

# Synthesis and Biosynthesis of Oligomeric Sebacates as Lubricant Oils

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This work presents the results of research carried out on synthesis of oligomeric esters of sebacic acid. The syntheses were conducted by the alcoholysis reaction of dimethyl sebacate with neopentyl glycol and 2-ethylhexanol. The catalyst used in the chemical synthesis was calcium methoxide. As a catalyst in the bioprocess, an immobilized lipase derived from *Rhizomucor miehei* strain (Lipozyme IM) was used. It was found that the reactions conducted in the presence of biocatalyst proceed with high yield, 95%, under mild conditions. On the other hand, chemical syntheses gave the same yield in a similar length of time but at much higher temperature. Some of the prepared esters were tested in terms of their suitability as additives to fully synthetic engine oils. The addition of these esters led to an improvement of the properties of the oils. The pour point was reduced by a few degrees in comparison with the tested base oil. The presence of esters significantly improved the viscosity index. A positive influence of esters on the lubricating properties of the formulated oil was also observed.

## Introduction

Global production of lubricating oils is up to 40 million tons.<sup>1,2</sup> More than half of this is emitted into the natural environment in the form of uncontrolled efflux, oil–water emulsion, and components of combustion gas. Very often these are substances that are toxic to living organisms and are hardly biodegradable. One way of avoiding such a hazard is to replace hydrocarbon oils derived from petroleum with synthetic oils, which are more environmentally friendly. Ideal substitutes include esters of carboxylic acids. These are compounds which, in their chemical structure, resemble natural triglycerides. Esters of dicarboxylic acids, especially the sebacates, have found a wide application as components of synthetic oils.<sup>3</sup>

The essential barrier to the wide application of esters is their relatively high cost of production, which is 4–15 times higher than that of oils derived from petroleum. Possibilities of applying compounds of unconventional structure, like complex esters, and natural product derivatives<sup>4,5</sup> are being considered. New low-waste and energy-saving methods of synthesizing ester oils using advanced catalytic systems are being designed.<sup>6</sup>

A convenient method of synthesizing esters of dicarboxylic acid is the process of transesterification of their methyl esters with appropriate alcohols.<sup>7</sup> In the reaction of dimethyl sebacate with monohydroxylic alcohols, straight dialkyl sebacates are obtained. Starting with dimethyl sebacate and dihydroxyl alcohols, the compounds with straight chain oligomers are formed.

A key factor for the synthesis is the selection of a suitable catalyst for the process. In addition to high activity it should be easily removable from the reaction products. The catalysts for basic alcoholysis of esters are alkoxide anions,<sup>8</sup> which could be introduced into the reaction mixture in the form of appropriate alcoholates. Alkoxide anions are also formed in the reaction of alcohols with alcoholates, oxides, hydroxides, or other basic compounds of some metals.<sup>9,10</sup>

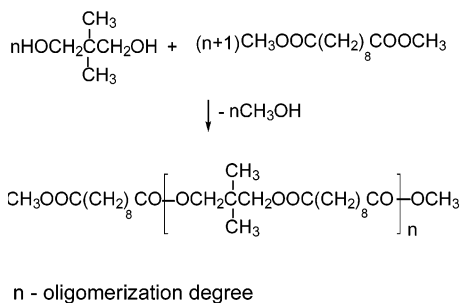
In recent years lipases have been widely used as catalysts of direct esterification,<sup>11,12</sup> transesterification,<sup>13</sup> and the opening of cyclic lactones.<sup>14</sup> Biocatalytical processes are widely used in the large-scale production of food,<sup>15</sup> flavor materials,<sup>16,17</sup> and pharmaceuticals,<sup>18</sup> as well as biodiesel fuel.<sup>19</sup> The biocatalysts show the following virtues: high and stable activity at low temperatures (around 50 °C), extremely high selectivity, possibility of repeated use, and, finally, ease of separation from the products in the case of their immobilization on the solid support. The application of lipases as catalysts in the synthesis of different polymer esters, especially biodegradable polyesters, can be also considered.<sup>20</sup> To our knowledge, there are not many reports on the use of enzymatic preparation in the manufacture of lubricants.

The aim of this work was to compare the synthesis of oligomeric esters of sebacic esters and neopentyl glycol using conventional catalysts such as magnesium, calcium, barium, and aluminum compounds, and lipase as a biocatalyst. The evaluation of obtained esters with respect to their application as a component of lubricating oils has been done.

## Experimental Section

**Materials.** Immobilized *Rhizomucor miehei* lipase, Lipozyme IM (EC 3.1.1.3), neopentyl glycol, 2-ethylhexanol, dimethyl sebacate, di-2-ethylhexyl sebacate, and 2,4,4-trimethylpentane were purchased from Fluka-Sigma-Aldrich (Steinheim, Germany). Magnesium oxide, calcium oxide, calcium hydroxide, and barium hydroxide were obtained from POCH Gliwice, Poland. Calcium methoxide, magnesium methoxide, and aluminum methoxide were synthesized by direct reaction of an appropriate metal with methanol. In the case of the synthesis of magnesium and aluminum methoxides, it was necessary to conduct the reaction in the presence of minute quantities of iodine and mercury (II) chloride, respectively, as catalysts. The components of prepared oils including polyalphaolefins base and additives was a gift from Lotos Group Company.

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**Figure 1.** Synthesis of oligomeric esters of sebacic acid using dimethyl sebacate and neopentyl glycol as starting material.

**Conventional Synthesis of Esters.** Dimethyl sebacate (0.15, 0.20, 0.25 mol), neopentyl glycol (0.1 mol), and 0.5 wt % of catalyst were used for the synthesis of oligomeric sebacates according to the reaction shown in Figure 1. The syntheses of the esters were conducted in a glass reactor fitted with a Dean–Stark cup. In the course of reaction, the formed methanol was continuously removed by azeotropic distillation with 2,4,4-trimethylpentane. When the process was over, the synthesized ester was separated from the catalyst by filtration. The unreacted substrates were removed by distillation under reduced pressure. The ester molecules obtained in this way are terminated with methoxyl groups.

**Biosynthesis of Esters.** The reaction mixture containing dimethyl sebacate (0.15, 0.20, or 0.25 mol), neopentyl glycol (0.1 mol), and 5.0 wt % of biocatalyst was magnetically stirred at 500 rev/min at 50 °C in an open glass beaker. The progress of the transesterification reaction was monitored by determining the amount of methanol evolved. Typically the process was over after 8–10 h. The remaining dimethyl sebacate was removed by vacuum distillation after separating the lipase by filtration. This way, biosynthesis of esters using a mixture of dimethyl sebacate (0.20 mol), neopentyl glycol (0.1 mol), and 2-ethylhexanol as starting materials was conducted.

**Preparation of Ester Oil Samples.** Selected esters, complemented with commercially available viscosity improver and a packet of additives gave a part of the composed lubricating oil, which was produced from a polyalphaolefin base with viscosity class SAE30. The prepared oil had a composition by mass as follows: polyalphaolefins PAO6 55.0%, polyalphaolefins PAO8 6.0%, pack of additives 18.0%, viscosity improver 6.0%, and ester 16.0%. For comparison, the oil without esters, i.e., esters were substituted with polyalphaolefines, was prepared.

**Testing of Catalysts.** For testing of catalysts, the transesterification of dimethyl sebacate with 2-ethylhexanol was used. Magnesium oxide, magnesium methoxide, calcium hydroxide, calcium oxide, calcium methoxide, barium hydroxide, and aluminum methoxide were tested as potential catalysts in the transesterification reaction. The criterion for choosing the optimal catalyst were its activity and ease of separation from the reaction products. The latter was evaluated basing on the determination of ash content in the reaction products.

**<sup>1</sup>H NMR Spectroscopy.** <sup>1</sup>H NMR spectra of oligomeric esters were taken on a Bruker DRX300 spectrometer for CDCl<sub>3</sub> with (CH<sub>3</sub>)<sub>4</sub>Si as internal standard.

**Gas Chromatographic Analysis.** The content of di-2-ethylhexyl sebacate in the ester samples were determined by gas chromatography. GC analysis was per-

**Table 1.** Catalytic Activity of Some Earth Metal Compounds in Alcoholysis Reaction of Dimethyl Sebacate with 2-Ethylhexanol

catalyst	reaction time <sup>a</sup> (h)	ash content in product (wt %)
MgO	no active	
Mg(OCH <sub>3</sub> ) <sub>2</sub>	10.5	0.119
Ca(OH) <sub>2</sub>	no active	
CaO	13.0	0.035
Ca(OCH <sub>3</sub> ) <sub>2</sub>	10.0	0.036
Ba(OH) <sub>2</sub>	13.5	0.305
Al(OCH <sub>3</sub> ) <sub>3</sub>	10.5	0.820
Lipozyme IM	8.0	0.008

<sup>a</sup> Time of 95% conversion.

formed using an HP 5890 Series II gas chromatograph with a capillary column (HP-5, 25 m × 0.32 mm) and flame ionization detector (FID). Nitrogen was used as the carrier gas. The oven temperature was programmed from 50 to 280 °C at 15 °C/min. The split ratio was 1:50. The inlet and detector were set at 250 and 270 °C, respectively. The result of analysis was taken from a standard graph developed for solutions of di-2-ethylhexyl sebacate in toluene. Every analysis was done three times.

**Physicochemical Properties.** Ash content, pour point, kinematics viscosity, and viscosity index (VI) were determined according to ASTM D-482, ASTM D-97, ASTM D-445, and ASTM D-2270, respectively.

Miscibility of ester oils (16% mass) in nonpolar polyalphaolefins of PAO4 base was determined. The tested temperature range was from –15 to 200 °C. The result was taken as positive when the solution formed a clear single phase.

Antiwear properties of prepared oils were tested in a four-ball test rig. The wear scar diameter (ASTM D-4172) and the weld load (ASTM D-2783) were determined.

## Results and Discussion

**Selection of Catalyst.** The catalytic activity of Mg, Ca, Ba, and Al compounds and the ash content in synthesized esters are given in Table 1. For comparison, the result of esters synthesis using Lipozyme IM are also shown.

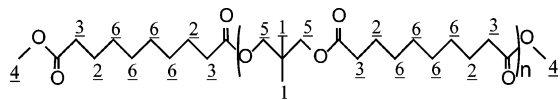
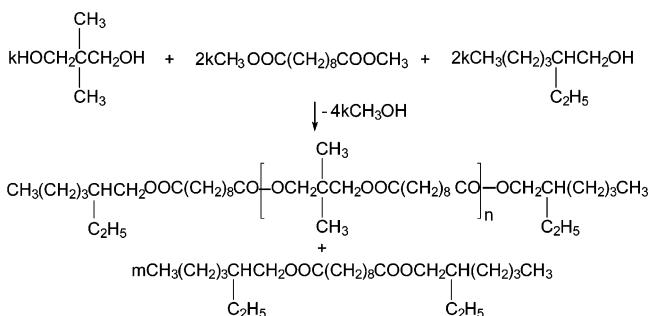
Most of the studied earth metal compounds were characterized by high activity in alcoholysis reaction. A 95% conversion level was achieved after 10–13.5 h. It was found that calcium methoxide shows the highest catalytic activity. Magnesium oxide and calcium hydroxide showed no activity. Compared to calcium catalysts, compounds of magnesium, barium, and aluminum were relatively more soluble in the reaction products, and as a result they were difficult to separate. Considering the above reasons, calcium methoxide was chosen as catalyst for the further synthesis of oligomeric sebacates. However, the shortest reaction time is reached when the enzymatic preparation Lipozyme IM was used as a catalyst for alcoholysis reaction of dimethyl sebacate with 2-ethylhexanol. Moreover, in this case the product formed was nearly free of ash.

**Synthesis and Biosynthesis of Oligomeric Esters.** The transesterification reaction of dimethyl sebacate with neopentyl glycol leads to the esters of straight oligomer structure. The presence of oligomers with terminal hydroxyl groups was eliminated by maintaining a substrate ratio of dimethyl sebacate to neopentyl glycol above 1. That is 1.5, 2.0, 2.5 in succession. Free

**Table 2. Chemical Structure of Oligomeric Sebates**

starting material (mol) <sup>a</sup>	catalyst	formula <sup>a</sup>	M <sup>b</sup>
NPG:SeMe <sub>2</sub> as 1:2.5	Ca(CH <sub>3</sub> O) <sub>2</sub>	<b>1:</b> MeSe[NPGSe] <sub>1.24</sub> Me	565
NPG:SeMe <sub>2</sub> as 1:2.0	Ca(CH <sub>3</sub> O) <sub>2</sub>	<b>2:</b> MeSe[NPGSe] <sub>1.26</sub> Me	570
NPG:SeMe <sub>2</sub> as 1:1.5	Ca(CH <sub>3</sub> O) <sub>2</sub>	<b>3:</b> MeSe[NPGSe] <sub>1.90</sub> Me	743
NPG:SeMe <sub>2</sub> as 1:2.5	Lipozyme	<b>1b:</b> MeSe[NPGSe] <sub>1.34</sub> Me	592
NPG:SeMe <sub>2</sub> as 1:2.0	Lipozyme	<b>2b:</b> MeSe[NPGSe] <sub>1.40</sub> Me	608
NPG:SeMe <sub>2</sub> as 1:1.5	Lipozyme	<b>3b:</b> MeSe[NPGSe] <sub>3.70</sub> Me	1229
NPG:SeMe <sub>2</sub> :EH as 1:2:2	Ca(CH <sub>3</sub> O) <sub>2</sub>	<b>4:</b> EHSe[NPGSe] <sub>1.85</sub> EH + 0.85SeEH <sub>2</sub>	590
NPG:SeMe <sub>2</sub> :EH as 1:2:2	Lipozyme IM	<b>4b:</b> EHSe[NPGSe] <sub>1.75</sub> EH + 0.75SeEH <sub>2</sub>	584

<sup>a</sup> Me = methyl; EH = 2-ethylhexanol or 2-ethylhexyl; Se = sebacic acid moiety; NPG = neopentyl glycol. <sup>b</sup> M = average molecular mass.

**Figure 2.** Chemical formula of oligomeric sebates. The specified numbers refer to the <sup>1</sup>H NMR chemical shift.**Figure 3.** Synthesis of oligomeric sebates using dimethyl sebacate, neopentyl glycol, and 2-ethylhexanol as starting materials.**Table 3. Physicochemical Properties of Oligomeric Sebates**

sample	pour point (°C)	viscosity 40 °C (cSt)	miscibility with polyalphaolefins
1	-34	47.00	not miscible
2	-34	48.22	not miscible
3	-27	71.31	not miscible
1b	-32	51.30	not miscible
2b	-33	63.12	not miscible
3b	-23	120.42	not miscible
4	-56	31.85	miscible
4b	-58	30.31	miscible

hydroxyl groups exert a negative influence on the physical properties of esters. They form hydrogen bonds which are easily broken off at higher temperatures and consequently lead to a sharp reduction in viscosity. A minimal change in viscosity with temperature is a positive parameter for characterizing lubricant oils.

The fundamental task in the preliminary evaluation of synthesized oligomeric sebates is to determine their average molecular mass. This was done on the basis of <sup>1</sup>H NMR measurements together with the calculation of degree of oligomerization. The structural formula of sebacic acid oligomers is presented in Figure 2 with the proton groups and their characteristic chemical shifts pointed out.

The results of the <sup>1</sup>H NMR spectroscopy are given below.

**a1:**  $\sigma_1$ , 0.93 (7.4H, s);  $\sigma_2$ , 1.53–1.62 (8.9H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (8.9H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (4.9H, s);  $\sigma_6$ , 1.14–1.26 (17.8H, q,  $J = 9.6$  Hz). **a2:**  $\sigma_1$ , 0.93 (7.6H, s);  $\sigma_2$ , 1.53–1.62 (9.0H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (8.9H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (5.0H, s);  $\sigma_6$ , 1.14–1.26 (17.0H, q,  $J =$

9.6 Hz). **a3:**  $\sigma_1$ , 0.93 (11.4H, s);  $\sigma_2$ , 1.53–1.62 (11.3H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (11.1H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (7.8H, s);  $\sigma_6$ , 1.14–1.26 (23.0H, q,  $J = 9.6$  Hz). **b1:**  $\sigma_1$ , 0.93 (8.0H, s);  $\sigma_2$ , 1.53–1.62 (9.4H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (9.3H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (5.5H, s);  $\sigma_6$ , 1.14–1.26 (18.6H, q,  $J = 9.6$  Hz). **b2:**  $\sigma_1$ , 0.93 (8.4H, s);  $\sigma_2$ , 1.53–1.62 (9.6H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (9.5H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (5.8H, s);  $\sigma_6$ , 1.14–1.26 (19.0H, q,  $J = 9.6$  Hz). **b3:**  $\sigma_1$ , 0.93 (22.2H, s);  $\sigma_2$ , 1.53–1.62 (18.0H, q,  $J = 6.9$  Hz);  $\sigma_3$ , 2.25–2.30 (17.8H, t,  $J = 7.5$  Hz);  $\sigma_4$ , 3.63 (6.0H, s);  $\sigma_5$ , 3.84 (14.1zH, s);  $\sigma_6$ , 1.14–1.26 (37.0H, q,  $J = 9.6$  Hz).

The degree of oligomerization was determined by calculating the intensity of signals from both the methyl group  $-\text{CH}_3$  protons and the terminal methoxyl group  $-\text{OCH}_3$ . The amount of methyl group protons in the molecule is proportional to the degree of oligomerization  $n$  and equals  $6n$ . On the other hand, the amount of methoxyl group protons in the molecule is constant (6), and is not dependent on the size of the ester molecule. The oligomerization degree can be described as follows:

$$n = \frac{\Sigma \text{H}_{\text{CH}_3}}{\Sigma \text{H}_{\text{OCH}_3}}$$

Having known the value of  $n$ , it was easy to calculate the average molecular mass.

$$M = 230 + 270n$$

Table 2 shows the structural parameters of oligomeric esters of sebacic acid and neopentyl glycol. For dimethyl sebacate and neopentyl glycol as starting material, the use of Lipozyme IM instead of calcium methoxide yields the esters of greater molecular mass. However, the formed oligomers are terminated with methoxyl group  $-\text{OCH}_3$ . This makes the ester molecules to be highly polarized, which limits their miscibility with synthetic hydrocarbon oils such as polyalphaolefins. To eliminate these terminal groups from the structure of ester oligomers, the starting material was changed. As substrates, dimethyl sebacate, neopentyl glycol, and 2-ethylhexanol at a molar ratio of 2:1:2 were used. In this case the reaction proceeds as shown in Figure 3. This type of co-oligomerization is a complex process. Beside oligomers terminated with 2-ethylhexyl group, di-2-ethylhexyl sebacate is also formed. To define the chemical composition of the product, the content of di-2-ethylhexyl sebacate was determined by GC method. This made it possible to calculate the degree of oligomerization of the second component of the postreaction mixture. The composition and chemical formula of the obtained sebates using calcium methoxide and Lipozyme IM as catalysts is shown in Table 2. It can be

**Table 4. Influence of Ester Content on Some Properties of Synthetic Oils**

sample	pour point [°C]	viscosity		VI	VI <sub>ad</sub> <sup>a</sup>	antiwear properties	
		40 °C	100 °C			scar diameter, mm	weld load, kG
oil-4	-42	81.0	12.9	160	145	0.30	148.5
oil-4b	-44	78.8	12.7	161	145	0.30	151.2
oil without ester	-40	89.4	13.13	144		0.40	95.0

<sup>a</sup> Viscosity index calculated as additive value.

seen that for both catalysts the structure of synthesized esters is similar.

**Physicochemical Properties of Esters.** The selected physicochemical properties of oligomeric sebacates including viscosity, pour point, and miscibility with hydrocarbon oil are shown in Table 3.

It was found that the viscosity of oligomeric esters of sebacic acid increases with the degree of oligomerization. This allows the production of ester oils with a wide spectrum of viscosity from the same initial materials. However, it should be noted that an increase in viscosity of esters is accompanied by an increase in pour point, which is a negative phenomenon.

Straight-chain oligomers of sebacic acid and neopentyl glycol with terminal methoxyl groups were not miscible with hydrocarbon oils of polyalphaolefin type. When the methoxyl group was replaced with a less polar 2-ethylhexyl group, a mixture of esters miscible with polyalphaolefines were obtained.

It is worth emphasizing that the problem of fluidal miscibility is a complex one. The general rule that like dissolves like pertains. However, this becomes difficult when it comes to a quantitative description of the theory involved. Mutual solubility of liquids is enhanced by similarity in polarity, molecular mass, and molecular structure. These parameters determine the strength of intermolecular interaction. Generally, liquids of good mutual solubility are characterized by similar strength of adhesion and cohesion. The miscibility of ester oils with hydrocarbons is of importance since esters are often used as components of lubricant oils to improve their polarity. This way, the stability of lubricant composition is improved and the lubricity properties of oils are better.

**Evaluation of Prepared Oils.** The basic properties of prepared samples of synthetic oils are presented in Table 4. Due to the immiscibility with PAO no oils were composed with esters 1, 1b, 2, 2b, 3, and 3b. In contrast, oligomeric esters 4 and 4b formed clear, stable solutions with polyalphaolefins and the packet of additives within a temperature range of -20 to 200 °C.

The addition of esters to the oil base stock resulted in a reduction in fluidity temperature to a level even lower than -40 °C and insignificantly reduced the viscosity of the final oil compositions.

Moreover, the presence of esters improved the viscosity index of the oil samples. Increase in viscosity index was seen to be higher than what should have been expected from the summation of all the components (the viscosity indices of pure esters 4 and 4b were 149 and 154, respectively). We therefore note a synergy effect of ester with the other components of oils.

The addition of ester clearly and positively affected the lubricity of oils. This effect was not very visible when the obtained values of the wear scar diameter were considered, but was clearly demonstrated through the increase of the weld load.

## Conclusions

The alcoholysis reaction of dimethyl sebacate with neopentyl glycol and 2-ethylhexanol leads to oligomeric esters of straight-chain structure which are potentially useful as liquid lubricants. In the process of synthesizing oligomeric esters of sebacic acid, basic compounds of magnesium, calcium, barium, and aluminum, as well as an enzymatic preparation (Lipozyme IM), appeared to be very effective as catalysts. Using the Lipozyme IM as catalyst made it possible to obtain products that are uncontaminated with catalyst residue and the reaction process proceeds with high yield under mild conditions.

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