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Rh-Mediated C1-Polymerization: Copolymers from Diazoesters and Sulfoxonium Ylides

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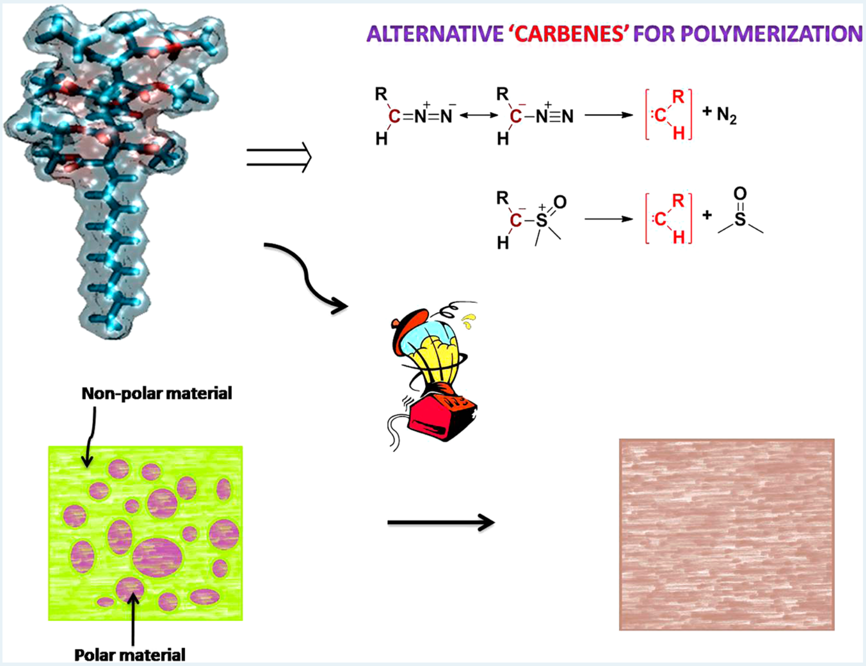
Supporting Information



ABSTRACT: In this paper, we present new results obtained in our investigations of Rh-catalyzed C1 (co)polymerization reactions using carbene units as monomers. We demonstrate here, for the first time, the use of transition metal catalysts in carbene polymerization 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 copolymerization 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 or polymethylene with poly(ethyl 2-ylidene-acetate). 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.

KEYWORDS: *carbene polymerization, block copolymer synthesis, diazo esters, sulfur ylides, rhodium, blending agents*

INTRODUCTION

Polymers bearing polar functionalities are an important class of materials because of their beneficial properties with respect to adhesion, paint- and printability, and miscibility.[1] Industrial focus on the production of such polymers is almost entirely focused on polymerization of vinylic monomers (C2 monomers).[2] However, despite the obvious advantages in terms of availability and cost aspects of vinylic monomers, these C2 polymerization techniques also have some important limitations. Examples are the poor stereocontrol of radical polymerization reactions,[3,4] the generally low reactivity of alkenes (especially ethylene) toward radical polymerization (hampering copolymerization reactions),[5] and difficulties in preparing stereoregular (co)polymers from coordination–

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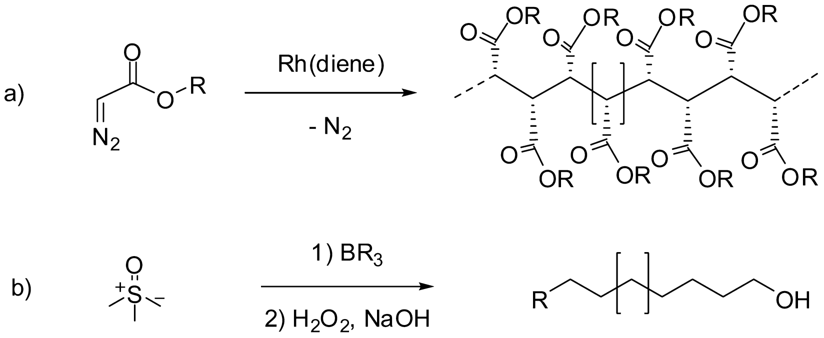
Scheme 1. Illustrative Examples of New C1 Polymerization Techniques[a]



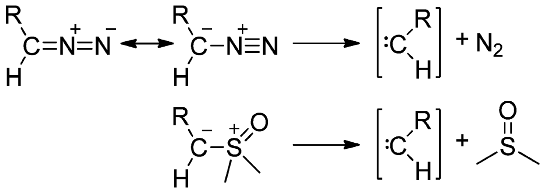
[a](a) Rh-mediated stereoselective "carbene polymerization" and (b) boron-mediated "poly-homologation".

insertion polymerization of functionalized olefins with (late) transition metals.[6−10] Synthesis of syndiotactic and isotactic (rich) homopolymers of a variety of polar vinyl monomers is possible via living coordination−addition polymerization (metal-controlled anionic polymerization or "group-transfer" polymerization).[11−14] However, these systems also have limitations, among which are the "stoichiometric" living character of these reactions (instead of true catalytic turnover) and limitations in polymerization of 1,2-bis-functionalized C2 monomers.

C1 polymerization (carbene polymerization) offers an interesting alternative synthetic approach to polymers that are currently not available via more traditional C2 polymerization, especially if densely functionalized stereoregular (co)polymers are desired.[1,6−10] Polymerization of functionalized C1 monomers is a powerful tool to obtain functionalized polymers with a large structural diversity.[15−35] Up to now, only a few reports (including diazo compounds and ylides) have shown the ability to achieve such polymerization reactions. The most important examples report the use of carbenes from either diazo compounds or sulfoxonium ylides as the C1 monomer precursors (Scheme 1). The recently reported rhodium-mediated carbene polymerization techniques developed in our group allow the formation of high M_w and highly stereoregular polymers that are functionalized with ester moieties at every carbon atom of the polymer backbone in good yields.[15−27] Other interesting examples are the boron-mediated polyhomologation techniques developed by Shea and co-workers using sulfoxonium ylides as monomers, which make it possible to prepare polymers with precise control over the nature of the end-group functionalities.[36−43] To the best of our knowledge, transition metal-catalyzed C1 polymerization reactions using sulfoxonium ylides as monomers have been thus far unknown.

A common feature of these reactions is that the applied C1 monomers, both diazo compounds and sulfoxonium ylides, can be considered as carbene precursors (Scheme 2). Hence, a combination of these reagents with a suitable C1 polymerization catalyst may allow the preparation of copolymers having both polar functionalized (:CHR) and nonfunctionalized (:CH_2) carbene monomers incorporated into the polymer carbon chain. Such reactions would provide an interesting alternative to the use of diazomethane in carbene copolymerization reactions.[44]

Scheme 2. Diazo Compounds and Sulfoxonium Ylides As "Carbene Precursors"



The boron homologation reactions reported by Shea and co-workers are not compatible with the use of polar-functionalized reagents. Attempts to (co)polymerize sulfoxonium ylides and ethyl diazoacetate (EDA) with the boron catalyst already leads to catalyst deactivation after the second "functionalized carbene" insertion step.[40] Transition metal catalysts, especially Rh^I(diene) complexes, perform well in EDA polymerization to prepare highly *syndiotactic* poly(ethyl 2-ylidene-acetate) (*st*-PEA). Therefore, we decided to investigate the activity of Rh catalyst in C1 polymerization employing sulfoxonium ylides as the carbene monomer source, aiming at desirable copolymerization reactions of functionalized and nonfunctionalized "carbenes". In principle, such copolymerization can also be achieved using diazomethane as the C1 comonomer instead of a sulfoxonium ylide,[44] 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[45−48]). Sulfoxonium ylides are quite stable, nonexplosive, and less toxic and are thereby much safer methylene carbene (:CH_2) precursors than diazomethane, which makes them much more interesting from a synthesis point-of-view.

Herein, we describe the preparation and characterization of new copolymers using diazo esters and methylene sulfoxonium ylides as monomers in Rh^I(diene)-mediated reactions. In addition, catalyst (de)activation pathways are disclosed.

■ RESULTS AND DISCUSSION

Rh-Mediated Homopolymerization of "Carbenes" from Sulfoxonium Ylides. Although boron-mediated synthesis of polymethylene ("poly homologation") is a known reaction,[36−40] there are no reports of any TM-mediated "carbene polymerization" reactions using sulfoxonium ylides as carbene precursors. Therefore, we first investigated the ability of different Rh^I(diene) compounds to mediate carbene polymerization using sulfoxonium ylides as carbene precursors. Rh^I(diene) complexes **1−6** (Figure 1) have shown good to excellent activities in carbene polymerization reactions using diazo esters as the carbene precursors, and therefore, we first evaluated the performance of these same catalysts for the synthesis of polymethylene from the dimethyl sulfoxonium

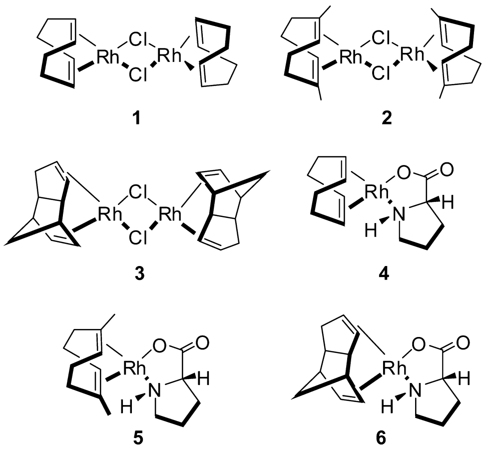
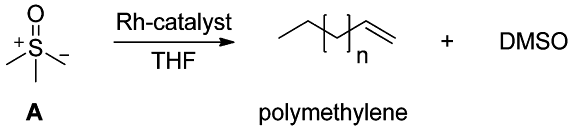


Figure 1. Rh^I(diene) catalysts **1**−**6** used in this study.

Scheme 4. Rh-Mediated Carbene Polymerization Using Dimethyl Sulfoxonium Methylide (A) as the Carbene (:CH_2) Precursor



methylide ylide **A** ($Me_2SO_2{=}CH_2$). These homopolymerization studies were aimed at gaining more information about the transition metal-catalyzed polymerization process with sulfoxonium ylides before actually using these same sulfoxonium ylides in copolymerization reactions of functionalized and nonfunctionalized carbene precursors.

We also prepared the new complex **7** that contains a more sterically hindered diene ligand. This compound was obtained according to the reaction route depicted in Scheme 3.

The catalytic C1 polymerization reactions of the Rh^I(diene) compounds **1**−**7** with sulfoxonium ylide **A**[49] as the substrate were carried out in THF under argon (Scheme 4). In all cases (except entry 5), the reactions reached full conversion (Table 1), but the different catalysts required various reaction times to convert all the monomer. The obtained polymer, identified as linear (low M_w) polymethylene (LPM, vide infra for detailed characterization),[50] which is 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 **1**−**7** produce, after full consumption of the monomer, polymethylene in different yields. As for EDA polymerization, the carbene polymerization reaction employing sulfoxonium ylide **A** is also substantially influenced by the diene applied as ligand. The best results were obtained with the most bulky dienes 1,5-dimethyl-1,5-cyclooctadiene (Me_2cod) and 1,5-di(4-methoxy)phenyl-1,5-cyclooctadien ((*p*-$MeOC_6H_4)_2$cod) (complexes **2**, **5**, and **7**) (entries 3−5, 8, and 10). The Me_2cod and (*p*-$MeOC_6H_4)_2$cod complexes also give higher yields and molecular weights in carbene polymerization of ethyl diazoacetate (EDA) than the corresponding cod complexes, suggesting that the polymerization of methylene (:CH_2) generated from **A** may follow similar activation and propagation pathways. However, in contrast to EDA polymerization, 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_2cod catalysts **2** and **5** as compared with the cod catalysts **1** and **3** suggests that increasing the steric bulk around the metal prevents or slows down chain-termination pathways.[7] Increased ligand bulk might also hinder the coordination of multiple substrates, and thereby slow down the competing formation of ethene via :CH_2 carbene dimerization.[51] If this is the case, even higher polymethylene yields should be attainable by further increasing the steric bulk at the diene ligand. Indeed, (*p*-$MeOC_6H_4)_2$cod rhodium complex **7** turned out to be the best catalyst for the synthesis of polymethylene via Rh-mediated carbene polymerization. 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 1, entry 11). Hence, changing the Me substituent of **2** to a *p*-$MeOC_6H_4$ substituent in **7** (Table 1, entries 3, 4, and 10) improves both the reaction rate (full conversion in 2 days instead of 4−10 days) and the obtained polymer yield (77% instead of 39−47%). The molecular weights produced by **7** are similar to those obtained with **1**−**5**.

Increasing the reaction temperature from 22 to 60 °C lowers the yield, whereas an increased ylide/Rh ratio is beneficial (entries 2 and 4).[52] In general, better yields are obtained 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 because the catalyst may (partly) coprecipitate from the solution. In the presence of (traces of) water, (partial) hydrolysis of **A** occurs, and hence, rigorous anhydrous conditions are required.

Scheme 3. Synthesis of the 1,5-Di(4-methoxyphenyl)-1,5-cyclooctadiene Ligand and Rhodium Complex 7

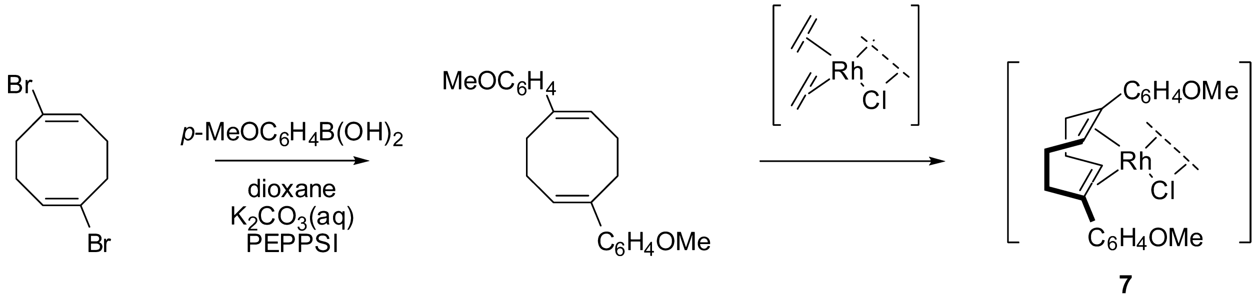


Table 1. Rh-Mediated Carbene Polymerization from Sulfoxonium Ylide A.[a]

entry	cat.	ylide:Rh	yield[b] PM (%)	reaction time	M_w (Da)	M_w/M_n	M_n NMR (Da)	M_n GPC (Da)
1	**1**	50:1	17	17 h	506	1.976	nd	256
2[c]	**1**	150:1	20	17 h	1039	3.799	nd	277
3	**2**	50:1	39	4 days	1430	3.287	nd	438
4[c]	**2**	150:1	47	10 days	3455	3.355	1778	1092
5[d]	**2**	500:1	24	nd	nd	nd	1485	nd
6	**3**	50:1	18	5 days	1083	2.927	1724	370
7	**4**	50:1	15	2 days	1788	1.924	nd	929
8	**5**	50:1	37	5 days	1289	3.303	nd	405
9	**6**	50:1	28	5 days	450	2.113	nd	213
10	**7**	100:1	77	2 days	1719	4.290	1169	815
11	**8**	100:1	80	2 days	nd	nd	1472	nd

[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.

The carbene polymerization reaction seems to be quite specific for Rh(diene) complexes because a variety of Ir^I, Pd^0 and Pd^{II} complexes gave very poor results in this reaction under similar reaction conditions.[53]

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 to 3500 Da).[54] However, the polydispersity also increases from PDI = 1.9 to 4.3 with increasing M_w. This seems to be caused in part by the precipitation of the polymer from THF.

Carbene Polymerization Attempts with Functionalized Sulfoxonium Ylides. Attempts to polymerize the more bulky sulfoxonium ylides **B** and **C** (Figure 2) were not successful. Reaction of **B** with catalysts **1**−**7** under different reaction conditions (variable temperatures, ylide/Rh ratios and different solvents) in all cases led to mostly carbene dimerization, producing diethyl maleate and diethyl fumarate (Scheme 5). Some short oligomers (C3−C7) were also observed in all cases. Only catalyst **6** at 40 °C in 2 mL of CH_2Cl_2 (0.014 mmol of **6** and 0.71 mmol of ylide **B**) produced after 1 week some longer oligomers (M_w = 2475 Da, PDI = 1.019) in isolable amounts, but only in rather poor yields (<5%).

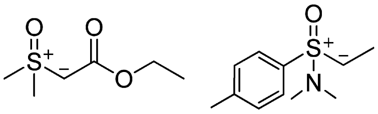


Figure 2. Structure of sulfoxonium ylides **B** and **C**.

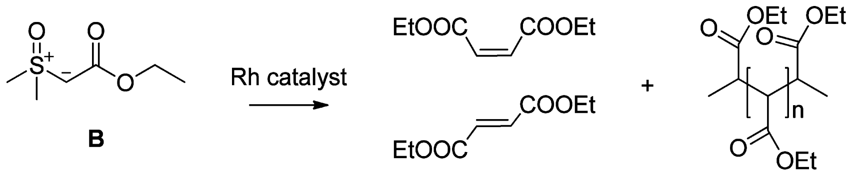
Reaction of **C** with the Rh compounds **1**−**7** did not produce any polymer. The addition of 1.27 mmol of **C** to 0.025 mmol of Rh^I(diene) at room temperature led to formation of *p*-tolyl-SO-NMe_2 (^{1}H NMR: δ = 7.49 and δ = 7.28, AB system ($CH{=}CH$), δ = 2.64 (NCH_3) and δ = 2.39 (CCH_3)) as the only detectable compound. The samples were treated in the same way as all other polymer reactions, leading to evaporation of the likely formed gaseous butene produced by carbene dimerization. Neither nonvolatile oligomers nor polymers were observed. A similar result was obtained by Shea and coworkers. Their attempts to homopolymerize this compound were also unsuccessful.[55] These bulkier ylides apparently produce only olefins by carbene dimerization.

Copolymerization of Carbenes from EDA and Sulfoxonium Ylide A. The ability of Rh(diene) complexes to polymerize "carbenes" generated from both EDA[15−27] and sulfoxonium ylides provides attractive opportunities in copolymerization reactions. Incorporation of the COOEt moieties employing C1 techniques provides an interesting alternative approach to prepare desirable copolymers containing both polar and nonpolar monomers. Two different approaches were investigated for such a reaction: (i) Rh-mediated copolymerization of the sulfoxonium ylides **A** and **B** and (ii) copolymerization of EDA and sulfoxonium ylide **A** (Scheme 6). Unfortunately, polymerization 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, we can discard the copolymerization reactions via route i.

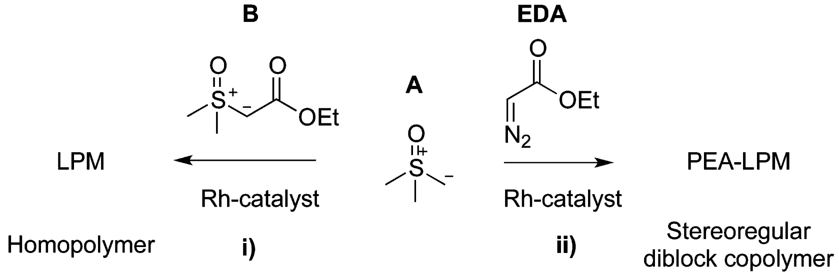
Copolymerization of EDA with sulfoxonium ylide **A** employing Rh(diene) complexes is more successful and produces copolymer by incorporating carbene units from both EDA and **A**. These polymers have a stereoregular PEA-LPM diblock structure (vide infra for detailed characterization).

Screening of the catalysts shown in Figure 1 indicated that all complexes can produce copolymer PEA−LPM, although in various yields. Although compounds **1**, **3**, **4**, and **6** have a poor activity (<5% yield), compounds **2**, **5**, and **7** proved to be more successful. However, we had to consider several issues to choose the right reaction conditions. Both EDA and sulfoxonium ylide **A** are rather reactive species and have been

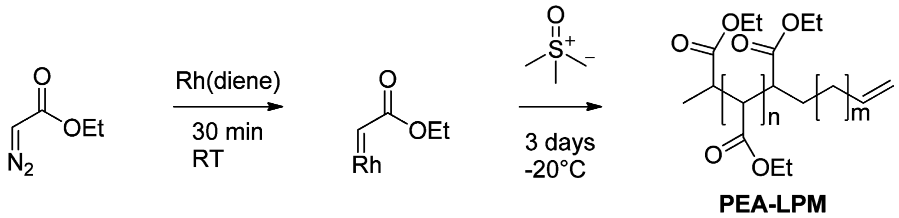
Scheme 5. Rh-Mediated Carbene Dimerization and Oligomerization Using Sulfoxonium Ylide B As the Carbene Precursor



Scheme 6. Attempts To Copolymerize Carbenes from Sulfoxonium Ylide A with (i) Sulfoxonium Ylide B and (ii) EDA



Scheme 7. Procedure for the Synthesis of the Diblock Copolymer PEA−LPM



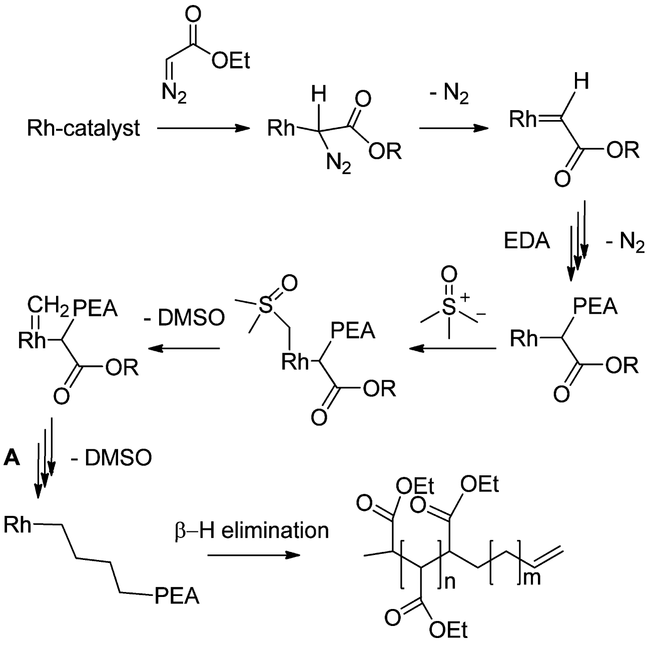
used for a variety of reactions, such as cyclopropanation,[56] heterocycle formation,[57] X-H insertion,[58] C-acylation,[59] olefination,[60] dimerization, etc. Therefore, a complex reaction mixture can be obtained with these reagents. So far, the reactivity between EDA and sulfoxonium ylide **A** has not been explored. As we expected, even in the absence of any catalyst, EDA and **A** in THF react strongly in an exothermic manner, producing a complex mixture of products. Low-temperature experiments at 0, −20, and −50 °C led to similar mixtures.

Successful copolymerization reactions required preactivation of the catalyst by EDA. The addition of sulfoxonium ylide **A** after 30 min of incubation time in a mixture at −20 °C affords the best reaction conditions. The copolymer is produced over the course of 3 days after warming the reaction mixture to room temperature (Scheme 7). Evaporation of the solvent followed by addition of MeOH leads to the precipitation of diblock copolymer PEA−LPM in ~15% yield. As is the case of the synthesis of LPM, the copolymer PEA−LPM precipitates in THF, thus explaining the high PDI and the rather low yield. Unfortunately, polymerization 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 copolymerization with EDA).[61]

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 °C. 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 8.

The best Rh catalysts for this reaction are compounds **2** and **7**, which produce the copolymer in 15% and 18% yield, respectively. The optimum ratio of Rh/ylide/EDA for both catalysts was found to be 1:50:50 (entries 2 and 6, Table 2). 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 **7** (entries 7−10, Table 2) and has hardly any effect on the obtained yields.

Scheme 8. Proposed Formation of Stereoregular Diblock PEA-LPM Copolymers



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 mostly affected by the catalyst rather than the reaction conditions. Catalyst **7** affords, on average, longer polymers than catalyst **2**. Interestingly, these copolymers are remarkably long compared with PEA obtained in EDA homopolymerization reactions.[18−27]

Characterization of the Obtained LPM Homopolymers. The obtained polymethylene samples generated from **A** (see Table 1) were characterized by FT-IR, ^{1}H, and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC).

The FT-IR spectra display vibrations typical and characteristic of polymethylene (identical to polyethylene). Clear vibrations are observed corresponding to the C−H stretch

Table 2. Rh-Mediated Carbene Copolymerization from Sulfoxonium Ylide A and EDA.[a]

entry	catalyst	EDA/ylide/Rh	yield[b] (%)	M_w[c] (kDa)	M_n[c] (kDa)	PDI[c]	% LPM[d]
1	**2**	20:50:1	6	210	117	1.78	58
2[e]	**2**	50:50:1	7	nd	nd	nd	25
3	**2**	50:50:1	16	481	237	2.03	33/79[f]
4	**2**	100:100:1	8	396	108	3.66	28/38[f]
5	**5**	50:50:1	<5	nd	nd	nd	nd
6	**7**	50:50:1	18	520	264	1.97	38
7	**7**	100:35:1	10	791	346	2.28	12
8	**7**	100:50:1	15	640	247	2.59	17
9	**7**	100:100:1	15.5	648	292	2.21	38
10	**7**	100:150:1	14	626	286	2.18	54
11	**8**	100:100:1	5	53	21	2.52	nd

[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 ^{1}H NMR spectra in *o*-dichlorobenzene-d_4 at 110 °C of total amount of copolymer. [e] Only 6 mL of THF. [f] The first number represents the $CDCl_3$ soluble fraction, and the second, the chloroform insoluble fraction.

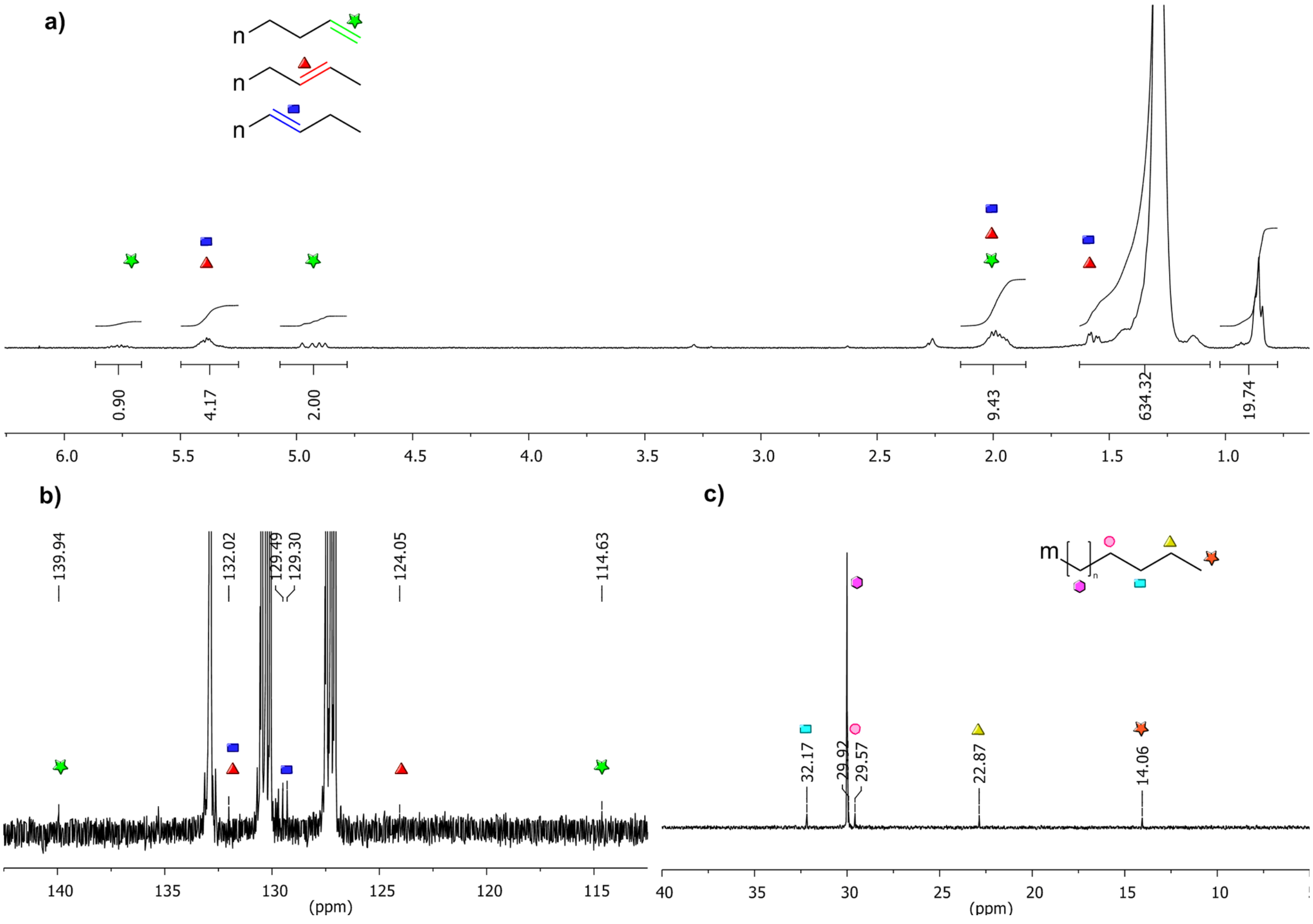


Figure 3. (a) ^{1}H NMR spectra of polymethylene, (b) ^{13}C NMR spectra (terminal olefins), and (c) ^{13}C NMR spectra (saturated chain) of polymethylene in 1,2-dichlorobenzene at 120 °C.

vibrations of the $-CH_2-$ and $-CH_3$ groups at 2916.5 and 2848.9 cm^{-1}, the $-CH_2$ bending vibrations at 1471.7 and 1462.1 cm^{-1}, and the $(-CH_2-CH_2-)_n$ rocking vibrations at 731.5 and 715.5 cm^{-1}.

Figure 3 shows the ^{1}H and ^{13}C NMR spectra of a representative polymethylene sample measured in 1,2-dichlorobenzene at 120 °C. The sharp peak at $\delta = 1.38$ corresponds to the $-CH_2-$ units of the polymer chain. The broad triplet peak at $\delta = 0.93$ corresponds to a $-CH_3$ 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 (^{1}H NMR at $\delta = 5.69$, $^3J_{H,H} = 17.1$, 10.2 Hz ($-CH{=}CH_2$), $\delta = 4.86$, $^3J_{H,H} = 17.1$, 3.7 Hz ($-CH{=}CH_2$) and $\delta = 4.80$, $^3J_{H,H} = 10.2$, 3.7 Hz ($-CH{=}CH_2$)). Isomerization from terminal to internal olefins by chain-walking[7] can, in principle, give access to the formation

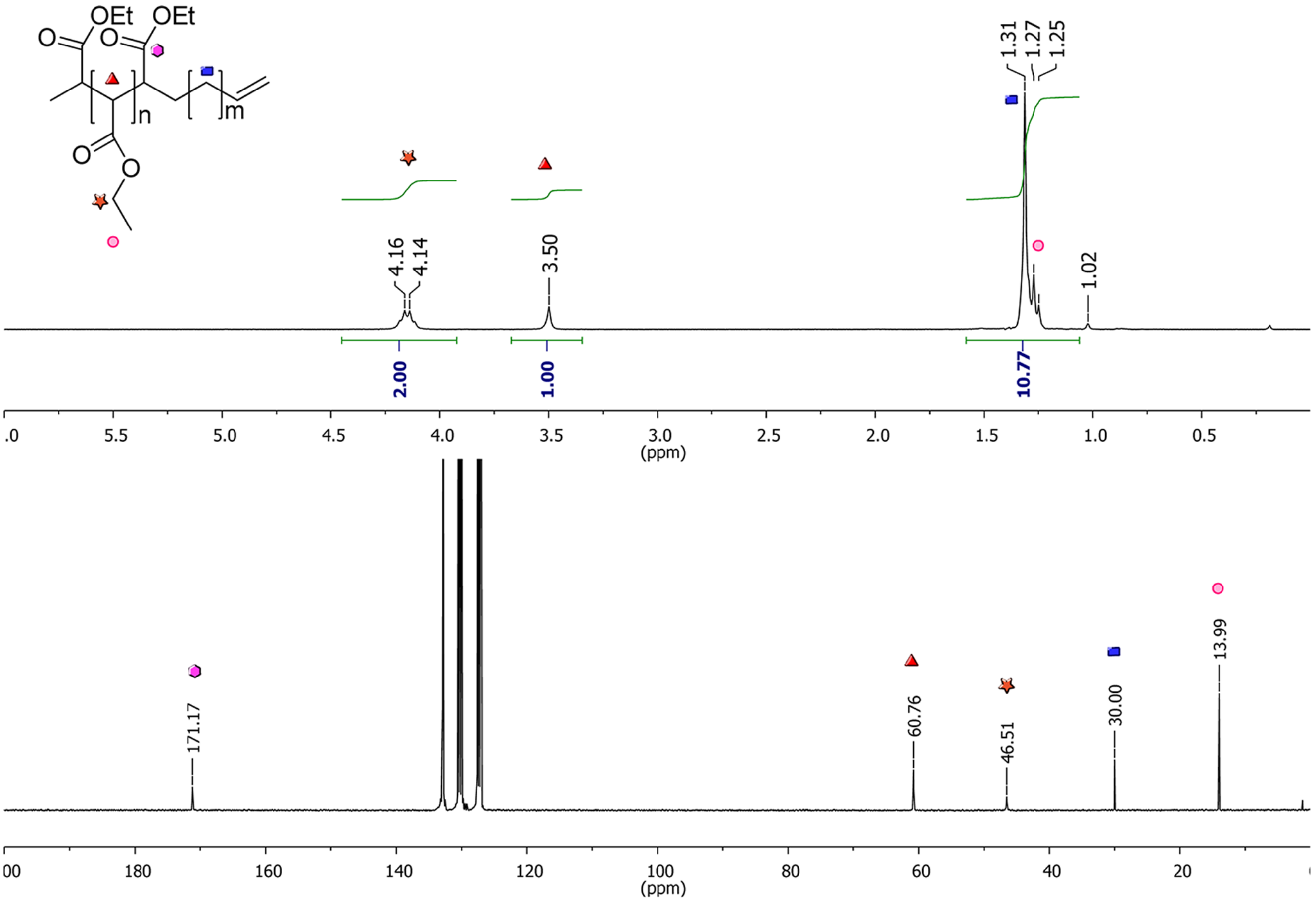


Figure 4. ^{1}H NMR and ^{13}C NMR spectra of chloroform insoluble stereoregular diblock *st*-PEA−LPM at 120 °C in 1,2-dichlorobenzene.

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: δ = 32.17 ppm ($-CH_2-CH_2-CH_3$), δ = 30.0 ppm ($-(CH_2)_n-$), δ = 29.57 ($-CH_2-(CH_2)_2CH_3$), δ = 22.87 ppm ($-CH_2-CH_3$), and δ = 14.06 ppm ($-CH_3$).[62] In agreement with this, determination of the average molecular weight based on ^{1}H NMR integration leads to values similar to those 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 $T_m \approx 120$ °C and $T_c \approx 105$ °C transitions ($\Delta H \sim 150$ J/g). The rather low melting point is most likely a consequence of the low M_w of these polymethylene samples.[63]

Characterization of the Stereoregular Diblock *st*-PEA−LPM Copolymers. The obtained stereoregular (syndiotactic) diblock *st*-PEA−LPM copolymers were also characterized by ^{1}H and ^{13}C NMR spectroscopy, GPC and DSC.

Different copolymers obtained with different catalysts or employing different 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 CH_2 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 functionalized copolymer from the less functionalized ones. The nonsoluble 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 homopolymer in the latter (chloroform-soluble) fraction cannot be entirely ruled out. However, the soluble and nonsoluble fractions reveal quite similar crystallization profiles in DSC (vide infra), suggesting that the soluble fraction is also dominated by diblock *st*-PEA-PM copolymers.

Figure 4 shows the ^{1}H NMR spectra of the most insoluble (in chloroform, RT) copolymer in 1,2-dichlorobenzene at 120 °C. The signals at δ = 4.15, 3.50, and 1.27 ppm correspond to $-OCH_2-$, $-CH-$ and $-CH_3$ of the stereoregular[17] *st*-PEA block, whereas the sharp peak at δ = 1.31 ppm corresponds to the $-CH_2-$ of the polymethylene block. The vinylic end groups can be observed for the shorter polymers at δ = 5.83 ppm ($-CH{=}CH_2$), δ = 5.04 ppm ($-CH{=}CH_2$), and δ = 4.95 ppm ($-CH{=}CH_2$). The ^{1}H NMR spectra ($CDCl_3$) of the copolymers with a high stereoregular *st*-PEA content show similar peaks, but as expected, the integrals show a higher ratio of $CHCOOEt/CH_2$, which provides more solubility in chloroform. The signals from the diblock can be observed as well in ^{13}C NMR spectra: δ = 171.17 ($C{=}O$), δ = 60.76 ($-OCH_2$),δ = 46.51($-CH-$), and δ = 13.99 ppm ($-CH_3$) from the *st*-PEA block and δ = 30.0 ppm (CH_2) 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

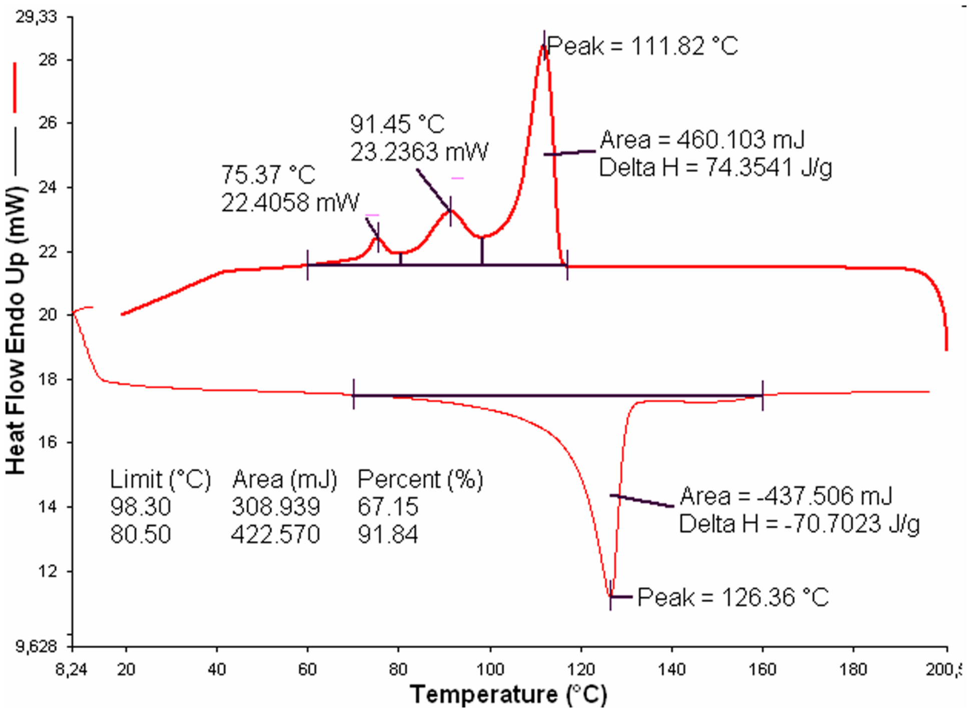


Figure 5. DSC second heating and cooling curve of PEA−PM copolymer (entry 3, Table 2).

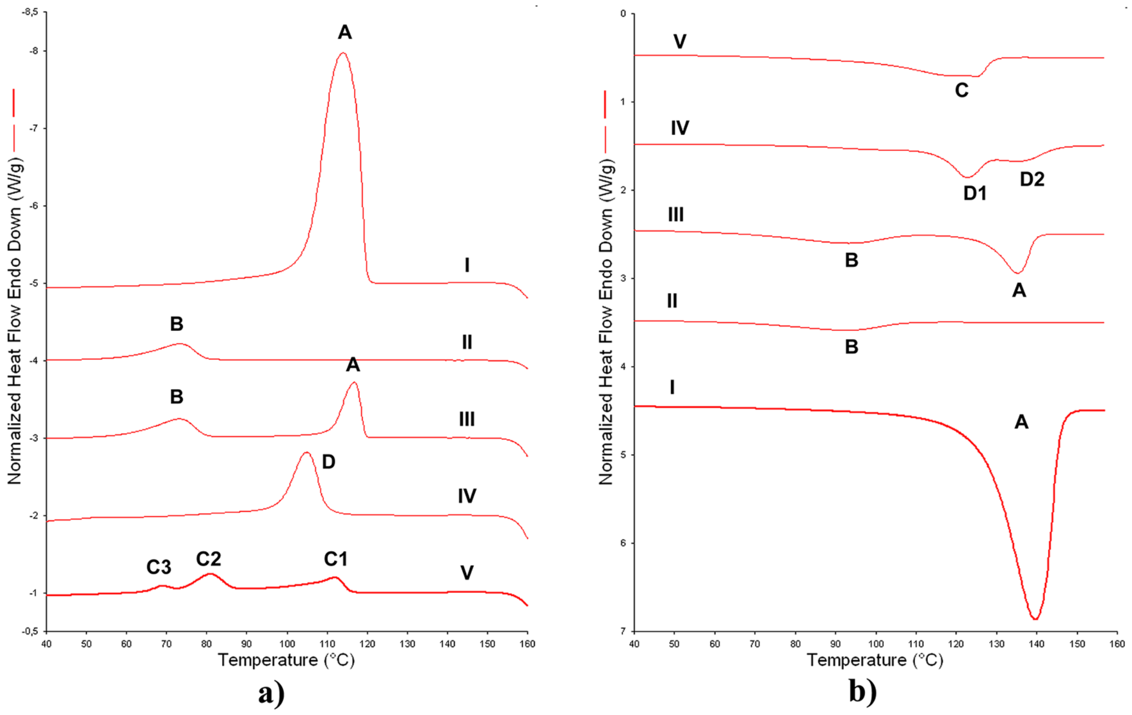


Figure 6. DSC second (a) cooling and (b) heating curves for homopolymers (I and II, for HDPE and *st*-PEA, respectively), copolymer (V), and blends (III for a 10/90/0 ratio and IV for a 10/90/50 ratio of HDPE/*st*-PEA/copolymer).

functionalized samples reveal a M_w of 520 kDa and PDI = 1.97. Reactions employing a 100:35:1 ratio of 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 with molecular weights reported for EDA polymerization 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 2).

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 CH_2) are present, as can be deduced from the variations in the heat capacity ($\Delta H_{PM} > 20$ kJ/mol $> \Delta H_{PEA}$). In the crystallization curve, we can observe the characteristic peak for PM (~110 °C), but we cannot distinguish a separate crystallization transition for *st*-PEA.[64] In a semicrystalline polymer, in which the different fragments can crystallize, we can assume that the block with the highest T_c or the predominant phase will crystallize first. As a result, the second fragment will have an unfavorable configuration for crystallization, and the crystallization process can be simply obstructed, meaning that thermodynamics no longer solely direct the crystallization process. Thus, the crystallization peaks we observe at lower temperatures (~90 and ~73 °C) can be assigned to nonfavored crystallizations 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 crystallization (T_c), which is also expected to dominate over *st*-PEA crystallization on the basis of the large differences in the crystallization enthalpies, the two lower-temperature crystallization peaks are most likely also PM crystallizations with hindered configurations.

Blending Experiments. An attractive approach to combine properties of different materials is to produce blends in which benefits from various phases can be obtained. Often, the problem in this field is the compatibility of different phases. Immiscible polymer blends often afford macrophase separation above a critical temperature, thus being a disadvantage in terms of production and handling.[65] 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 insight into the different interactions between the polar *st*-PEA block and the nonpolar PM block and the potential application of these copolymers, we studied blends containing HDPE[66] and *st*-PEA[67] in which the phase behavior, thermal properties, and crystallization of PM/PEA blends were investigated by DSC experiments.

Figure 6 shows the heating (a) and crystallization (b) curves of the second run obtained for the different blends. Curves I and II are the homopolymers HDPE and *st*-PEA, respectively. DSC curve III is measured using a simple 10/90 mixture of HDPE/*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 crystallization 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 interlamellar region or out of the interlamellar region, and therefore, crystallization patterns are expected to be more complex than those occurring in the respective homopolymers and block copolymers. Therefore, DSC curve III simply represents the expected behavior of macrophase-separated HDPE in a *st*-PEA matrix (nonmiscible mixture).

The behavior of HDPE/*st*-PEA mixtures changes markedly upon addition of *st*-PEA-LPM copolymer. In the presence of *st*-PEA-LPM copolymer, as we can see in curve IV (10/90/50 ratio of HDPE/*st*-PEA/copolymer), the only detected crystallization peak is $T_c = 104.9$ °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.[68] In the copolymer curve V, the PM microdomains dominate the crystallization process ($T_c = 120°$). The observed lower T_c peaks are likely also from PM micro domains, but in a thermodynamically less favorable orientation for crystallization (perhaps shorter blocks).

In contrast, curve IV (10/90/50 ratio of 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 of the solubility of HDPE in the PM domains of the copolymer, thus resulting in an overall higher crystallinity ($\Delta H_D = 45$ J/g vs $\Delta H_{C1} = 27$ J/g). These results suggest that the *st*-PEA-LPM copolymer acts as a blending agent for HDPE and *st*-PEA.[68] Remarkably, the unusual T_c's observed in the copolymer ($T_c = 81$ °C, 69 °C) do not appear in the blend, which is likely the result of the interaction of the HDPE with every PM domain and, therefore, homogenization of the nonpolar phase of the blend. This phenomenon also affects the *st*-PEA phase. Peak B completely disappears in curve IV, indicating that the prearrangement of the PM-HDPE chains hinders the cocrystallization of the *st*-PEA blocks with the homopolymer *st*-PEA.

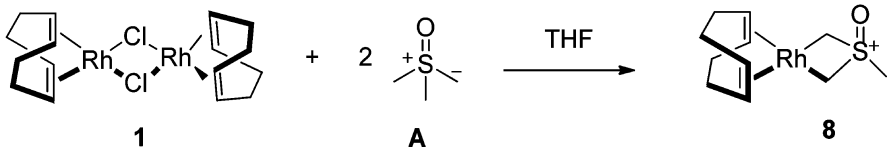
Rather relatively large amounts of copolymer are required to observe the above-mentioned effects. HDPE/*st*-PEA/copolymer mixtures with smaller amounts of copolymer and a larger HDPE content than *st*-PEA show a gradual decrease of T_c from the PM/PE domains and no T_c for the *st*-PEA domains (see Supporting Information, Figure S17). Only in mixtures with high *st*-PEA contents does the T_c of PEA become apparent. Mixtures of PEA and HDPE with small amounts of copolymer thus seem to behave as macrophase-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.

Model Studies To Identify Catalytic Intermediates, Side Reactions, and Deactivation Pathways. As described above, the best results in the carbene copolymerization of sulfur ylide **A** with EDA are clearly obtained with catalysts containing 1,5-disubstituted cod ligands, such as 1,5-Me_2cod and 1,5-(*p*-$MeOC_6H_4)_2$cod (i.e., complexes **2** and **7**). Catalysts without steric bulk at the 1,5-positions afford hardly any copolymer. Catalysts with more bulky diene ligands also perform best in the homopolymerization of sulfur ylide **A**, leading to linear polymethylene (good yields with catalyst **2** and **7**; see Table 1), but the homopolymerization reactions do tolerate the use of catalysts with less bulky diene ligands (moderate polymethylene yields with catalysts **1** and **4**), while these perform poorly in the copolymerization reactions.

One contributing factor to the higher yields obtained with more bulky catalysts in the homopolymerization of **A** could well be suppressed carbene dimerization (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 copolymerization of sulfur ylide **A** with EDA. Therefore, in an attempt to understand these observations, we performed some stoichiometric model studies with compounds **1** and **7** to identify possible intermediates, side reactions, and deactivation pathways.

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

Scheme 9. Reactivity of Compound 1 and A Leading to Compound 8



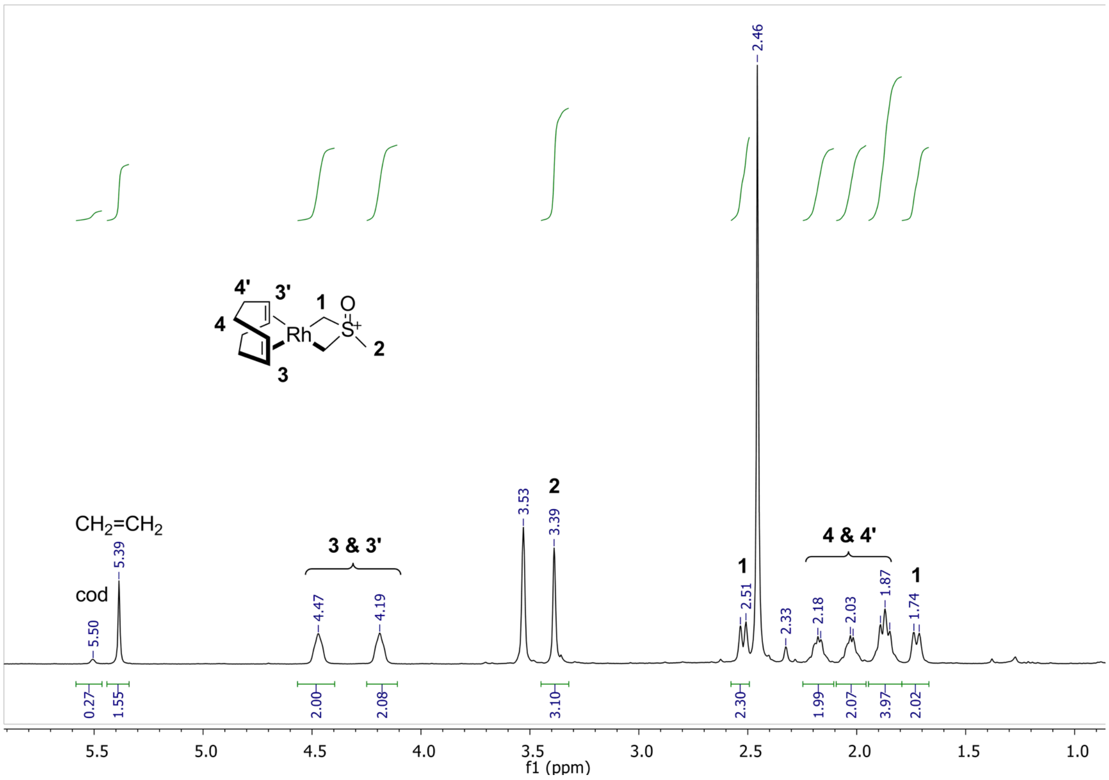


Figure 7. ^{1}H NMR spectrum of species **8** formed from **1** with sulfur ylide **A** in dioxane.

mild coordinating solvents, such as THF or dioxane. The reaction affords a yellow solution and a white salt precipitate. The soluble part of the reaction mixture is a clean solution of complex **8** (see Scheme 9). The salt precipitate was identified as trimethyl sulfoxonium chloride ([Me_3SO]Cl). Complex **8** was characterized with mass spectrometry and a combination of NMR techniques (an illustrative ^{1}H NMR spectrum is shown in Figure 7). In addition to an intact cod ligand, the rhodium complex **8** 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 **8** is best described as an anionic bis-alkyl Rh^I compound with an internal sulfoxonium counterion. Stoichiometric reactions give incomplete conversion of **1** to **8**. Complex **8** was formed much more selectively in experiments in which a Rh/ylide ratio of 1:2 was used, thus showing that the ylide itself acts as a base for deprotonation of the CH_2 group of a second ylide, leading to complex **8**. The reaction is accompanied by formation of a negligible amount of ethylene. Large-scale synthesis allowed us to isolate **8** as a bright yellow compound in high yield (Scheme 9).

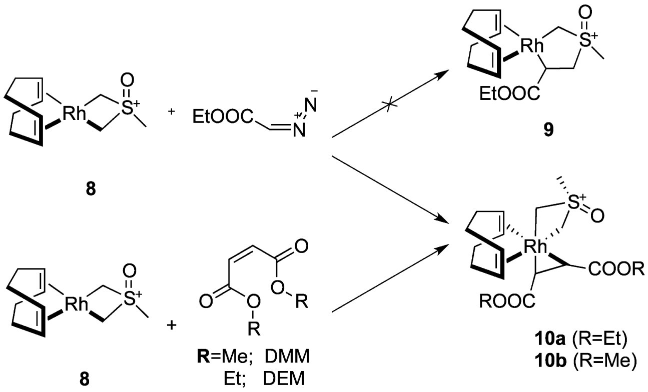
Similar experiments with complex **7** (1:20 Rh/ylide ratio) resulted in a faster consumption of ylide **A** (complete conversion in less than 30 min), and NMR spectra of the resulting solution revealed a complex mixture of rhodium compounds, independent of the solvent used. Attempts to form a complex analogous to **8** by performing reactions of **7** with **A** at lower temperatures (−20 and −73 °C) were not successful, in each case leading to formation of ethylene and a nonidentified mixture of rhodium compounds. This suggests that the steric bulk of the (p-$MeOC_6H_4$)$_2$cod ligand in **7** prevents formation of a complex analogous to **8**, probably by preventing coordination of a second ylide moiety to the metal center and thus favoring the carbene transfer mechanism.

We tested the activity of complex **8** as a precatalyst in both the homopolymerization of sulfur ylide **A** and in the copolymerization of **A** with EDA. Remarkably, although **8** performs very poorly in the copolymerization of **A** with EDA (similar to **1**), higher polymethylene yields were obtained in the homopolymerization of sulfur ylide **A** with **8** than with **1**. Complete conversion of **A** also requires shorter reaction times with **8** than with **1** (entry 11, Table 1). The improved performance of **8** over **1** in the homopolymerization of **A** appears to be related to a reduced carbene dimerization activity.

To exclude the possibility that the observed formation of polymethylene is actually due to polymerization of in situ-generated ethylene, some control experiments were performed in which we tested catalyst **8** as an ethylene polymerization catalyst. However, a solution of **8** in THF treated with 3 bars of ethylene atmosphere for two days showed neither the presence of oligomers nor that of any polymer.

As mentioned above, the activity of complex **8** toward copolymerization of **A** with EDA is poor, which contrasts with its improved behavior in the homopolymerization of **A** compared to **1**. The poor performance of **8** in the copolymerization reaction is most likely due to its poor compatibility toward EDA because **8** also performs very poorly in the homopolymerization 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 **8** towards EDA, we studied the reaction of **8** with limited amounts of EDA on the NMR scale, expecting to observe carbene insertion reactions into the Rh−C bonds of ylide-based ligand moiety with formation of complex **9** (Scheme 10).

Scheme 10. Reactivity of Complex 8 in the Presence of Diethyl (Methyl) Maleate[a]



[a]Production of deactivated catalyst **10** for copolymerization.

Treatment of complex **8** with 2 equiv of EDA in THF leads to fast evolution of N_2 and an immediate color change of the solution from yellow to orange-brown. At lower temperatures (−78 °C), the reactivity is more controlled and, thus, affords a cleaner reaction mixture. In situ experiments in THF-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 because of an ^{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 **8** was treated with 1 equiv of diethyl maleate produced the same species as observed in the reaction of **8** 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 **10b**.

It is noteworthy that the complexes of type **10**, formed by reaction of **8** with maleates, proved to be virtually inactive toward homopolymerization of **A** (<5% yield after 3 days at RT). These model studies therefore give a good explanation of the poor performance of complexes **1** and **8** in the copolymerization of **A** with EDA: they are both rapidly deactivated by reaction of **8** (complex **8** is formed under the catalytic condition from **1** and **A**) with in situ-generated diethyl maleate from EDA, thus producing the inactive complex **10a**. The more bulky catalyst precursors **2** and **7** containing steric bulk at the 1,5-position of the diene ligand do not form complexes similar to **8** and, hence, do not react with diethyl maleate to form inactive compounds similar to **10**.

■ CONCLUSIONS

In this paper, we present the first examples of transition metal-catalyzed carbon-chain polymer formation using sulfoxonium ylides as monomers. We demonstrated that polymethylene is formed via a transition metal carbene polymerization reaction using dimethyl sulfoxonium methylide as the carbene ($:CH_2$) source. Rhodium-mediated homopolymerization of sulfoxonium ylide **A** affords linear polymethylene (LPM ≅ LPE). Other (substituted) sulfoxonium ylides could not be polymerized, presumably because of steric hindrance. However, we successfully demonstrated that functionalized copolymers can be prepared in the Rh(diene)-mediated copolymerization of nonfunctionalized carbenes generated from sulfoxonium ylides and polar-functionalized carbenes generated from diazoesters.

The best results in the copolymerization reactions were obtained with Rh(diene) complexes containing bulky 1,5-disubstituted cod ligands, such as 1,5-Me_2cod and 1,5-(p-$MeOC_6H_4$)$_2$cod. Model reactions between [{Rh(cod)(μ-Cl)}$_2$] complex **1** and dimethyl sulfoxonium methylide **A** allowed the isolation of [Rh(cod){$(CH_2)_2SOMe$)}] complex **8**. This species is also formed under the catalytic homopolymerization reaction conditions. In the copolymerization of EDA with sulfur ylide **A**, complex **8** reacts with in situ-generated diethyl maleate (generated from EDA) to form the inactive diethyl maleate complex **10a**, which explains the poor activity of complex **8** in the copolymerization reactions. This copolymerization deactivation pathway is blocked by the use of more bulky complexes containing 1,5-substituted diene ligands, such as Rh(Me_2cod) complex **2** and Rh((p-$MeOC_6H_4$)$_2$cod) complex **7**. In the homopolymerization of dimethyl sulfoxonium methylide **A**, complex **8**, Rh(Me_2cod) complex **2**, and Rh((p-$MeOC_6H_4$)$_2$cod) complex **7** perform comparably well and each much better than [{Rh(cod)(μ-Cl)}$_2$] complex **1**. This last fact is mainly due to suppressed carbene dimerization (ethylene formation) activity for **2**, **7**, and **8** compared with **1**.

PEA−LPM block copolymers can be prepared only by starting the carbene polymerization with EDA as the functionalized carbene precursor, followed by addition of sulfur ylide **A**. This procedure requires that (most of) the EDA substrate is consumed before addition of sulfur ylide **A**. However, the polymethylene content and thereby the solubility of the copolymer can be easily tuned by varying the ylide/EDA ratio. In this way, different diblock copolymers with different properties can be prepared. This new C1 polymerization procedure provides an attractive synthetic protocol to prepare stereoregular diblock copolymers carrying a highly syndiotactic ester-functionalized carbon-chain block and a nonfunctionalized, nonpolar polymethylene block. The blending properties of these new copolymers makes them attractive for application as additives in polymer blends or glues between functionalized and nonfunctionalized polymers.

■ 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. [{Rh^I(1,5-cyclooctadiene)(μ-Cl)}$_2$][69] (**1**), [{Rh^I(1,5-dimethyl-1,5-cyclooctadiene)(μ-Cl)}$_2$][70,51] (**2**), [{Rh^I(1,5-dimethyl-1,5-cyclooctadiene)(μ-Cl)}$_2$][71] (**3**), [(L-prolinate)Rh^I(1,5-cyclooctadiene)][72] (**4**), [(L-prolinate)-Rh^I(1,5-dimethyl-1,5-cyclooctadiene)][51] (**5**), and [(L-prolinate)Rh^I(*endo*-dicyclopentadiene)][20] (**6**) were prepared according to literature procedures. Sulfoxonium ylide **A**[73] was prepared according to the procedures reported by Shea and co-workers,[36] and the concentrations of the solutions were determined by titration before use. Sulfoxonium ylides **B**[74] and **C**[75] were also prepared according to literature procedures.

NMR spectroscopy experiments were carried out on a Bruker AV-400 spectrometer (400 and 100 MHz for ^{1}H and ^{13}C, respectively) or a BrukerDRX-500 spectrometer (500 and 125 MHz for ^{1}H and ^{13}C, respectively). Molecular weight distributions were measured using size-exclusion chromatography 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 α-p FT-IR spectrometer with ATR module. The thermal behavior of polymer LPM and copolymer PEA−LPM was measured on a Perkin-Elmer Jade DSC under N_2 atmosphere (flow 5 mL/min) on encapsulated samples (∼5 mg) in aluminum pans. The heating program was carried at 10 °C/min in a 30−180 °C range. The melting and crystallization temperatures were determined from the second heating−cooling curves.

Homopolymerization of Carbene Units from Dimethyl Sulfoxonium Methylide. A magnetic stirrer and a glass stopper with a Teflon sleeve and a solution of dimethyl sulfoxonium methylide was added into a flamed Schlenk equipped with the catalyst. The reaction was monitored by titration of hydrolyzed aliquots (∼200 μL) in the presence of phenoftalein. After full consumption of the ylide (2−3 days), evaporation of the solvent, followed by the addition of 5 mL of MeOH, afforded the polymer as a white solid. The samples were centrifuged, washed with MeOH (3 × 10 mL), and dried until constant weight.

Copolymerization of EDA and Dimethyl Sulfoxonium Methylide. A magnetic stirrer and a glass stopper with Teflon sleeves, 2 mmol of EDA, and 2 mL of DCM were added into a flamed dried Schlenk equipped with 0.02 mmol of the corresponding catalyst. After 30 min of stirring, the reaction was cooled to −20 °C, and 2 mmol of **A** in 2 mL of THF was added slowly. The reaction was monitored by titration of hydrolyzed aliquots (∼200 μL) in the presence of phenoftalein. After full consumption of the ylide, the samples were treated as described above for the homopolymerization reactions. The resulting copolymer was washed with chloroform to separate the most functionalized copolymer (soluble) from the less functionalized 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 K_2CO_3 (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 °C, the solution was extracted with CH_2Cl_2 (3 × 10 mL). The organic layer was washed with $NaHCO_3$ and water, then dried over $MgSO_4$ and treated with activated carbon (norit), filtered over an alumina bed, and concentrated. The residue was purified by column chromatography (0.4486 g, 1.40 mmol, 61.9%). ^{1}H NMR (400 MHz, $CDCl_3$) 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).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.49 (2 × C), 139.93 (2 × C), 137.34 (2 × C^{olefin}), 127.20 (4 × $CH_2{}^{Ar}$), 125.45 (2 × CH^{olefin}), 113.61 (4 × $CH_2{}^{Ar}$), 55.39 (O−CH_3), 31.25 (2 × CH_2), 27.63 (2 × CH_2). Calcd. for $C_{22}H_{24}O_2$: m/z = 320.1776. Found: m/z = 320.1816.

[{Rh(1,5-(4-methoxyphenyl)-1,5-cyclooctadiene)(μ-Cl)}$_2$] (7). A 0.129 mmol portion of [Rh(ethylene)$_2$(μ-Cl)]$_2$ (50.2 mg,) was dissolved in dichloromethane (10 mL). To the red-brown solution, 0.257 mmol of 1,5-bis(4-methoxyphenyl)-cycloocta-1,5-diene (82.3 mg,) was added. The solution was stirred overnight at 40 °C and filtered over Celite. The resulting solution was concentrated to afford [Rh((p-$MeOC_6H_4)_2COD)_2Cl]_2$ as a red-brown solid (59.1 mg, 49.9%). ^{1}H NMR (500 MHz, $CDCl_3$) 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). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.11 (s, 2 × C), 139.69 (s, 2 × C), 128.23 (s, 4 × $CH_2{}^{Ar}$), 113.85 (s, 4 × $CH_2{}^{Ar}$), 93.98 (d, J = 15.4 Hz, 2 × C^{olefin}), 70.77 (d, J = 13.2 Hz, 2 × CH^{olefin}), 55.38 (s, CH_3), 37.36 (s, 2 × CH_2), 33.78 (s, 2 × CH_2). Calcd. for $C_{44}H_{48}O_4Rh_2Cl_2$: m/z = 916.1040. Found: m/z = 916.1042.

[Rh(1,5-cyclooctadiene)(η^2-$(CH_2)_2SOCH_3$)] (8). To a flame-dried Schlenk containing 10 mL of dry THF was added 0.203 mmol of [Rh(1,5-cycloocta-1,5-diene)Cl]$_2$. A solution of 0.8 mmol of dimethyl sulfoxonium methylide **A** was added slowly. After 2 h of reaction, the solution was filtered using the cannula technique. A bright yellow powder was obtained after evaporation of the solvent under vacuum (110 mg, 90%). ^{1}H NMR (400 MHz, dioxane) δ 4.50 (br, 2 × CH^{olefin}), 4.22 (br, 2 × CH^{olefin}), 3.42 (s, $SOCH_3$), 2.55 (d, J = 10.1 Hz, 2 × $CH\mathit{H}SO^{exo}$), 2.20 (m, 2H), 2.05 (m, 2H), 1.90 (t, J = 8.5 Hz, 4H), 1.76 (d, J = 9.8 Hz, 2 × $CH\mathit{H}SO^{endo}$). ^{13}C 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). Calcd. for $C_{11}H_{19}ORhS$: m/z = 302.0206. Found: m/z = 302.0213.

[Rh(1,5-cyclooctadiene)(η^2-$(CH_2)_2SOCH_3$)(η^2-dimethyl-maleate)] (10). 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. ^{1}H 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, CH^{DMM}), 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, $SOCH\mathit{H}^{exo}$), 2.87−2.94 (m, $CH\mathit{H}^{cod\text{-}exo}$), 2.78 (dd, J = 9.3, 1.4 Hz, CH^{DMM}), 2.63−2.53 (m, $CH\mathit{H}^{cod\text{-}endo}$), 2.50 (d, J = 10.1 Hz, $SOCH\mathit{H}^{endo}$), 2.44−2.35 (m, $CH\mathit{H}^{cod\text{-}exo}$), 2.34−2.26 (m, $CH\mathit{H}^{cod\text{-}endo}$), 2.19−2.08 (m, $CH\mathit{H}^{cod\text{-}endo}$), 2.07−1.93 (m, $CH\mathit{H}^{cod\text{-}exo}$), 1.85 (d, J = 11.0 Hz, $SOCH\mathit{H}^{exo}$), 1.82−1.72 (m, $CH\mathit{H}^{cod\text{-}exo}$), 0.61 (d, J = 11.0 Hz, $SOCH\mathit{H}^{endo}$). ^{13}C NMR (101 MHz, THF) δ 171.51 (s, COO), 171.45 (s, COO), 105.69 (d, J = 4.6 Hz, C^{olefin}), 94.65 (d, J = 4.6 Hz, C^{olefin}), 84.09 (d, J = 6.9 Hz, C^{olefin}), 78.29 (d, J = 8.1 Hz, C^{olefin}), 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, $SOCH_3$), 34.82 (s, CH_2), 30.78 (s, CH_2), 24.77 (s, CH_2), 23.63 (s, CH_2), 20.99 (d, J = 20.4 Hz, $SOCH_2$), 12.56 (d, J = 18.8 Hz,

$SOCH_2$). Calcd. for $C_{34}H_{54}O_{10}Rh_2S_2$: $m/z = 446.0629$. Found: 302.0 as most abundant peak.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra of complexes **8** and **10a**. DSC curves of homopolymers, copolymers, and blends. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(49) 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 a few weeks at −20 °C.

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

(53) The palladium complexes $[\{Pd(cod)(\mu\text{-}Cl)\}_2]$, $[(Allyl)PdCl]$, $[Pd(MeCN)_2Cl_2]$, and $[Pd(dba)_2]$ only catalyze ylide dimerization to ethylene, and the related iridium complexes $[\{Ir(cod)(\mu\text{-}Cl)\}_2]$ and $[\{Ir(cod)(\mu\text{-}OMe)\}_2]$ showed only poor activities, giving rise to very low polymer yields. This behaviour is similar to what was observed in EDA polymerization reactions.

(54) 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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(64) Attempts to blend separately prepared PEA and PM were not successful and resulted in rather inhomogeneous mixtures. DSC measurements of thus obtained mixtures (with various different PEA/PM ratios) show only separate crystallization and melting peaks of PM and PEA, with no sign of the low-temperature peaks observed for the copolymer.

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(66) The polyethylene sample employed was synthetized by ethylene polymerization by the commercially available catalyst Cp_2ZrCl_2.

(67) The PEA was synthetized by C1-homopolymerization of EDA with compound **2** and quenched with methanol to obtain low-molecular-weight polymer.

(68) Proper characterization of such blends would require detailed microscopy and SAX/WAXS measurements, which is beyond the scope of the present paper.

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