chloride dimer complexes 8 and 10 – 12 produce polymer with comparable length as their prolinate analogous complexes 9 and 13 – 15 (see Table 1 and ref. 7).

6.2.2 Rh-mediated homo-polymerisation of ‘carbenes’ from sulfoxonium ylides.

While boron-mediated synthesis of polymethylene (‘poly-homologation’) is a known reaction,\textsuperscript{9} there are no reports of any TM-mediated ‘carbene polymerisation’ reactions using sulfoxonium ylides as carbene precursors. Therefore, we first investigated the ability of different RhI(diene) compounds to mediate carbene polymerisation using sulfoxonium ylides as carbene precursors. RhI(diene) complexes 8–13 (Figure 4) have shown good to excellent activities in carbene polymerisation reactions using diazo esters as the carbene precursors, and hence we first evaluated the performance of these same catalysts for the synthesis of polymethylene from the dimethyl sulfoxonium methylide ylide A (Me₂SO₂=CH₂). These
homo-polymerisation studies were aimed at gaining more information about the transition metal catalysed polymerisation process with sulfoxonium ylides before actually using these same sulfoxonium ylides in co-polymerisation reactions of functionalised and non-functionalised carbone precursors.

The catalytic C1 polymerisation reactions of the Rh I(diene) compounds $8$–$15$ with sulfoxonium ylide $A^{14}$ as the substrate were carried out in THF under argon (Scheme 5). In all cases (except entry 5), the reactions reached full conversion (Table 2), but the different catalysts required various reaction times to convert all the monomer. The obtained polymer, identified as linear (low $M_n$) polymethylene (LPM, *vide infra* for detailed characterisation)$^{15}$ and essentially (almost) the same material as linear polyethylene (LPE), was isolated from the reaction mixture by evaporation of the solvent, followed by addition of MeOH and filtration.

The Rh I(diene) complexes $8$–$15$ produce, after full consumption of the monomer, polymethylene in different yields. As for EDA polymerisation, the carbone polymerisation reaction employing sulfoxonium ylide $A$ is also substantially influenced by the applied diene as ligand. The best results were obtained with the most bulky dienes 1,5-dimethyl-1,5-cyclooctadiene (Me$_2$cod) and 1,5-di(4-methoxy)phenyl-1,5-cyclooctadien ($p$-MeOC$_6$H$_4$)$_2$cod) (complexes $9$, $12$ and $14$) (entries 3–5, 8 and 10). The Me$_2$cod and ($p$-MeOC$_6$H$_4$)$_2$cod complexes also give higher yields and molecular weights in carbone polymerisation of ethyl diazoacetate (EDA) than the corresponding cod complexes, suggesting that the polymerisation of methylene (:CH$_2$) generated from $A$ may follow similar activation and propagation pathways. However, in contrast to EDA polymerisation, the yields are hardly influenced by the presence of the prolinate ligand, and very similar results are obtained with the chloride-bridged compounds.

The higher polymer yields using the Me$_2$cod catalysts $9$ and $12$ as compared to the cod catalysts $8$ and $10$ suggests that increasing the steric bulk around the metal prevents or slows-down chain-termination pathways.$^{5b}$ Increased ligand bulk might also hinder the coordination

![Scheme 5. Rh–mediated carbone polymerisation using dimethyl sulfoxonium methyldide (A) as the carbone (:CH$_2$) precursor.](image-url)

**Scheme 5.** Rh–mediated carbone polymerisation using dimethyl sulfoxonium methyldide (A) as the carbone (:CH$_2$) precursor.
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of multiple substrates, and thereby slow-down the competing formation of ethene via :CH2 carbene dimerisation.16 If this is the case, even higher polymethylene yields should be attainable by further increasing the steric bulk at the diene ligand. Indeed, (p–MeOC6H4)2cod rhodium complex 14 turned out to be the best catalyst for the synthesis of polymethylene via Rh-mediated carbene polymerisation. Addition of the ylide to the catalyst in 2 mL of THF using a Rh:ylide ratio of 1:100 produced the polymer in 77% yield after 2 days (Table 2, entry 11). Hence, changing the Me substituent of 9 to a p-MeOC6H4 substituent in 14 (Table 2, entries 3, 4 and 10) improves both the reaction rate (full conversion in two days instead of 4–10 days) and the obtained polymer yield (77% instead of 39–47%). The molecular weights produced by 14 are similar to those obtained with 8–13.

Increasing the reaction temperature from 22 to 60 °C lowers the yield, whereas an increased ylide:Rh ratio is beneficial (Entries 2 and 4).17 In general, better yields are obtained

### Table 2. Rh-mediated carbene polymerisation from sulfoxonium ylide A.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat.</th>
<th>Ylide:Rh</th>
<th>Yieldb PM (%)</th>
<th>Reaction time</th>
<th>Mw (Da)</th>
<th>Mn/Mw</th>
<th>Mw/Mn</th>
<th>Mw (Da) NMR</th>
<th>Mw (Da) GPC</th>
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<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>50:1</td>
<td>17</td>
<td>17 hours</td>
<td>506</td>
<td>1.976</td>
<td>nd</td>
<td>256</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>8</td>
<td>150:1</td>
<td>20</td>
<td>17 hours</td>
<td>1039</td>
<td>3.799</td>
<td>nd</td>
<td>277</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>50:1</td>
<td>39</td>
<td>4 days</td>
<td>1430</td>
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<td>nd</td>
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</tr>
<tr>
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<td>150:1</td>
<td>47</td>
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<td>1778</td>
<td>1092</td>
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</tr>
<tr>
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<td>24</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>1485</td>
<td>nd</td>
<td></td>
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<td>1724</td>
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<td>nd</td>
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</tr>
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<td>9</td>
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<td>28</td>
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<td>nd</td>
<td>nd</td>
<td>1472</td>
<td>nd</td>
<td></td>
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</table>

a General reaction conditions: 0.02 mmol of [Rh] catalyst, 2.10 mmol of sulfoxonium ylide A (0.55-0.70 N solution depending on the batch), room temperature b After precipitation with MeOH. c 6.30 mmol of sulfoxonium ylide A. d Reaction not finished after 3 weeks.
with longer reaction times, and the faster reacting catalysts seem to form mostly shorter, MeOH-soluble oligomers.

Screening experiments using solvents other than THF, such as toluene, dichloromethane, or chloroform led to formation of only small amounts of short oligomers (C8-C12). This is unfortunate, because polymethylene precipitates from THF during the reaction, thereby limiting the chain-growth process as the catalyst may (partly) co-precipitate from the solution. In the presence of (traces of) water, (partial) hydrolysis of A occurs, and hence rigorous anhydrous conditions are required.

The carbene polymerisation reaction seems to be quite specific for Rh(I)(diene) complexes, as a variety of IrI, Pd0, and PdII complexes gave very poor results in this reaction under similar reaction conditions.18

The obtained polymethylene materials have a low $M_w$ of ~1000–2000 Da. An increase in the ylide/Rh ratios clearly increases the polymer yields and the $M_w$ of the polymer ($M_w$ ranging from ~1000 – 3500 Da).19 However, also the polydispersity increases from PDI = 1.9 to 4.3 with increasing $M_w$. This seems to be partially caused by the precipitation of the polymer from THF.

6.2.3 Carbene polymerisation attempts with functionalised sulfoxonium ylides.

Attempts to polymerise the more bulky sulfoxonium ylides B and C (Figure 2) were not successful. Reaction of B with catalysts 8–15 under different reaction conditions (variable temperatures, ylide:Rh ratio’s and different solvents) in all cases led to mostly carbene dimerisation, producing diethyl maleate and diethyl fumarate (Scheme 6). Some short oligomers (C3-C7) were also observed in all cases. Only catalyst 13 at 40 ºC in 2 mL of CH2Cl2 (0.014 mmol of 6 and 0.71 mmol of ylide B), produced after one week some longer oligomers ($M_w = 2475$ Da, PDI = 1.019) in isolable amounts, but only in rather poor yields (<5%).

Reaction of C with the Rh compounds 8–15 did not produce any polymer. The addition of 1.27 mmol of C to 0.025 mmol of Rh(I)(diene) at room temperature led to formation of $p$-tolyl-SO-NMe2 ($^1$H NMR: $\delta = 7.49$ and $\delta = 7.28$, AB system (CH=CH), $\delta = 2.64$ (NCH3) and $\delta = 2.39$ (CCH3) ppm) as the only detectable compound. The

Figure 2. Structure of sulfoxonium ylides B and C.
samples were treated in the same way as all other polymer reactions, leading to evaporation of the likely formed gaseous butene produced by carbene dimerisation. Neither non-volatile oligomers nor polymers were observed. A similar result was obtained by Shea and coworkers. Their attempts to homo-polymerise this compound were also unsuccessful. These bulkier ylides apparently only produce olefins by carbene dimerisation.

### 6.2.4 Copolymerisation of carbenes from EDA and sulfoxonium ylide A.

The ability of Rh(I)(diene) complexes to polymerise ‘carbenes’ generated from both EDA and sulfoxonium ylides provides attractive opportunities in copolymerisation reactions. Incorporation of the COOEt moieties employing C1 polymerisation techniques provides an interesting alternative to prepare desirable copolymers containing both polar and nonpolar monomers. Two different approaches were investigated for such reaction: (i) Rh-mediated copolymerisation of the sulfoxonium ylides A and B, and (ii) copolymerisation of EDA and sulfoxonium ylide A (Scheme 7). Unfortunately, polymerisation attempts with stoichiometric amounts of ylide A and B in the presence of Rh(diene) catalysts produced only polymethylene without any incorporation of ester groups. Hence, the copolymerisation reactions via route i is impossible.

Copolymerisation of EDA with sulfoxonium ylide A employing Rh(I)(diene) complexes is

### Scheme 6. Rh-mediated carbene dimerisation and oligomerisation using sulfoxonium ylide B as the carbene precursor.

### Scheme 7. Attempts to copolymerise carbenes from sulfoxonium ylide A with i) sulfoxonium ylide B and ii) EDA.
more successful and produces copolymer by incorporating carbene units from both EDA and A. These polymers have a stereoregular PEA–LPM diblock structure (vide infra for detailed characterisation).

All the catalysts shown in Figure 1 can produce copolymer PEA–LPM, although in various yields. While compounds 8, 10, 11, and 13 have a poor activity (< 5% yield), compounds 9, 12, and 14 give high yields if the right reaction conditions were chosen. Both EDA and sulfoxonium ylide A are rather reactive species and have been used for a variety of reactions such as cyclopropanation21, heterocycle formation22, X–H insertion23, C-acylation24, olefination25, dimerisation, etc. Therefore, a complex reaction mixture can be obtained if these reagents are used. So far, the reactivity between EDA and sulfoxonium ylide A has not been explored. As we expected, even in the absence of any catalyst, EDA and A in THF react

Table 3. Rh mediated carbene copolymerisation from sulfoxonium ylide A and EDA.a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>EDA:Ylide:Rh</th>
<th>Yieldb (%)</th>
<th>Mw c (kDa)</th>
<th>Mn c (kDa)</th>
<th>PDIc</th>
<th>%LPMd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11</td>
<td>20:50:1</td>
<td>6</td>
<td>210</td>
<td>117</td>
<td>1.78</td>
<td>58</td>
</tr>
<tr>
<td>2e</td>
<td>11</td>
<td>50:50:1</td>
<td>7</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
<td>50:50:1</td>
<td>16</td>
<td>481</td>
<td>237</td>
<td>2.03</td>
<td>33/79f</td>
</tr>
<tr>
<td>4</td>
<td>11</td>
<td>100:100:1</td>
<td>8</td>
<td>396</td>
<td>108</td>
<td>3.66</td>
<td>28/38f</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>50:50:1</td>
<td>&lt;5</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>50:50:1</td>
<td>18</td>
<td>520</td>
<td>264</td>
<td>1.97</td>
<td>38</td>
</tr>
<tr>
<td>7</td>
<td>8</td>
<td>100:35:1</td>
<td>10</td>
<td>791</td>
<td>346</td>
<td>2.28</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
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<td>100:50:1</td>
<td>15</td>
<td>640</td>
<td>247</td>
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<td>15.5</td>
<td>648</td>
<td>292</td>
<td>2.21</td>
<td>38</td>
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<tr>
<td>10</td>
<td>8</td>
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<td>626</td>
<td>286</td>
<td>2.18</td>
<td>54</td>
</tr>
<tr>
<td>11</td>
<td>16</td>
<td>100:100:1</td>
<td>5</td>
<td>53</td>
<td>21</td>
<td>2.52</td>
<td>Nd</td>
</tr>
</tbody>
</table>

a General reaction conditions: 2 mmol EDA, 2 mmol A and 2 or 1 mol% Rh, 3 mL dichloromethane and 3 ml THF. b Yield is referred to the total mol addition of both substrates. c Data collected from soluble fraction at room temperature. d Calculated from the 1H NMR spectra in o-dichlorobenzene-d4 at 110 °C of total amount of copolymer. e Only 6 ml of THF. f the first number represents the CDCl3 soluble fraction and the second the non-soluble fraction.
Rh-mediated C1-polymerisation: copolymers from diazoesters and sulfoxonium ylides.

strongly in an exothermic manner producing a complex mixture of products. Low-temperature experiments at 0, −20, and −50 ºC led to similar mixtures.

Successful copolymerisation reactions were performed by first preactivation of the catalyst by addition of 50 eq. of EDA and subsequently addition (after 30 minutes) of sulfoxonium ylide A in a mixture at −20 ºC. The copolymer is produced over the course of three days after warming-up the reaction mixture to room temperature (Scheme 8). Evaporation of the solvent followed by addition of MeOH leads to the precipitation of diblock copolymer PEA–LPM that was formed in ~15% yield. As is the case in the synthesis of LPM, the copolymer PEA–LPM precipitates in THF, thus explaining the high PDI and the relative low yield. Unfortunately, the polymerisation of A in pure chlorinated solvents (in which the polymer of EDA is soluble) results in very poor yields, and the presence of THF is necessary (also in the case of copolymerisation with EDA).

No copolymer is obtained when the sulfoxonium ylide A and EDA are added at the same time, even if the reaction is performed at 0 or −50 ºC. This indicates that most of the EDA must be converted to a (still living) growing polymer chain before addition of sulfoxonium ylide A. Furthermore, the active species generated by the reaction between EDA and the catalyst likely have to be formed before the addition of the sulfoxonium ylide. A proposed mechanism is shown in Scheme 9.

The best Rh catalysts for this reaction are compounds 8 and 14, which produce the copolymer in 15% and 18% yield respectively. The optimum ratio Rh:ylide:EDA for both catalysts was found to be 1:50:50 (entries 2 and 6, Table 3). Decreasing the amount of EDA in the reaction helps to incorporate more methylene units (entry 1), but this leads to dramatically lower yields. However, the polymethylene content (% LPM) can be easily increased by simply increasing the amount of ylide. This works best with catalysts 14 (entry 7–10, Table 3), and has hardly any effect on the obtained yields. These results strongly
suggest that chain-initiation is effected by EDA (formation of an active growing polymer chain from which the LPM block can grow further).

The length of the copolymers seems to be only affected by the catalyst and not by the reaction conditions. Catalyst 14 affords on average longer polymers than catalyst 9. Interestingly, these copolymers are remarkably long compared to PEA obtained in EDA homopolymerisation reactions.7

6.2.5 Characterisation of the obtained LPM homo-polymers.

The obtained polymethylene samples generated from A (see Table 2) were characterised by FT-IR, ¹H and ¹³C NMR spectroscopy, Gel Permeation Chromatography (GPC), and Differential Scanning Calorimetry (DSC).

The FT-IR spectra display vibrations typical and characteristic for polymethylene (identical to polyethylene). Clear vibrations are observed corresponding with the C–H stretch vibrations of the –CH₂– and –CH₃ groups at 2916.5, 2848.9 cm⁻¹, the –CH₂ bending vibrations at 1471.7 and 1462.1 cm⁻¹, and the (–CH₂–CH₂–)ᵣ rocking vibrations at 731.5 and 715.5 cm⁻¹.

Figure 3 shows the ¹H and ¹³C NMR spectra of a representative polymethylene sample measured in 1,2-dichlorobenzene at 120°C. The sharp peak at δ = 1.38 ppm corresponds to the –CH₂– units of the polymer chain. The broad triplet peak at δ = 0.93 ppm corresponds to a –CH₃ chain-end.

The clear olefinic signals observed in the NMR data reveal the presence of vinylic end-groups, thus pointing to β–H elimination as the mechanism for chain-transfer or chain-termination. Integration of this signal reveals a roughly 1:4 to 1:6 ratio of terminal vs. internal alkene signals (¹H NMR at δ = 5.69, ³J_H,H = 17.1, 10.2 Hz (–CH=CH₂), δ = 4.86, ³J_H,H = 17.1, 3.7 Hz (–CH=CH₂) and δ = 4.80, ³J_H,H = 10.2, 3.7 Hz (–CH=CH₂)). Isomerisation from

terminal to internal olefins by chain-walking\textsuperscript{5b} can, in principle, give access to the formation of branched polymers. However, long time accumulation $^{13}$C NMR experiments showed no evidence for any branching, and only characteristic signals for linear polymethylene are observed: $\delta = 32.17$ ppm ($-\text{CH}_2-\text{CH}_2-\text{CH}_3$), $\delta = 30.0$ ppm ($-(\text{CH}_2)_n-$), $\delta = 29.57$ ($-\text{CH}_2-(\text{CH}_2)_2\text{CH}_3$), $\delta = 22.87$ ppm ($-\text{CH}_2-\text{CH}_3$), and $\delta = 14.06$ ppm ($-\text{CH}_3$).\textsuperscript{27} In agreement with this, determination of the average molecular weight based on $^1$H NMR integration leads to similar values as obtained by GPC analysis. The relative integral of the end groups of different samples does not change much from one sample to another, indicative of similar mechanisms for all the catalysts.

Thermal analysis with DSC reveals the $T_m \approx 120$ °C and $T_c \approx 105$ °C transitions ($\Delta H \sim 150$ J g$^{-1}$). The rather low melting point is most likely a consequence of the low $M_w$ of these polymethylene samples.\textsuperscript{28}

6.2.6 Characterisation of the stereoregular diblock st-PEA–LPM copolymers

The obtained stereoregular (syndiotactic) diblock st-PEA-LPM copolymers were also characterised by $^1$H and $^{13}$C-NMR spectroscopy, GPC and DSC.

![Figure 3](image-url)  
**Figure 3.** a) $^1$H NMR spectra of polymethylene, b) $^{13}$C NMR spectra (terminal olefins), and c) $^{13}$C NMR spectra (saturated chain) of polymethylene in 1,2-dichlorobenzene at 120 °C.
From this experiments, it is clear that the copolymers obtained with the different catalysts or employing various ylide:EDA ratios, have different solubility properties. This depends mainly on the length of each block. Copolymers with higher ester contents are soluble in regular chlorinated solvents at RT. Copolymers containing more CH2 units in the backbone are less soluble in dichloromethane or chloroform, and copolymers with a dominating LPM fragment become completely insoluble in conventional organic solvents. By washing the sample with chloroform, it is possible to separate the most functionalised copolymer from the one with less functional groups. The non soluble fraction consists entirely of diblock copolymers with a dominating LPM block. The chloroform-soluble part consists of copolymers with shorter LPM blocks and longer st-PEA blocks. The presence of some st-PEA homo-polymer in the latter (chloroform soluble) fraction cannot be entirely ruled out. However, the soluble and non-soluble fractions reveal quite similar crystallisation profiles in DSC (vide infra), suggesting that also the soluble fraction is dominated by diblock st-PEA-PM copolymers.

Figure 4 shows the $^1$H NMR spectra of the most insoluble (in chloroform, r.t.) copolymer in 1,2-dichlorobenzene-$d_4$ at 120 °C. The signals at δ = 4.15, 3.50 and 1.27 ppm correspond to

![NMR Spectra](image_url)

**Figure 4.** $^1$H NMR spectra of insoluble stereoregular diblock st-PEA-LPM at 130 °C in 1,2-dichlorobenzene-$d_4$. 
Rh-mediated C1-polymerisation: copolymers from diazoesters and sulfoxonium ylides.

The sharp peak at δ = 1.31 ppm corresponds to the –CH₃ of the stereoregular st-PEA block, whereas the sharp peak at δ = 5.83 ppm (–CH=CH₂), δ = 5.04 ppm (–CH=CH₂) and δ = 4.95 ppm (–CH=CH₂). The ¹H NMR spectra (CDCl₃) of the copolymers with a high stereoregular st-PEA content show similar peaks, but as expected the integrals show a higher ratio CHCOOEt:CH₂ that provides more solubility in chlorinated solvents. The signals from the diblock can also be observed in ¹³C NMR spectra, δ = 171.17 (C=O), δ = 60.76 (–OCH₂), δ = 46.51 (–CH–) and δ = 13.99 (–CH₃) ppm from the st-PEA block and δ = 30.0 (–CH₂–) ppm from PM block (Figure 4).

For a regular reaction (50:50:1 ratio EDA/ylide/Rh) molecular weights obtained by GPC analysis from the most functionalised samples reveal a $M_w$ of 520 kDa and PDI = 1.97. Reactions employing a 100:35:1 ratio EDA:ylide:Rh leads to chloroform soluble polymer with $M_w = 700$ kDa and PDI = 2.5 and ~12% incorporation of polymethylene. The $M_w$ value is high compared to molecular weights reported for EDA polymerisation in THF ($M_w = 130$ kDa, $M_w/M_n = 2.4$). On average, the total content of polymethylene varies from 12 to 54% depending on the applied reaction conditions (see Table 3).

Thermal analysis of the copolymer shows important features that distinguish the homopolymer from the copolymer. All copolymer samples show one melting peak at around $T_m = 120$ °C (Figure 5). Although the melting point of both fragments overlap, it is clear that both components (CHCOOEt and CH₂) are present, as can be deduced from the variations in the heat capacity ($\Delta H_{PM} > 20$ kJ mol⁻¹ > $\Delta H_{PEA}$). In the crystallisation curve, we can observe the characteristic peak for PM (~110 °C), but we cannot distinguish a separate crystallisation transition for st-PEA. In a semi-crystalline copolymer, where the different fragments can crystallise, we can assume that the block with the highest $T_c$ or the predominant phase will crystallise first. As a result, the second fragment will have an unfavourable configuration for crystallisation, and the crystallisation process can be simply obstructed, meaning that steric constraints play an important role and thermodynamics no longer solely direct the crystallisation process. Thus, the crystallisation peaks we observe at lower temperatures (~90 and ~73 °C) can be assigned to non-favoured crystallisations of PM or st-PEA fragments in the copolymer. These peaks are characteristic for formation of a copolymer, and are atypical for mixtures of homopolymers (blends). Since the first peak corresponds to PM crystallisation ($T_c$), which is also expected to dominate over st-PEA crystallisation on the basis of the large
differences in the crystallisation enthalpies, the two lower-temperature crystallisation peaks are most likely also PM crystallisations with hindered configurations.

6.2.7 Blending experiments.

An attractive approach to combine properties of different materials is to produce blends where benefits from various phases can be obtained. An often encountered problem in this field is the incompatibility of different phases. Immiscible polymer blends often lead to macro-phase separation above a critical temperature, being a disadvantage in terms of production and handling.\textsuperscript{30} In contrast, phase separation in block copolymers leads to microphase separation because macrophase separation is prevented by the connectivity of the polymer chains.

To have an insight in the different interactions between the polar \textit{st}-PEA block and the non-polar PM block and the potential application of these copolymers we studied blends containing HDPE\textsuperscript{31} and \textit{st}-PEA\textsuperscript{32} in which the phase behaviour, thermal properties and crystallisation of PM/PEA blends were investigated by DSC experiments.

Figure 6 shows the heating (a) and crystallisation (b) curves of the second run obtained for the different blends. Curve I, and II are the homopolymers, HDPE and \textit{st}-PEA, respectively. DSC curve III is measured using a simple 10/90 mixture of HDPE/\textit{st}-PEA without any copolymer as a blending agent. In this curve, we can distinguish the \(T_c\) and the \(T_m\) with no significant shift between the values of the respective homopolymers and those measured in the mixture. In a miscible blend of two crystalline components, after the crystallisation of the highest \(T_c\) component and before the lower \(T_c\) component, the amorphous phases of both components are expected to interact either in the confined inter-lamellar region or out of the inter-lamellar region. Therefore, crystallisation patterns are expected to be more complex than those occurring in the respective homopolymers and/or block copolymers, because DSC curve III simply represents the expected behaviour of macrophase separated HDPE in a \textit{st}-PEA matrix (non miscible mixture).

The behaviour of HDPE/\textit{st}-PEA mixtures changes markedly upon addition of \textit{st}-PEA-LPM copolymer. In presence of \textit{st}-PEA-LPM copolymer, as we can see in curve IV (10/90/50 ratio
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HDPE/st-PEA/copolymer), the only detected crystallisation peak is $T_c = 104.9 \, ^\circ C$. Apparently, the st-PEA-LPM copolymer acts as a blending agent, probably by coupling of the macrophase separation of the blend components with the microphase separation of the block copolymer.\textsuperscript{33} In the copolymer curve V, the PM micro domains dominate the crystallisation process ($T_c = 120 \, ^\circ C$). The observed lower $T_c$ peaks are likely also from PM micro domains, but in a thermodynamically less favourable orientation for crystallisation (perhaps shorter blocks).

In contrast, curve IV (10/90/50 ratio HDPE/st-PEA/copolymer) shows a homogeneous phase with a lower $T_c$ than in HDPE (Figure 6, C1 vs A). This single $T_c$ is indicative for the solubility of HDPE in the PM domains of the copolymer, thus resulting in an overall higher crystallinity ($\Delta H_D = 45 \, J \, g^{-1}$ vs. $\Delta H_{C1} = 27 \, J \, g^{-1}$). These results also suggest that the st-PEA-LPM copolymer acts as a blending agent for HDPE and st-PEA.\textsuperscript{33} Remarkably, the unusual $T_c$’s observed in the copolymer ($T_c = 81, 69 \, ^\circ C$) do not appear in the blend, which is likely the result of the interaction of the HDPE with every PM domain and therefore homogenisation of the non-polar phase of the blend. This phenomenon also affects the st-PEA phase. The peak B completely disappears in curve IV, indicating that the prearrangement of the PM-HDPE chains hinders the cocrystallisation of the st-PEA blocks with the homopolymer st-PEA.

![Figure 6. DSC second a) cooling and b) heating curves for homopolymers (I and II, for HDPE and st-PEA respectively), copolymer (V) and blends (III for a 10/90/0 ratio and IV for a 10/90/50 ratio of HDPE/st-PEA/copolymer).](image-url)
Rather relatively large amounts of copolymer are required to observe the abovementioned effects. HDPE/st-PEA/copolymer mixtures with smaller amounts of copolymer and a larger HDPE content than st-PEA show a gradual decrease of $T_c$ from the PM/PE domains, and no $T_c$ for the st-PEA domains. Only in mixtures with high st-PEA contents the $T_c$ of PEA becomes apparent. Mixtures of PEA and HDPE with small amounts of copolymer thus seem to behave as macro-phase separated mixtures, but in which the copolymer interacts with both the HDPE and the st-PEA phases. The interplay between micro- and macrophase separation with various blending ratios should thus allow a variety of possible morphologies.

### 6.2.8 Model studies to identify catalytic intermediates, side reactions and deactivation pathways.

As described above, the best results in the carbene copolymerisation of sulfur ylide A with EDA are clearly obtained with catalysts containing 1,5-disubstituted cod ligands such as 1,5-\text{Me}_2\text{cod} and 1,5-\text{p-MeOC}_6\text{H}_4\text{c cod} (i.e. complex 9 and 14). Catalysts without steric bulk at the 1,5-positions afford hardly any copolymer. Catalyst with more bulky diene ligands also perform best in the homo-polymerisation of sulfur ylide A, leading to linear polymethylene (good yields with catalyst 9 and 14, see Table 3). However, the homopolymerisation reactions do tolerate the use of catalysts with less bulky diene ligands (moderate polymethylene yields with catalysts 8 and 11) while these perform poorly in the copolymerisation reactions.

One contributing factor to the higher yields obtained with more bulky catalysts in the homo-polymerisation of A could well be suppressed carbene dimerisation (i.e. formation of ethylene from sulfur ylide A). However, this factor alone cannot explain the complete lack of activity of the less bulky catalyst (catalysts without R-groups at the diene 1,5-positions) in the copolymerisation of sulfur ylide A with EDA. Therefore, in an attempt to understand these observations, we performed some stoichiometric model studies with compound 8 and 14 to identify possible intermediates, side reactions and deactivation pathways.

*In situ* NMR experiments with complex 8 and species A (1:20 Rh:ylide ratio) have shown slow evolution of ethylene and formation of a new rhodium complex (complex 16) within 2 hours. The reaction proceeds cleanly, but only in the presence of mild coordinating solvents

\[ \text{Scheme 10. Reaction of compound 8 with A leading to compound 16.} \]
Rh-mediated C1-polymerisation: copolymers from diazoesters and sulfoxonium ylides. The reaction affords a yellow solution and a white salt precipitate. The soluble part of the reaction mixture is a clean solution of complex 16 (see Scheme 10). The salt precipitate was identified as trimethyl sulfoxonium chloride ([Me3SO]Cl).

Complex 16 was characterised with mass spectrometry and a combination of NMR techniques (an illustrative $^1$H NMR spectrum is shown in Figure 7). Besides an intact cod ligand, the rhodium complex 16 contains a new ligand derived from sulfur ylide A. Surprisingly, this ligand is not simply ylide A that coordinates with the ylide carbon and the S=O group, but a deprotonated form of A that coordinates with two carbon atoms to rhodium. Complex 16 is best described as an anionic bis-alkyl Rh I compound with an internal sulfoxonium counter ion. Stoichiometric reactions give incomplete conversion of 8 to 16. Complex 16 is formed much more selectively in experiments in which a Rh:ylide ratio of 1:2 was used, thus showing that the ylide itself acts a base for deprotonation of the CH$_2$ group of a second ylide leading to complex 16. The reaction is accompanied with formation of a negligible amount of ethylene. Large scale synthesis allowed us isolate 8 as a bright yellow compound in high yield (Scheme 10).

Similar experiments with complex 14 (1:20 Rh/ylide ratio) resulted in a faster consumption of ylide A (complete conversion in less than 30 minutes), and NMR spectra of the resulting solution revealed a complex mixture of rhodium compounds, independent of the solvent used. Attempts to form a complex analogous to 16 by performing reactions of 14 with A at lower temperatures (−20 and −73 °C) were not successful, in each case leading to formation of ethylene and a complex mixture of rhodium compounds. This suggest that the steric bulk of the (p-MeOC$_6$H$_4$)$_2$cod ligand in 14 prevents formation of a complex analogous to 16,
probably by preventing coordination of a second ylide moiety to the metal centre and thus favouring the carbene transfer mechanism.

We tested the activity of complex 16 as a pre-catalyst in both the homo-polymerisation of sulfur ylide A, and in the copolymerisation of A with EDA. Remarkably, while 16 performs very poorly in the copolymerisation of A with EDA (similar to 10), higher polymethylene yields were obtained in the homo-polymerisation of sulfur ylide A with 16 than with 8. Complete conversion of A also requires shorter reaction times with 16 than with 8 (entry 11, Table 2). The improved performance of 16 over 8 in the homo-polymerisation of A appears to be related to a reduced carbene dimerisation activity.

To exclude the possibility that the observed formation of polymethylene is actually due to polymerisation of in situ generated ethylene, some control experiments were performed in which we tested catalyst 16 as an ethylene polymerisation catalyst. However, a solution of 16 in THF treated with three bars ethylene atmosphere did not show formation of oligomers or polymer, even after several days.

As mentioned above, the activity of complex 16 towards copolymerisation of A with EDA is poor, which contrasts with its improved behaviour in the homo-polymerisation of A compared to 8. The poor performance of 16 in the copolymerisation reaction is most likely due to its poor compatibility with EDA, as 16 also performs very poorly in the homo-polymerisation of EDA (15% yield, producing only short polymers of ~65 kDa, PDI = 3.15). To obtain more information about the reasons behind the poor compatibility of 16 towards EDA, we studied the reaction of 16 with limited amounts of EDA on NMR scale, expecting to observe carbene insertion reactions into the Rh–C bonds of ylide-based ligand moiety with formation of complex 17 (Scheme 11).

Treatment of complex 16 with two equivalents of EDA in THF leads to fast evolution of N₂ and an immediate colour
change of the solution from yellow to orange-brown. At lower temperatures (−78 °C) the reaction affords a cleaner reaction mixture. *In situ* experiments in THF-\textit{d}_8 reveal the immediate formation of diethyl maleate and diethyl fumarate, short oligomeric PEA and a rhodium complex different from the starting material. In addition, the signals of diethyl maleate start to disappear simultaneously with the appearance of the NMR signals belonging to this new Rh compound. Filtration of the precipitate from the reaction mixture showed a fraction of polymer and residues of diethyl fumarate, but no diethyl maleate. APT $^{13}$C NMR studies show quite clean spectra but not all signals could be assigned due to a $^1$H NMR overlapping of signals of the oligomeric chains with some of the characteristic NMR signals of the new rhodium species formed. A separate reaction in which complex 16 was treated with 1 equivalent of diethyl maleate produced the same species as observed in the reaction of 16 with EDA (Scheme 10). To simplify the NMR assignment, further studies were carried out with dimethyl maleate (DMM). Clear 2D NMR data revealed the coordination of the DMM to rhodium, affording complex 18b (See experimental section).

It is noteworthy that the complexes of type 18, formed by reaction of 16 with maleates, proved to be virtually inactive towards homo-polymerisation of A (<5% yield after 3 days at RT). These model studies give a good explanation for the poor performance of complexes 8 and 16 in the copolymerisation of A with EDA; they are both rapidly deactivated by reaction of 16 (complex 16 is formed under the catalytic condition from 8 and A) with *in situ* generated diethyl maleate from EDA, thus producing the inactive complex 18a. The more bulky catalyst precursors 9 and 14 containing steric bulk at the 1,5-position of the diene ligand do not form complexes similar to 16, and hence do not react with diethyl maleate to form inactive compounds similar to 18.

6.3 Conclusions

In this chapter, we present the first examples of transition metal catalysed carbon-chain polymer formation using sulfoxonium ylides as monomers. As a proof of concept, we achieved the use of dimethyl sulfoxonium methylide as the carbene source (:CH$_2$) to prepare the linear homopolymer polymethylene (LPM ≅ LPE) via the rhodium-mediated homo-polymerisation of sulfoxonium ylide A. Other (substituted) sulfoxonium ylides could not be polymerised, presumably due to steric hindrance. However, by applying sulfoxonium ylide A as new substrate, we successfully demonstrated that copolymers can be prepared in the Rh(diene) mediated copolymerisation of non-functionalised carbenes generated from sulfoxonium ylides and functionalised carbenes generated from diazoesters.
Chapter 6

The best results in carbene polymerisation with diazo esters were obtained with electron rich and bulky substituents \([\text{Rh}'(\text{diienes})(\text{N,O–ligand})]\) that can promote oxidative addition of an allylic C–H bond of the diene ligand (low \(\pi\)-back donation and availability of allylic protons), in particular 1,5-substituted cyclooctadiene \((\text{R}_2\text{C}_8\text{H}_{10})\) rhodium species allowing formation of allylic \([[(\text{R}_2\text{C}_8\text{H}_9)\text{Rh}^{\text{III}}–\text{R}]+\) active species during the catalyst activation process. Similarly, the best yields in copolymerisation reactions were obtained with Rh(diene) complexes containing bulky 1,5-disubstituted cod ligands such as 1,5-Me\(_2\)cod and 1,5-(\(p\)-MeOC\(_6\)H\(_4\))\(_2\)cod. Model reactions between \([(\text{cod})\text{Rh}(\mu-\text{Cl})\text{Rh(cod)})]\) complex 8 and dimethyl sulfoxonium methylide \(\text{A}\) allowed the isolation of \([\text{Rh(cod)}\{(\text{CH}_2\text{)}_2\text{SOMe})\}]\) complex 16. This species is also formed under the catalytic homo-polymerisation reaction conditions of \(\text{A}\). In the copolymerisation of EDA with sulfur ylide \(\text{A}\), complex 16 reacts with \textit{in situ} generated diethyl maleate (generated from EDA) to form the inactive diethyl maleate complex 18\(_a\), which explains the poor activity of complex 16 in the copolymerisation reactions. This copolymerisation deactivation pathway is blocked by the use of more bulky complexes containing 1,5-substituted diene ligands such as Rh(Me2cod) complex 9 and Rh((PhOMe)2cod) complex 14. In the homo-polymerisation of dimethyl sulfoxonium methylide \(\text{A}\), the \([\text{Rh(cod)}\{(\text{CH}_2\text{)}_2\text{SOMe})\}]\) complex 16, Rh(Me2cod) complex 9 and Rh((PhOMe)2cod) complex 14 perform comparably well and each much better than \([(\text{cod})\text{Rh}(\mu-\text{Cl})\text{Rh(cod)})]\) complex 8. This last fact is mainly due to suppressed carbene dimerisation (ethylene formation) activity for 9, 14 and 16 compared to 8.

PEA–LPM block copolymers can only be prepared by starting the carbene polymerisation with EDA as the functionalised carbene precursor, followed by addition of sulfur ylide \(\text{A}\). This procedure requires that (most of) the EDA substrate is consumed before addition of sulfur ylide \(\text{A}\). However, the polymethylene content and thereby the solubility of the copolymer can be easily tuned by varying the ylide to EDA ratio. In this way different di-block copolymers with different properties can be prepared. This new C1 polymerisation procedure provides an attractive synthetic protocol to prepare stereoregular diblock copolymers carrying a highly syndiotactic ester-functionalised carbon-chain block and a non-functionalised, non-polar polymethylene block. The blending properties of these new copolymers make them attractive for application as additives in polymer blends or glues between functionalised and non-functionalised polymers.
6.4 Experimental Section

General procedures. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. THF distilled from sodium was used for the catalysis. All other chemicals were used as received without further purification. [{RhI(tricycle[6,2,1,02,7]undeca-4,9-diene-3,6-dione)(μ-Cl)}]234 (1), [{Rh(1,5-cyclooctadiene)(hydroquinone)}BF4•Et2O]35 (4), [K{Rh(1,5-cyclooctadiene)(1,4-quinone)}]35 (5), [{Rh((R,R)-Me2-tetrafluorobenzobicyclo[2.2.2]octatriene)(μ–Cl)}]236 (6), [{Rh(tetrafluorobenzobicyclo[2.2.2]octatriene)(μ–Cl)}]237 (7), [{RhI(1,5-cyclooctadiene)(μ-Cl)}]238 (8), [{RhI(1,5-dimethyl-1,5-cyclooctadiene)(μ-Cl)}]239,16 (9) [{RhI(endo-dicyclopentadiene)(μ-Cl)}]12 (10), and [{L-prolinate}RhI(1,5-cyclooctadiene)]40 (11), [{(L-prolinate)RhI(1,5-dimethyl-1,5-cyclooctadiene)}]16 (12), and [{(L-prolinate)RhI(endo-dicyclopentadiene)}]7 (13) were prepared according to literature procedures. Sulfoxonium ylide A41 was prepared according to the procedures reported by Shea and coworkers9 and the concentration of the solutions were determined by titration before use. Sulfoxonium ylides B42 and C43 were also prepared according to literature procedures. NMR spectroscopy experiments were carried out on a Bruker AV-400 spectrometer (400 and 100 MHz for 1H and 13C, respectively) or a BrukerDRX-500 spectrometer (500 and 125 MHz for 1H and 13C, respectively). Molecular weight distributions were measured using size-exclusion chromatography (SEC) on a Shimadzu LC–20AD system with two PLgel 5 μm MIXED-C (300 mm × 7.5 mm) columns (Polymer Laboratories) in series and a Shimadzu RID-10A refractive-index detector, using dichloromethane as the mobile phase at 1 mL/min and T = 35 °C. Polystyrene standards in the range of 760–1 880 000 g/mol (Aldrich) were used for calibration. FT-IR measurements were carried out in a Bruker alpha-p FT-IR spectrometer with ATR module. The thermal behaviour of polymer LPM and copolymer PEA–LPM was measured on a Perkin-Elmer Jade DSC under N2 atmosphere (flow 5mL min⁻¹) on encapsulated samples (−5 mg) in aluminium pans. The heating program was carried at 10 °C min⁻¹ in a 30–180 °C range. The melting and crystallisation temperatures were determined from the second heating-cooling curves.

Homo-polymerisation of carbene units from dimethyl sulfoxonium methylide. Into a flamed-dried schlenk equipped with the catalyst, a magnetic stirrer and a glass stopper with a Teflon sleeve, a solution of dimethyl sulfoxonium methylide was added. The reaction was monitored by titration of hydrolysed aliquots (~200 μL) in the presence of phenohtalein. After full consumption of the ylide (2–3 days), evaporation of the solvent followed by the addition
of 5 mL MeOH afforded the polymer as a white solid. The samples were centrifuged, washed with MeOH (3 x 10 mL) and dried until constant weight.

**Copolymerisation of EDA and dimethyl sulfoxonium methyldie.** Into a flamed dried schlenk equipped with 0.02 mmol of the corresponding catalyst, a magnetic stirrer and a glass stopper with Teflon sleeves, 2 mmol of EDA and 2 mL of DCM was added. After 30 minutes stirring, the reaction was cooled down to −20 ºC and 2 mmol of A in 2 ml of THF was added slowly. The reaction was monitored by titration of hydrolysed aliquots (~200 μL) in the presence of phenoftalein. After full consumption of the ylide, the samples were treated as described above for the homopolymerisation reactions. The resulting copolymer was washed with chloroform to separate the most functionalised copolymer (soluble) from the less functionalised material.

**1,5-(4-methoxyphenyl)-1,5-cyclooctadiene.** 1,5-dibromocycloocta-1,5-diene (600 mg, 2.26 mmol) was added to a schlenk containing dioxane (11.3 mL). PEPPSI catalyst (52.1 mg, 0.045 mmol) was added to this solution. A solution of K₂CO₃ (1.9 g) was dissolved in water (3 mL) and added to the schlenk. The boronic acid (2.01 g, 13.2 mmol) was slowly added. After overnight stirring at 60 ºC the solution was extracted with CH₂Cl₂ (3x10 mL). The organic layer was washed with NaHCO₃ and water, then dried over MgSO₄ and treated with activated carbon (norit), filtered over an alumina bed and concentrated. The residue was purified by column chromatography (0.4486 gram, 1.40 mmol, 61.9 %). ¹H NMR (400 MHz, CDCl₃) δ 7.25 (d, J = 7.1 Hz, 4H), 6.82 (d, J = 8.8 Hz, 4H), 5.81 (t, J = 6.6 Hz, 2H), 3.80 (s, 3H), 2.84 (t, J = 7.1 Hz, 4H), 2.57 (dd, J = 13.8, 6.9 Hz, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 158.49 (2xC), 139.93 (2xC), 137.34(2xColefin), 127.20(4xCH₂Ar), 125.45 (2xCH₁olefin), 113.61 (4xCH₂Ar), 55.39 (O-CH₃), 31.25 (2xCH₂), 27.63 (2xCH₂). Calc. for C₂₂H₂₄O₂: m/z = 320.1776 Found: m/z = 320.1816.

[Rh(1,5-(4-methoxyphenyl)-1,5-cyclooctadiene)(μ-Cl)]₂ (14): 0.129 mmol of [Rh(ethylene)₂(μ-Cl)]₂ (50.2 mg,) were dissolved in dichloromethane (10ml). To the red-brownish solution 0.257 mmol of 1,5-bis(4-methoxyphenyl)cycloocta-1,5-diene (82.3 mg,) were added. The solution was stirred overnight at 40 ºC and filtered over celite. The resulting solution was concentrated to afford [Rh((p-MeOC₆H₄)₂COD)₂Cl₂] as a yellow solid (59.1 mg, 49.9%). ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, J = 8.4 Hz, 4H), 6.82 (d, J = 8.3 Hz, 4H), 4.87 (d, J = 6.5 Hz, 2H), 3.77 (s, 6H), 3.26 (m, 2H), 2.51 (m, 2H) 2.27 (m, 2H), 1.87 (m, 2H) ¹³C NMR (101 MHz, CDCl₃) δ 159.11 (s, 2xC) 139.69 (s, 2xC), 128.23 (s, 4xCH₂Ar), 113.85 (s, 4xCH₂Ar), 93.98 (d, J = 15.4 Hz, 2xColefin), 70.77 (d, J = 13.2 Hz, 2xCH₁olefin), 55.38 (s, CH₃),
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37.36 (s, 2xCH₂), 33.78 (s, 2xCH₂). Calc. for C₄₄H₄₈O₄Rh₂Cl₂: m/z = 916.1040. Found: m/z: 916.1042

[Rh(1,5-cyclooctadiene)(η²-(CH₂)₂SOCH₃)] (16): In a flame dried schlenk containing 10 ml of dry THF were added 0.203 mmol of [Rh(1,5-cycloocta-1,5-diene)Cl]₂. A solution of 0.8 mmol of dimethyl sulfoxonium methyle A were added slowly. After 2 hours of reaction the solution was filtered over with cannula technique. A bright yellow powder was obtained after evaporation of the solvent under vacuum. (110 mg, 90%) ¹H NMR (400 MHz, Dioxane) δ 4.50 (br, 2xCH olefin), 4.22 (br, 2xCH olefin), 3.42 (s, SOCH₃), 2.55 (d, J = 10.1 Hz, 2xCHHSOexo), 2.20 (m, 2H), 2.05 (m, 2H), 1.90 (t, J = 8.5 Hz, 4H), 1.76 (d, J = 9.8 Hz, 2xCHHSOendo). ¹³C NMR (101 MHz, Dioxane) δ 80.30 (d, J = 10.7 Hz), 78.68 (d, J = 9.4 Hz), 48.86 (s), 36.31 (d, J = 21.0 Hz), 31.90 (s) 31.56 (s). Calc. for C₁₁H₁₉ORhS: m/z = 302.0206. Found: m/z: 302.0213.

[Rh(1,5-cyclooctadiene)(η²-(CH₂)₂SOCH₃)(η²-dimethylmaleate)] (18): To a stirred solution of 0.165 mmol of 8 in THF under inert atmosphere was added 0.17 mmol of DMM. After overnight stirring the solvent and excess of maleate were evaporated to afford a yellow-orange powder in 85% yield. ¹H NMR (500 MHz, THF) δ 4.12 (dt, J = 8.6, 8.3 Hz, 1H olefin), 4.05 (dd, J = 9.3, 2.0 Hz, CHDMM), 4.04 – 3.94 (m, CH olefin), 3.48-3.53 (m, CH olefin), 3.12-3.03 (m, CH olefin), 2.94 (d, J = 10.2 Hz, SOCHFexo), 2.87-2.94 (m, CHFcod-exo) 2.78 (dd, J = 9.3, 1.4 Hz, CHDMM), 2.63-2.53 (m, CHFcod-endo), 2.50 (d, J = 10.1 Hz, SOCHFendo), 2.44-2.35 (m, CHFcod-exo), 2.34-2.26 (m, CHFcod-endo), 2.19-2.08 (m, CHFcod-endo), 2.07-1.93 (m, CHFcod-exo), 1.85 (d, J = 11.0 Hz,SOCHFexo), 1.82-1.72 (m, CHFcod-exo), 0.61 (d, J = 11.0 Hz, SOCHFendo). ¹³C NMR (101 MHz, THF) δ 171.51 (s, COO), 171.45 (s, COO), 105.69 (d, J = 4.6 Hz, Colefin), 94.65 (d, J = 4.6 Hz, Colefin), 84.09 (d, J = 6.9 Hz, Colefin), 78.29 (d, J = 8.1 Hz, Colefin), 47.84 (s, Me), 47.76 (s, Me), 46.87 (d, J = 9.9 Hz), 42.01 (d, J = 10.0 Hz),39.57(s, SOCH₃), 34.82 (s, CH₂), 30.78 (s, CH₂), 24.77 (s, CH₂), 23.63 (s, CH₂),20.99 (d, J = 20.4 Hz, SOCH₂), 12.56 (d, J = 18.8 Hz, SOCH₂). Calc. for C₃₄H₃₄O₁₀Rh₂S₂: m/z: 446.0629. Found: 302.0 as most abundant peak.
Figure 8. $^1$H, $^{13}$C, and 2D NMR studies for species 16.
Figure 9. $^1$H, $^{13}$C, and 2D NMR studies for species 18b.
References


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13 However, carbene polymerisation is also observed for non-oxidised rhodium(I) diene complexes where strict inert conditions are applied.

14 Dimethyl sulfoxonium methylide (A) is accessible by deprotonation of trimethyl sulfoxonium chloride, and can be stored either as a solid or as a solution in THF for few weeks at –20 ºC.

15 Linear polymethylene (no branches) differs from the linear low density polymethylene which contains a significant amount of branches.


17 The influence and possible deactivating role of DMSO was investigated. The polymer reaction carried out in neat, dry DMSO as a solvent affords no polymer, but coordination of DMSO to the catalyst when present in smaller amounts (similar to those in the reaction mixture after complete conversion A) was not observed.

18 The palladium complexes [\([\text{Pd(cod)}(\mu-\text{Cl})]\)\(_2\)], [\((\text{Allyl})\text{PdCl}\)], [\(\text{Pd(MeCN)}\text{Cl}_2\)] and [\(\text{Pd(dba)}\text{Cl}_2\)] only catalyse ylide dimerisation to ethylene, and the related iridium complexes [\([\text{Ir(cod)}(\mu-\text{Cl})]\)\(_2\)] and [\([\text{Ir(cod)}(\mu-\text{OMe})]\)\(_2\)] showed only poor activities, giving rise to very low polymer yields. This behaviour is similar to what was observed in EDA polymerisation reactions.

19 Poor solubility of LPM did not allow us to carry out full GPC analysis. However, the molecular weights determined by NMR integration are in agreement with those obtained by GPC analysis.

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26 For reactions performed in pure THF (e.g. entry 3, Table 2) yields are rather low. Better yields are obtained starting the reaction with EDA in dichloromethane followed by addition of THF and sulfoxonium ylide A.


28 The low T_c and T_m values could alternatively point to the formation of LLDPM (=LLDPE) having a branched structure. However, NMR shows no sign for any branching. Therefore the low values are more likely the result of the relatively low molecular weights (and broad PDI).

29 Attempts to blend separately prepared PEA and PM were not successful, giving rather inhomogeneous mixtures. DSC measurements of thus obtained mixtures (with various different PEA:PM ratios) show only separate crystallisation and melting peaks of PM and PEA, with no sign of the low temperature peaks observed for the copolymer.


31 The Polyethylene sample employed was synthetised by ethylene polymerisation by the commercially available catalyst Cp2ZrCl2.

32 The PEA was synthetised by C1–homo polymerisation of EDA with compound 2 and quenched with methanol in order to obtain low molecular weight polymer.

33 Proper characterisation of such blends would require detailed microscopy and SAX/WAXS measurements, which is beyond the scope of the present paper.


