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(54) Title: METHOD OF OLIGOMERIZATION OF 1-BUTENE

(57) Abstract

The invention is concerned with a method of oligomerization of 1-butene to a hydrogen carbon comprising in average 12-48 carbon atoms and an unsaturated double bond, wherein the reaction temperature is ca -30...90 °C, the total pressure ca 1-15 bar and the retention time in the reaction ca 5 minutes...10 hours by using a complex of BF_3 and water, C_2-C_{10} monoalcohol or C_2-C_8 monocarboxylic acid as catalyst. The product obtained can be used as solvent or lubricant and as intermediate when preparing different chemicals for example lubricants or additives of those.

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Method of oligomerization of 1-butene

This invention is concerned with a method of oligomerization of 1-butene.

KNOWN TECHNIQUE

The butene used for preparation of oligomers of butene has conventionally been iso- or tert-butene, that has been oligomerized to an oligomer of a suitable molar mass. These oligo- and polymers that are formed in the oligomerization of isobutene are called with a common name, poly-i-butenes or polybutylenes depending on the composition of the starting material. The source of i-butene has mainly been the so called raffinate I flow. In this raffinate I flow there are 1- and 2-butenes as well as butanes in addition to the isobutene. Alternatively the starting material used has been purified isobutene.

One of the most important mechanisms of polymerization of olefines are the cationic mechanism and the coordination polymerization. Of these mechanisms, coordination polymerization is primarily used for preparation of poly-1-butene plastics if the structure of the product to be formed is wished to define very exactly in forehand. The cationic mechanism produces only oligomers or viscotic fluids, so called liquid polymers, in the polymerization of 1-butene.

The catalysts used in the cationic mechanism have been Lewis acids such as BF_3, $AlCl_3$, $AlBr_3$, $TiCl_4$, $SnCl_4$ etc. It is known that Lewis acid catalysts cannot alone initiate a polymerization reaction but need a proton donor or a cocatalyst. Such cocatalysts are for example water, alcohols, carboxylic acids, inorganic acids, given alkyl halides or halogenes. The oligomerization can be carried out in bulk, in other words without any auxiliary solvent or in the presence of an inert solvent. Such inert solvents are for example alkanes such as hexane and heptane and cycloalkanes such as cyclohexane and cycloheptane.

Oligomers suitable for different applications have thus conventionally been prepared by oligomerization of isobutene or of the raffinate I flow. The catalyst used has been for example BF_3 and $AlCl_3$. Generally, water, short-chained alcohols and organic acids have been mentioned as cocatalysts. 1-Butanol has generally been used together with BF_3 as cocatalyst when the intention has been to produce fractions suitable as lubricants and additives of those. These fractions have generally been produced by copolymerization. Larkin et al.
(US 4 417 082, 4 395 578 and 4 434 309) used 1-butene as short chained olefine and $C_6...C_{18}$ alkene as long chained olefine in the copolymerization. The catalyst system was consisted of BF_3 and –1-butanol and possibly a transition metal cation. Nipe et al. (US 4 225 739) also used BF_3 as 1-butanol catalyst for the copolymerization but the short chained olefine was propene instead of 1-butene. Watts et al. (US 4 413 156) used a mixture of C_3-C_4 olefine as starting material from which $C_9...C_{24}$ inner olefines were prepared by means of a disproportion reaction. By further oligomerization of this fraction with BF_3 as 1-butanol, catalyst fractions of a product that were suitable for preparation of additives for lubricants were obtained. The processes described in the above mentioned patents are either two step polymerizations or copolymerizations.

The catalysts used in the oligomerization of the raffinate I flow partly depends on the wished product distribution. Torck et al. (GB 1 312 950) for example used a BF_3-HF complex in tetra methylene sulphone solution as di- and trimerization catalyst. Chen et al. (US 4 849 572) used water and/or methanol as cocatalyst and thus the M_n of the product was 520....1500 g/mol. Halaska et al. (EP 337 737) was using BF_3 or alkyl aluminium chlorides for the oligomerization of a raffinate II flow that contains 1- and 2-butenes as main components which chlorides have the common formula of R_2AlCl or $RAlCl_2$, wherein R is C_{1-8} alkyl. They used HF, HCl or compounds containing a reactive chlorine or fluorine atom bond to a tertiaric, benzylic or allylic carbon atom as cocatalyst. These catalyst systems are the same as the catalysts used by Loveless et al. (US 4 041 098) for oligomerization of $C_3...C_{14}$ olefines, preferably $C_8...C_{10}$ olefines.

Carboxylic acid cocatalysts are very little known for oligomerization of short-chained olefines. Sheng et al. (US 4 263 465) used a carboxylic acid with not more than five carbon atoms as cocatalyst. Their process was carried out in two steps. The first step comprised 1-butene as a fraction for oligomerization, the numerical average length of the carbon chain of which was 8...18, preferably 10...16 carbon atoms. In the second step the product fraction of the first step is cooligomerized together with C_8...C_{18} alfaolefines. Carboxylic acids containing for example five carbon atoms, have been used for oligomerization of long-chained olefines. According to patent publication GB 1 378 449 there has for example been used n- and i-valerianic acid, methyl butanoic acid and mixtures of those to catalyst the oligomerization of C_6...C_{12} olefines together with BF_3.

During the last ten years the production of MTBE or methyl-tert-butylether, that has strongly increased and is further increased, restricts the availability of isobutene (by increasing the production costs at the same time). The object of this invention is to show that it is possible to produce fractions that substitute low oligomers of isobutene by oligomerization of 1-butene to poly-n-butene (M_n = 110...ca 650 g/mol or even 850 g/mol). Poly-i butene and polybutylene have been produced already in many years even in an industrial scale, but the production of poly-n-butene by oligomerization of 1-butene is not known.

In this invention the oligomerization of 1-butene is carried out in a one step process by using a boron trifluoride cocatalyst complex as catalyst, wherein the cocatalyst is water, C_2-C_{10} monoalcohol or C_2-C_8 monocarboxylic acid, preferably valerianic acid.

By the method of this invention the light fractions of poly-i-butene and polybutylene can be substituted the numerical average molar mass being 110...ca 650 or even 850 g/mol.

The object of this invention is an oligomerization method of 1-butene by which poly-n-butenes can be produced, the numerical average molar mass being in the aforesaid range.

USE

Oligomers of short-chained olefines are technically important intermediates which can be used for preparation of very different end products. The most important of the short-chained olefines are propene and different isomers of butene and pentene. The oligomers of butene, M_n of which is 110...2500 g/mol, is used for example as solvents, fuels, in preparation of chemicals and in preparation of lubricants and additives for those.

The oligomers of 1-butene prepared according to this invention and which also are known as poly-n-butenes, contain an olefinic double bond in the polymer chain, the reactivity of which is increased. The polydispersity of their molar masses is $M_w/M_n = 1.02...1.5$. Of the properties of the oligomers there can be mentioned for example resistance against oxidation caused by heat, a low freezing point, low volatility, and a good temperature- viscosity relation. The aforesaid properties are important, especially when the oligomers are used for producing lubricants and additives for those. Because of the reactive double bond, the oligomers can be used as intermediates in the production of different chemical compounds. In the preparation of chemicals, oligomers of 1-butene are used for preparation of for example alkyl benzenes, alkyl phenols and alkyl succinic acid anhydride. Surfactants are prepared from alkyl benzenes and phenols by sulphonation. In the additives of lubricants, the oligomers of 1-butene can be used for example for preparing sulphonates, phenates, thiophosponates and ashless dispersants, alkenyl succinic imides. The molar mass of the hydrocarbon part in these compounds is ca 350...1200 g/mol, even 2500 g/mol in alkenyl succinic imide. Other applications are for example as lubricant in two stroke spark ignition engines, as working oil for metallurgic materials in rolling and drawing, in the leather and rubber industry and to make different surfaces hydrophobic. By hydration of the oligomers it is possible to obtain transformator oils, electrically isolating and cable oils of high quality and non-toxic cosmetic oils and white oils.

EXAMPLES

The following examples have been presented to describe in detail the oligomerization of 1-butene of the invention which, however, are not meant to restrict the scope of invention in any way.

The oligomerization reactions of 1-butene was carried out as following if not otherwise mentioned:

A steel reactor with the volume of 300 ml was internally cooled by a cooling coil and, when necessary, externally heated by a outer electric bath. The reactor was equipped with a mixer. 1-Butene and the catalyst were fed into the reactor via a valve to the liquid phase. The temperature of the reaction mixture was studied by a thermocouple. The temperature of the reaction mixture was tried to keep at the wished value with the precision of ± 1°C from the desired value. 100 ml n-heptane was added as solvent to the reactor in nitrogen atmosphere and also cocatalyst the amount of which is mentioned in the example. The solvent had been dried with molecular sieves. Thereafter 60...70 g of liquid 1-butene was added to the reactor. After the addition of the monomer, the reactor was pressurized with BF_3 gas and the catalyst complex was formed in situ and the reaction started immediately. The pressure of the reactor was kept constant by means of BF_3 gas. The reaction parameters were the following: the pressure 2.5...10 bar expressed as over pressure, the reaction temperature 10...70°C and the reaction time 1...121 minutes or 1...6 hours. The reaction was finished by adding an excess of either NaOH solution or water to the reactor. The product fraction was washed with NaOH solution and thereafter with water until the pH of the fraction was neutral. The product distribution was analyzed by the GC method.

Examples 1 and 2

The cocatalyst used was 14.2 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 4.0 bar and the temperature 20°C. The reaction time in Example 1 was 9 minutes and in Example 2 49 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

		The selectivities						
	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 1	77.4%	-	10.5	51.5	28.2	8.0	1.8	-
Ex. 2	91.0%	0.3	5.0	15.8	15.3	22.8	18.5	22.3

The numerical average molar mass of the product distributions of the Examples were 237 g/mol and 310 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 2, whereby M_n = 360 g/mol.

Examples 3 and 4

The cocatalyst used was 5.1 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 4.0 bar and the temperature 20°C. The reaction time in Example 3 was 9 minutes and in Example 4 49 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

		The selectivities						
	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 3	84.6%	-	7.7	23.2	36.2	24.0	8.9	-
Ex. 4	92.7%	0.4	1.2	4.1	12.8	18.9	14.8	47.0

The numerical average molar mass of the product distributions of the Examples were 268 g/mol and 383 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 4, whereby M_n = 407 g/mol. The viscosity index 81 was defined for this unhydrated product, measured in 100°C, the kinematic viscosity being 4.3 cSt.

Examples 5 and 6

The cocatalyst used was 37.8 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 4.0 bar and the temperature 20°C. The reaction time in Example 5 was 9 minutes and in Example 6 49 minutes. After the reaction times mentioned the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

		Selectivities						
	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 5	72.5%	0.5	34.3	32.4	10.4	16.9	5.5	-
Ex. 6	97.0%	0.7	9.2	11.2	14.8	25.5	23.0	15.6

The numerical average molar mass of the product distributions of the Examples were 220 g/mol and 302 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 6, whereby M_n = 357 g/mol.

Example 7

The cocatalyst used was 13.4 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 2.5 bar and the temperature 20°C. The reaction time was in Example 7 49 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

		The selectivities						
	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 7	81.8%	0.6	43.3	40.7	10.5	3.9	1.0	-

The numerical average molar mass of the product distributions of the Example were 202 g/mol.

Example 8

The cocatalyst used was 13.0 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 4.0 bar and the temperature 20°C. The reaction time was 6 hours. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

Selectivities

	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 8	ca 99%	0.9	4.2	9.0	8.0	7.5	8.4	58.4

The numerical average molar mass of the product distributions of the Example were 386 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 8, whereas M_n = 467 g/mol.

Examples 9 and 10

The cocatalyst used was 4.8 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 10 bar and the temperature 10°C. The reaction time in Example 9 was 9 minutes and in Example 10 121 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

The selectivities

	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 9	53.5%	0.3	7.6	43.3	36.8	7.1	5.0	-
Ex. 10	ca 99%	0.1	1.2	4.7	23.5	21.0	18.2	31.3

The numerical average molar mass of the product distributions of the Examples were 247 g/mol and 349 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 6, whereby M_n = 365 g/mol.

Examples 11 and 12

The cocatalyst used was 4.9 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 10 bar and the temperature 40°C. The reaction time in Example 11 was 4 minutes and in Example 12 121 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

		The selectivities						
	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 11	60.6%	-	6.1	21.6	36.2	23.9	12.2	-
Ex. 12	ca 99%	-	5.7	7.3	9.3	13.3	13.1	51.4

The numerical average molar mass of the product distributions of the Examples were 275 g/mol and 371 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 6, whereby M_n = 429 g/mol. The viscosity index 82 was defined for this unhydrated product measured in 100°C, the kinematic viscosity being 7.0 cSt.

Examples 13 and 14

The cocatalyst used was 5.0 mmol n-valerianic acid per one mole of 1-butene. The pressure of the reactor was 10 bar and the temperature 70°C. The reaction time in Example 13 was 9 minutes and in Example 14 121 minutes. After the reaction times mentioned, the reaction was stopped by means of NaOH solution. The hydrogen carbon phases were analyzed and the results were the following:

The selectivities

	C_4-conv.	C_8	C_{12}	C_{16}	C_{20}	C_{24}	C_{28}	C_{32+}
Ex. 13	63.2%	0.9	27.1	40.3	24.4	7.3	-	-
Ex. 14	ca 98%	-	8.8	19.7	19.0	29.5	13.4	9.6

The numerical average molar mass of the product distributions of the Examples were 219 g/mol. The lower fractions (C_{16-}) were separated by vacuum distillation from the product of Example 14, whereas M_n = 341 g/mol.

Examples 15...21

1-butene can be oligomerized also with other organic acid cocatalysts than n-valerianic acid, both with alcohols and water as Examples 15...21 show. The pressure of the reactor was 4.0 bar and the temperature 20°C, the reaction time being 36 minutes. The cocatalysts were acetic acid (Ex. 15), n-octanoic acid (Ex. 16), ethanol (17), 1-pentanol (18), 1-octanol (19) and water (20). The comparison examples is a reaction carried out in the same conditions with n-valerianic acid. The cocatalyst used was 14.5...15.9 mmol cocatalyst per one mole as 1-butene.

cocat.	n_{kk}	$C_8...C_{16}$	$C_{20}...C_{28}$	C_{32+}	C_4-conversion
C_2 acid	15.1	57.0	43.0	-	77.0%
C_8 acid	14.8	17.4	59.4	23.2	83.9%
ethanol	14.5	5.4	75.4	19.2	80.4%
pentanol	15.9	10.0	69.9	20.1	74.8%
octanol	14.5	22.7	61.1	16.2	79.2%
water	15.0	12.7	87.3	-	61.2%
n-valer.acid	15.0	18.3	59.7	22.0	86.7%

Patent claims

1. Method of oligomerization of 1-butene, **characterized** in that n-butene is oligomerized in one step by means of a complex consisting of BF_3 and water, C_2-C_{10} monoalcohol or C_2-C_8 monocarboxylic acid to a hydrogen carbon containing 12-48 carbon atoms.

2. Method of claim 1, **characterized** in that the monocarboxylic acid mentioned is n-valerianic acid, i-valerianic acid, methyl butanoic acid or a mixture of those.

3. Method of claim 1 or 2, **characterized** in that the temperature in the oligomerization is -30 - 90°C.

4. Method of claim 1,2 or 3, **characterized** in that the total pressure in the oligomerization reaction is 1-15 bar.

5. Method of any of claims 1-4, **characterized** in that the reaction time of the oligomerization reaction is 5 min - 10 hours.

6. The use of oligomerization of 1-butene prepared with the method of any of claims 1-5 as solvent or intermediate in preparing lubricants or additives of those.

AMENDED CLAIMS

[received by the International Bureau on 8 December 1992 (08.12.92);
original claims 1 - 6 replaced
by amended claims 1 - 7 (1 page)]

1. Method of oligomerization of 1-butene, **characterized** in that 1-butene is oligomerized in one step by means of a complex consisting of BF_3 and water, C_2-C_{10} monoalcohol or C_2-C_8 monocarboxylic acid to a hydrogen carbon containing 12-48 carbon atoms, in such a way that the BF_3-complex is made in situ in a constant BF_3-pressure by feeding at first inert solvent, cocatalyst and the 1-butene to the reactor.

2. Method of claim 1, **characterized** in that the monocarboxylic acid mentioned is n-valerianic acid, i-valerianic acid, methyl butanoic acid or a mixture of those.

3. Method of claim 1 or 2, **characterized** in that the temperature in the oligomerization is 0 - 90°C.

4. Method of claim 1,2 or 3, **characterized** in that the total pressure in the oligomerization reaction is 1-15 bar.

5. Method of any of claims 1-4, **characterized** in that the reaction time of the oligomerization reaction is 0,5 min - 10 hours.

6. Method of any of claims 1-5, **characterized** in that the inert solvent is an alkane or a cycloalkane, preferably n-heptane.

7. The use of oligomerization of 1-butene prepared with the method of any of claims 1-6 as solvent or intermediate in preparing lubricants or additives of those.

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI 92/00199

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 07 C 2/22, 11/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 07 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

SE,DK,FI,NO classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 4263465 (SHENG ET AL) 21 April 1981, see column 2, line 5 - line 11; example 1, part A --	1-6
X	MAKROMOL.CHEM., Vol. 191, 1990 Aldo Priola: "Presence of fragmentation products in the cationic oligomerization of 1-butene", pp 725-730 -- --------	1-6

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search 3rd November 1992	Date of Mailing of this International Search Report 05 -11- 1992
International Searching Authority SWEDISH PATENT OFFICE	Signature of Authorized Officer Jack Hedlund

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/FI 92/00199

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the Swedish Patent Office EDP file on 30/09/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4263465	81-04-21	NONE	