A new temperature-dependent solvent system based on polyethylene glycol 1000 and its use in rhodium catalyzed cooligomerization

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Dedicated to Professor Eckhard Dinjus on the occasion of his 60th birthday.

Abstract

The rhodium catalyzed cooligomerization of conjugated methyl linoleate with ethylene was studied using a new temperature-dependent solvent system based on polyethylene glycol 1000. Under mild ethylene pressure, two hours' reaction at 80 °C gave 95% conversion of conjugated methyl linoleate and 98% selectivity of cooligomers. By using this polyethylene glycol 1000 based temperature-dependent solvent system, an easy separation of product and catalyst phases has been achieved.
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Keywords: Temperature-dependent solvent system; Polyethylene glycol 1000; Cooligomerization; Conjugated methyl linoleate; Phase separation; Catalyst recycling

1. Introduction

Homogeneous catalysis is of great importance in modern synthetic chemistry. In petrochemistry various commercial-scale processes have already been established, e.g. the Ruhrchemie/Rhône-Poulenc oxo process (aqueous/organic biphasic hydroformylation of propene or butene) or the SHOP process (polar/non-polar biphasic oligomerization of ethylene) [1]. However these two liquid/liquid biphasic processes succeeded only in the range of low olefins. For long-chain olefins, which have no or only slight solubility in the catalyst phase, the resulting reaction rates are too low. The best way to avoid the problem of mass transfer is to carry out the catalytic reaction in a single phase and to separate the product and the catalyst afterwards by distillation of the product, as realized e.g. in the Wacker-Hoechst-process (the palladium/copper catalyzed oxidation of ethylene to acetaldehyde) or in the Monsanto/Cativa-Process (the rhodium/iridium catalyzed carbonylation of methanol to acetic acid) [1]. Never-

theless the application of single phase catalysis is also limited. The temperature-dependent solvent system [2] is a novel recycling system which combines aspects of the liquid/liquid two-phase technique with the principles of the thermo-regulated phase-transfer catalysis (TRPTC) [3,4]. By using temperature-dependent solvent systems, great improvements can be achieved in maintaining both a high reaction rate and a good separation of catalyst and product phases [5,6].

A temperature-dependent solvent system usually comprises three liquid components, a polar (S1), a non-polar (S2) and a semi-polar (S3) solvent or reactant. The addition of a semi-polar solvent suppresses the miscibility gap of the polar and non-polar solvents in such a way that the solvent mixture forms into one phase at a higher temperature but separates into two phases at a lower temperature. This phenomenon makes it possible that the catalytic reaction can be carried out in a single phase at a higher temperature whereas after the reaction, the separation of product and catalyst phases can be achieved at a reduced temperature.

The extremely low solubility of alkenes in polyethylene glycol [7] suggests a success in introducing polyethylene glycol 1000 as a polar solvent into the temperature-dependent

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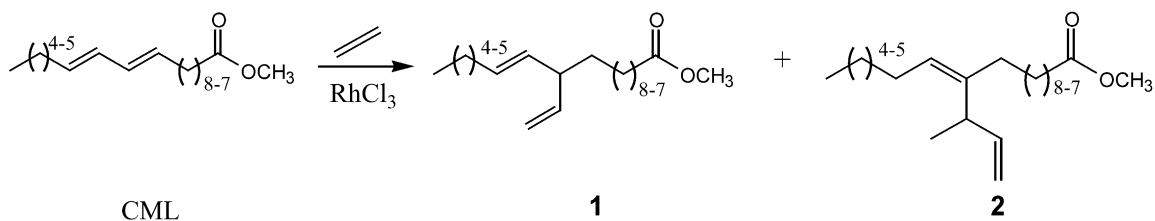
Scheme 1. Cooligomerization of conjugated methyl linoleate with ethylene.

solvent system. Rated as a polar solvent, polyethylene glycol 1000 is commercially and economically available. Recent results from the literature showed that polyethylene glycols were widely studied to modify ligands [3,4,8–11] and ionic liquids [12,13], or used as solvent [14–18] in catalytic syntheses.

In the present paper, the rhodium catalyzed cooligomerization of conjugated methyl linoleate (CML) with ethylene (Scheme 1) was studied in the temperature-dependent solvent system, PEG1000/toluene/CML. The rhodium catalyzed cooligomerization of fatty dienes and ethylene was firstly examined by Behr and Laufenberg [19,20]. Using rhodium (III) trichloride trihydrate (RhCl$_3$·3H$_2$O) as the catalyst precursor, phosphines and phosphites as ligands and the CML as the fatty substance, yields over 90% were achieved in a single phase reaction after 20 h with chloroform as solvent. This cooligomerization gives branched fatty substances, which are of great interest for lubricants and cosmetics because of their excellent physical properties, e.g. low melting points and low pour points [21,22]. In the current paper we present an easy separation of catalyst and product phases and a successful catalyst recycling in the presence of ligands.

2. Experimental

2.1. Materials

Sunflower fatty acid methyl ester (SFAME) (contains 60.5% conjugated methyl linoleate) is synthesized by acid-catalyzed esterification of conjugated sunflower fatty acid with methanol. Conjugated sunflower fatty acid was supplied as UKD6010 by Cognis Deutschland GmbH. The catalyst RhCl$_3$·3H$_2$O was used as received from Umicore AG & Co. KG, i.e. without any further purification. Ethylene 2.7 was supplied from Messer-Griesheim. Polyethylene glycol

1000 was from Acros and used without any further treatment. Phosphorous ligands **3** (*N,N*-diisopropylaminopoly-ethoxy *o*-phenylenephosphite), **4** (*N,N*-diisopropylaminopolyethoxy diphenylphosphonite) and **5** (polyethoxy triphenyl phosphine) were synthesized according to the literature [23,24] (Scheme 2).

2.2. Homogeneous cooligomerization

Generally, given amounts of catalyst RhCl$_3$·3H$_2$O, promoter, solvents and fatty substrates were weighed and transferred into a Schlenk tube. Heating and ultrasonic treatment were applied to offer a fast and complete dissolution of the catalyst in the solvent. The mixture was then transferred into a 300 ml Parr stainless steel autoclave, which was rinsed with argon and pre-vacuumed. The reaction mixture was saturated with 5 bar ethylene under mild stirring. The autoclave was heated up to reaction temperature, pressurized to desired ethylene pressure and the reaction was considered to start when isothermal conditions were reached. Samples were taken from the autoclave at regular intervals. The catalytic phase was separated from the product phase after a certain time standing at room temperature and can be recycled for the next run. All reactions were carried out under argon using the standard Schlenk technique.

2.3. Analysis and product characterization

Routine gas chromatographic analysis were carried out on an HP 6890 instrument (Hewlett-Packard GmbH, Waldbronn, Germany) equipped with an FI-detector and a HP-5 capillary column (30 m, coating 5% diphenyl-95% dimethyl-polysiloxane, diameter 0.25 mm, film thickness 0.25 μm), connected with an auto-sampler. Methyl palmetate was used as an internal standard. ICP-OES analysis were carried out on an Iris Interpid DUO ER/S (Thermo Elemental, USA).

Ligand **3**   Ligand **4**   Ligand **5**
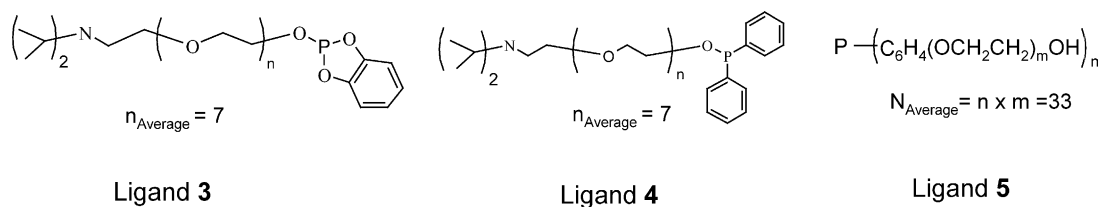
Scheme 2. Phosphine, phosphonite and phosphite ligands.

Table 1
Cooligomerization in different solvent combinations

PEG1000, S1 (g)	Solvent, S3 (g)	Conversion (%)	Selectivity (%)	
			Product **1**	Product **2**
20	Dioxane, 20	90	92	7
20	Dichloromethane, 27	88	90	10
20	Toluene, 18	89	91	8
10	Toluene, 18	96	81	10
20	Water, 5	45	98	2
20	–	85	93	7

Reaction conditions: 11.3 g CML (S2), RhCl₃·3H₂O, 0.5 mol% of substrates; cinnamyl chloride as promoter, 25-fold of catalyst (molar ratio); 100 °C, 30 bar, 2 h.

3. Results and discussion

3.1. PEG1000/toluene /CML multi-solvent system

The temperature-dependent solvent systems needs at least three components, a polar, a non-polar and a semi-polar liquid component. Here polyethylene glycol 1000 was used as polar (S1) solvent and CML as non-polar liquid component (S2). Results in Table 1 show some pre-tests for the evaluation of several semi-polar solvents (S3).

Cooligomerization in different solvent combinations showed that under the same reaction conditions, conversions of CML were nearly the same when dioxane, dichloromethane and toluene were used as semi-polar solvents, while the addition of water in the system inhibits the reaction rate of the cooligomerization. Since dioxane and dichloromethane are much more of a potential hazard, toluene was chosen as the semi-polar solvent.

To get a phase-diagram of the system PEG1000, toluene and CML, miscibility tests were carried out in glass tubes at 40 and 80 °C. Given amounts of PEG1000 and CML were transferred into the tube and heated in a water bath for 30 min. The toluene was then added into the tube step by step till the mixture was miscible and remained stable as one phase. The phase-diagram of this solvent system is shown in Fig. 1.

3.2. Selection of solvent composition for the cooligomerization

As shown in the phase-diagram of Fig. 1, the big miscibility gap of this solvent system (between 40 and 80 °C) facilitated a good operation range for the cooligomerization. According to the three chosen operation points P1, P2 and P3, the reaction mixture remained as two phases at room temperature and dissolved into a single phase at elevated temperatures (i.e. 80 °C). The reactions given in Table 2 were carried out for the evaluation of solvent compositions.

As shown in Table 2, the conversion of CML was increased with greater catalyst concentration. Catalyst concentration higher than 7.9×10^{-4} g/g is not attainable because of the solubility limitation of RhCl₃·3H₂O in PEG1000. Hence, the solvent composition according to the operation point P1 was selected as a practical one for the further study
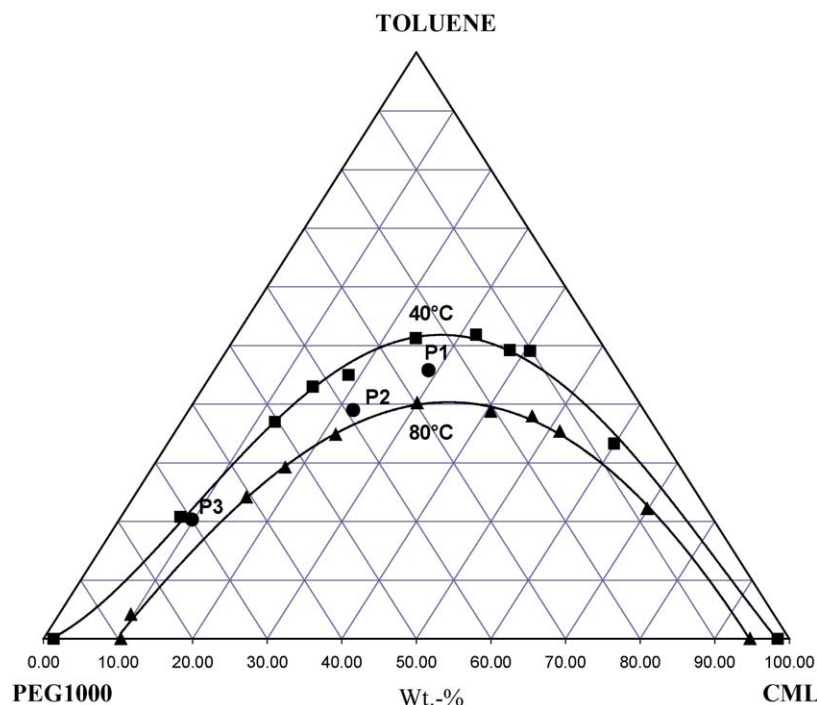

Fig. 1. Phase-diagram of the solvent system PEG1000/toluene/CML (operation points P1, P2 and P3, see text).

Table 2
Cooligomerization in the solvent system PEG1000/toluene/CML with different ratios of solvents

Operation point	PEG1000/toluene/CML (wt. ratio)	Catalyst concentration[a] (g/g)	Conversion (%)	Selectivity (%)	
				Product **1**	Product **2**
P1	10/18/11.3	7.9×10^{-4}	96	81	10
P2	20/18/11.3	6.0×10^{-4}	89	91	8
P3	35/6/4.8	2.6×10^{-4}	79	93	7

Reaction conditions: 0.5 mol% $RhCl_3 \cdot 3H_2O$ of CML, cinnamyl chloride as promoter, 100 °C, 30 bar, 2 h.

  [a] $RhCl_3 \cdot 3H_2O$, g/total mixture, g.
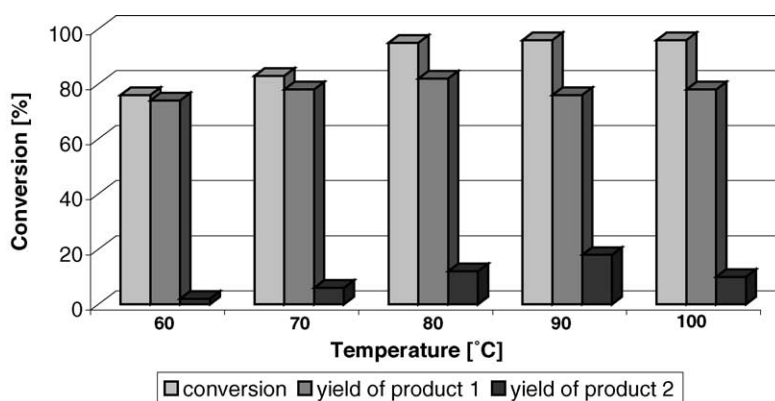

Fig. 2. Influence of the reaction temperature. Conditions: 0.5 mol% $RhCl_3 \cdot 3H_2O$ of CML; cinnamyl chloride as promoter; 30 bar, 2 h.

on cooligomerization of conjugated methyl linoleate with ethylene.

3.3. Cooligomerizations in PEG1000/toluene/CML system

3.3.1. Influence of reaction temperature

As shown in Fig. 2, the conversion of CML increases to 95% at a reaction temperature of 80 °C and product **1** reaches the highest yield of 82%. Reactions at a higher temperature gave no noticeable increase in the total conversion of CML but only an increase in forming by-products. At 100 °C, 96% of CML were converted and the total selectivity of products **1** and **2** reached 91%. Small amounts of differ-

ent non-isolated by-products were detected on the GC after product **2** and can be proposed to be the isomers of product **2**.

3.3.2. Influence of reaction time

The influence of the reaction time was measured by sampling at time periods of about 20 min. The results are shown in Fig. 3.

The reaction proceeded very quickly in the first 60 min. The conversion of CML was already 89% after an hour's reaction and only 6% more in the second hour's reaction. The following two hours' reaction afforded no further increase of the total conversion but only slight conversion of product **1** to product **2**.
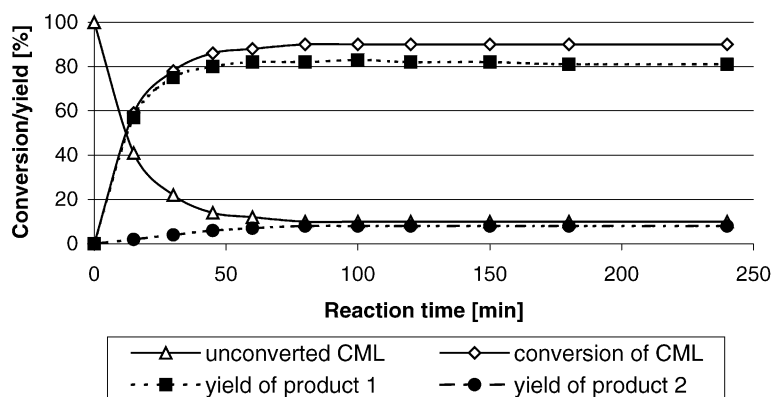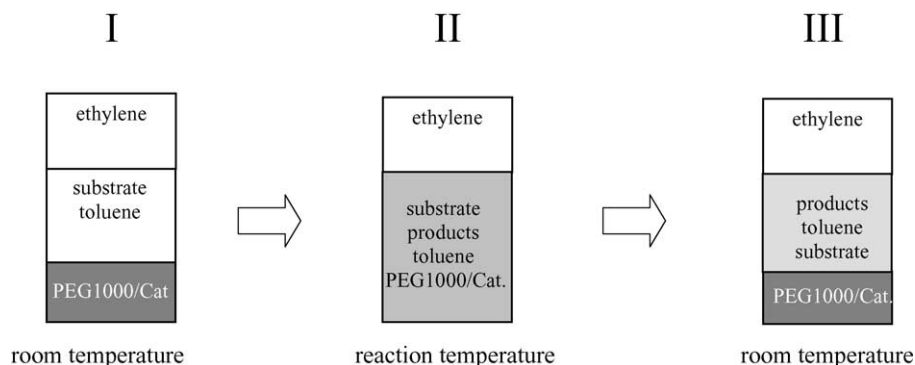

Fig. 3. Influence of the reaction time. Conditions: 0.5 mol% $RhCl_3 \cdot 3H_2O$ of CML; cinnamyl chloride as promoter; 30 bar, 80 °C.

Scheme 3. Illustration of solvent behavior during reaction process.

3.4. Catalyst recycling

As illustrated in Scheme 3, the use of the PEG1000/toluene/CML system affords an easy separation of the catalyst and the product phase. After the reaction, more than 95% of the fatty substance was found in the separated product phase.[1] The separated catalyst phase was directly used in the next run.

Catalyst recycling was studied with or without the addition of ligands. In the absence of a ligand, rhodium black was formed during the recycle runs due to the reduction of rhodium catalyst by olefins [25]. To enhance the stability and maintain the activity of the catalyst, phosphorous ligands such as phosphines, phosphonites and phosphites were added into the reaction mixture to coordinate with the rhodium catalyst. These polyethylene glycol modified ligands are readily soluble in PEG1000 and ligand **5** was successfully used by Jin et al. for the stabilization and recycling of rhodium catalyst in thermo-regulated phase-transfer catalysis [26]. In Fig. 4 the results of these recycling runs were compared with the runs without addition of ligand.

Owing to the steric hindrance of the ligands, the complexes of rhodium catalyst with ligands resulted in lower conversions of CML. However these complexes showed greater abilities in maintaining their activity than the catalyst without addition of ligand. In the absence of ligand, the rhodium catalyst had only about 55% of its original activity in its fourth run while those complexes of rhodium catalyst with ligands **3**, **4** and **5** had respectively, 74, 79 and 60% of their original activities in the fourth runs. These results proved the stabilization of the rhodium catalyst by complexing with ligands **3**, **4** and **5**.

Though the catalyst was stabilized by the presence of ligands, small amounts of rhodium catalysts were still detected in the product phase. An explanation for this leaching may be the strong competition of ethylene with the ligands to
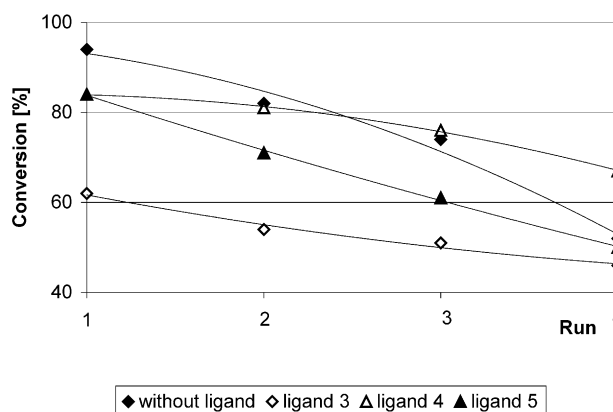

Fig. 4. Study of catalyst recycling. Conditions: 0.5 mol% $RhCl_3 \cdot 3H_2O$ of CML; cinnamyl chloride as promoter; L/Rh, 1:1 (molar ratio); 80 °C, 2 h, 30 bar.

coordinate to the rhodium. As a result, the polarities of these ethylene coordinated rhodium species are reduced so that they can be extracted into the non-polar product phase. Fig. 5 shows the results of the ICP-OES analysis. The rhodium leaching was found to decrease with an increasing recycle number.
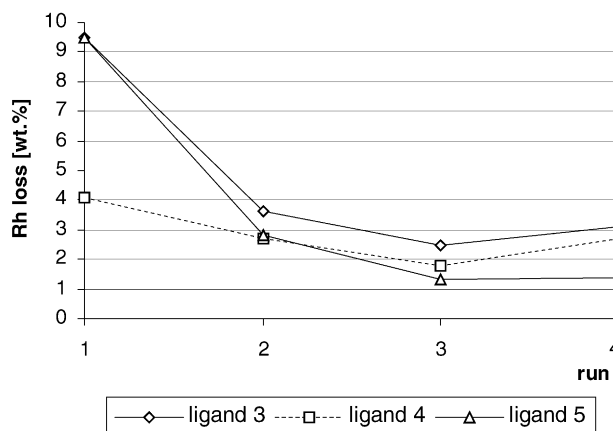

Fig. 5. Rhodium leaching in the recycle runs.

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[1] The calculation was based on the weight of fatty substance collected after distillation of solvent.

4. Conclusion

In this paper, a new temperature-dependent solvent system was developed by using PEG1000, toluene and conjugated methyl linoleate. In using this "smart" solvent system, the cooligomerization of conjugated methyl linoleate with ethylene was studied. Under mild ethylene pressures and at a temperature of 80 °C, 2 h reaction gave a 95% conversion of conjugated methyl linoleate and a total 98% selectivity of products **1** and **2**. An easy separation of the catalyst from the product has been achieved. Compared with the catalyst complex without ligand, those complexes of RhCl$_3$·3H$_2$O with ligands **3**, **4** or **5** showed higher stabilities and an improvement in maintaining their catalytic activities.

Acknowledgements

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