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<p>(21) International Application Number: PCT/FI95/00105</p> <p>(22) International Filing Date: 27 February 1995 (27.02.95)</p> <p>(71) Applicant (for all designated States except US): NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): KAPANEN, Mika [FI/FI]; Pormestarinkatu 5 B 11, FIN-06100 Porvoo (FI). HALME, Erkki [FI/FI]; Kyläkunnantie 7, FIN-00660 Helsinki (FI). KOSKIMIES, Salme [FI/FI]; Hämeenapajantie 7, FIN-00850 Helsinki (FI). KEINÄNEN, Kari [FI/FI]; Tornipolku 3 C 49, FIN-06400 Porvoo (FI).</p> <p>(74) Agent: NESTE OY; Patent Services, P.O. Box 310, FIN-06101 Porvoo (FI).</p>		<p>(81) Designated States: AT, AU, BR, CA, CH, CN, CZ, DE, DK, EE, ES, GB, HU, JP, KR, LT, LV, MX, NL, NO, NZ, PL, PT, RO, RU, SE, SI, SK, TJ, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. In English translation (filed in Finnish).</i></p>
<p>(54) Title: PROCESS FOR OLIGOMERIZATION OF AROMATIC AND ALICYCLIC HYDROCARBONS HAVING OLEFINIC SIDE GROUP</p> <p>(57) Abstract</p> <p>The application relates to a process for the oligomerization of aromatic or alicyclic hydrocarbons by means of a complex made up of BF₃ and a cocatalyst. The aromatic hydrocarbon may preferably be styrene, alpha-methyl styrene, or a mixture thereof, and the alicyclic hydrocarbon may be vinyl cyclohexane, vinyl cyclohexene, allyl cyclohexane, allyl cyclohexene, or a mixture thereof. The cocatalyst is an aliphatic alcohol, carboxylic acid, or inorganic acid. The oligomerization may be performed with or without a medium, at a temperature above 0 °C, the pressure being adjusted by means of BF₃ to 1 - 10 bar. An oligomer prepared by the process can be used as a solvent or an additive in fuels or lubricants, in surfactants, in white oils and cosmetic oils requiring extra purity, and in PVC and polyolefin plastics. In polyester and vinyl ester resins this oligomer can be used to replace in part a monomer (e.g. styrene), thus reducing the evaporation of monomer, and to inhibit shrinkage at the hardening stage, and it also improves the optical properties of the said resins.</p>		

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Process for oligomerization of aromatic and alicyclic hydrocarbons having olefinic side group.

The patent relates to a process for the oligomerization of aromatic or alicyclic hydrocarbons at a temperature above 0 °C by means of a complex made up of a boron fluoride catalyst and a cocatalyst. The pressure in the oligomerization reaction is adjusted to 1 - 10 bar by means of the gaseous catalyst BF_3 .

The oligomerization and polymerization of hydrocarbons which contain different olefinic groups is commonly known technology. These reactions can occur thermally without a catalyst, as a radical reaction with, for example, peroxide catalysts, with coordination polymerization catalysts, through an anionic mechanism with basic catalysts, through a cationic mechanism with Friedel-Crafts catalysts, and through polymerization by using molecular sieves, e.g. zeolites.

The anionic mechanism is mainly used for olefin dimerization reactions, for example for the dimerization of propylene to 4-methyl-1-pentene. Coordination polymerization is mainly used for the preparation of various plastics, such as polyethylene, polypropylene and poly-1-butene, in which it is desired to determine in advance very precisely the structure of the product to be formed. The cationic mechanism and polymerization with molecular sieves produce in the polymerization of olefinic hydrocarbons light oligomers or viscous liquids, so-called liquid polymers. The various mechanisms are described, for example, in the books Principles of Polymerization (Odián, G., J. Wiley & Sons, New York, 2nd ed., 1981) and Textbook of Polymer Science (Billmeyer, F.W. Jr, J. Wiley & Sons, New York, 3rd ed., 1984).

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 require a proton donor, i.e. a cocatalyst. Such cocatalysts include water, alcohols, carboxylic acids, inorganic acids, certain alkyl halides, and halogens. The oligomerization can be performed in bulk, i.e. without an auxiliary solvent, or in the presence of an inert solvent. Such inert solvents include alkanes, such as hexane and heptane, and cycloalkanes, such as cyclohexane and cycloheptane, as well as certain aromatic solvents, such as toluene and benzene.

The books mentioned above mainly discuss polymerization, the molar mass of the product ranging from several tens of thousands to hundreds of thousands, up to millions, in which case the degree of polymerization is considerably over one hundred. Actual oligomerization, the molar mass of the product being hundreds or at maximum a few hundred thousands, has been passed by completely.

Vinyl cyclohexane

Kennedy et al. used aluminum trichloride in an ethyl chloride solvent as the catalyst for the polymerization of vinyl cyclohexane, the reaction temperature being +7...-100 °C, in which case the number-average molar mass of the product was respectively $M_n = 2000 \dots 6500$ g/mol, and the degree of polymerization was thus 18 - 59. The product was white and pulverous. Ketley and Ehring arrived at similar results, although they used as the catalyst aluminum chloride in an ethyl chloride solvent, the temperature being -50 °C; the number-average molar mass of the product was $M_n = 10500$ g/mol, the degree of polymerization thus being 95. Ketley and Ehring also polymerized allyl cyclohexane with the same catalyst-solvent combination at -78 °C, the number-average molar mass of the product being $M_n = 13100$ g/mol and the degree of polymerization thus being 119.

4-Vinyl cyclohexene

Butler and Miles polymerized 4-vinyl cyclohexene with several different catalysts, such as BF_3 gas, BF_3 etherate, and titanium tetrachloride. In the polymerization with BF_3 gas at $-70\text{ }^\circ\text{C}$ in a methyl chloride solvent, the conversion was 28 %. With BF_3 etherate catalyst in a methyl chloride solvent at $0\text{ }^\circ\text{C}$, the conversion was 35 %.

Marconi et al. (in the Kennedy book mentioned above, pages 194 - 197) polymerized 4-vinyl cyclohexene with acid initiators, in which case the product was a solid, amorphous polymer having a low molar mass and an irregular structure.

α -Methyl styrene

α -Methyl styrene polymerized by means of a cationic mechanism is used to a limited extent in certain commercial resins. According to the literature, it is possible to produce from α -methyl styrene with AlCl_3 catalyst in suitable conditions (solvent, temperature) polymers the molar mass of which is up to $2 \cdot 10^6$ g/mol (i.e. degree of polymerization approx. 17000). There is no detailed information regarding the molar masses of products obtained with boron trifluoride catalysts, BF_3 gas or BF_3 etherate, at low temperatures ($-78 \dots +10\text{ }^\circ\text{C}$) in a suitable solvent, such as toluene, methyl chloride or n-hexane, or a mixture thereof. The only mention is a product polymerized with BF_3 etherate in toluene at $-78\text{ }^\circ\text{C}$, with a degree of polymerization of $\text{DP} = 5570$, which corresponds to a molar mass of approx. 660000 g/mol.

Styrene

The cationic polymerization of styrene is very well known and investigated in academic research, owing to the relatively easy control and monitoring of its polymerization, in particular

with respect to the reaction velocity and the molar mass. However, because of the relatively poor properties of the product, industrial research has not shown great interest in the said product. The molar masses were 45000 - 340000. In the course of years, styrene polymerization has been studied using nearly all cationic catalysts, such as Brönstedt acids, Lewis acids, alkyl aluminums, etc. Styrene, as well as α -methyl styrene, has been polymerized using BF_3 catalysts. The catalyst was a complex formed in a reaction between BF_3 and a cocatalyst. In these complexes the cocatalyst has been water, tetrahydrofuran or ethanol. In addition, there are several examples of the use of BF_3 etherate as a catalyst for the polymerization of styrene. The solvent has in most cases been benzene, carbon tetrachloride, methyl chloride, or a mixture thereof. 0...30 °C is mentioned as the reaction temperature.

BF_3 -catalyzed oligomerization has been known at least since 1873, when Butlerov and Gorianov reported the oligomerization of isobutene and propylene with BF_3 treatment at room temperature. The first BF_3 -catalyzed polycondensation was performed by Canizzaro in 1854, at which time he reacted benzyl alcohol with BF_3 , and the product obtained was a resin-like hydrocarbon. (Kennedy, J., Cationic polymerization of olefins, J. Wiley & Sons, New York, 1975, p. 8).

The present invention relates to the oligomerization of alicyclic or aromatic hydrocarbons which contain an olefinic group to a liquid product by using as the catalyst a complex formed by boron trifluoride and a cocatalyst. The cyclic hydrocarbon may contain a group containing a heteroatom, mainly a hydroxyl or ester group, which may be significant in some uses. The product is thus neither solid nor crystalline, and its degree of polymerization is low, clearly below one hundred. In the invention, the cyclic compound which contains an olefinic pendant group is preferably vinyl cyclohexane, vinyl cyclohexene, or various isomers thereof, allyl cyclohexane, or allyl cyclo-

hexene or various isomers thereof. The aromatic compound which contains an olefinic pendant group is preferably styrene or α -methyl styrene. The catalyst system comprises a complex made up of boron trifluoride and a cocatalyst, which may be an alcohol, a carboxylic acid, water, or an inorganic acid. The cocatalyst is preferably a carboxylic acid or an alcohol. The oligomerization takes place in the presence of an active catalyst complex. Such a catalyst complex may be prepared by a reaction between BF_3 and a cocatalyst, separately from the oligomerization reactor or in situ in the reactor.

The oligomerization temperature is above 0 °C, preferably 10 - 30 °C. The pressure is 1 - 10 bar, and it can be adjusted by means of gaseous BF_3 . The reaction time is relatively short, in general 0.5-1 hour, at maximum 3 hours.

The oligomerization process according to the present invention differs from the state-of-the-art techniques in particular with respect to the catalyst complex mentioned above and in that the reactions are performed by using a considerably higher reaction temperature. One of the advantages achieved by using a higher reaction temperature is the possibility to use water for the cooling of the reactor as an inexpensive alternative instead of expensive specialized apparatus.

The examples show that it is possible to produce oligomers in which the degree of polymerization is 2 - 100, in which case the number-average molar mass is a few hundred to a few thousand with the catalyst complex according to the invention and with a high monomer conversion. In oligomerization by the process of the invention, the oligomerization reaction proceeds at a considerable speed.

By the process according to the present invention it is possible to oligomerize alicyclic or aromatic hydrocarbons which contain an olefinic pendant group. Such oligomerization is not

previously known in the literature. The invention is characterized by the characteristics stated in the patent claims hereinafter.

The oligomers of olefinic hydrocarbons are technologically important intermediates, which can be used for the preparation of highly varied end products.

The oligomers prepared according to the present invention contain in the polymer chain an olefinic double bond having increased reactivity. The properties of the oligomers include resistance to thermal oxidation, a low pour point, a low volatility, and a good temperature-viscosity dependence. The above properties are important, especially if the oligomers are used for the production of lubricants and their additives. On the other hand, the process according to the invention can also be used for producing oligomers having a low viscosity index. These oligomers and their derivatives are used mainly for applications other than lubricants and their additives.

Owing to the reactive double bond, the oligomers can be used as intermediates in the production of various chemical compounds. In the preparation of chemicals, the oligomers are used, for example, for the preparation of alkyl benzenes, alkyl phenols and alkyl succinic acid anhydride. Surfactants are prepared from alkyl benzenes and alkyl phenols by sulfonation. In the additives of lubricants, the oligomers can be used in the preparation of, for example, sulfonates, phenates, thiophosphonates, and ash-free dispersants, alkenyl succinimides. In these compounds, the molar mass of the hydrocarbon component is approx. 350...1200 g/mol, in alkenyl succinimide as high as 2500 g/mol. Other uses include lubricants in two-stroke spark-ignition engines, as a machining oil in the rolling and drawing of metallurgical materials, in the leather and rubber industries, and in rendering various surfaces hydrophobic. By hydrogenation of the oligomers it is possible to prepare high-

standard transformer oils, electrical insulation and cable oils, and non-toxic oils and white oils. In particular, the lightest oligomers of styrene and α -methyl styrene can be used to replace in part the monomer in polyester resins and vinyl ester resins. Thereby it is possible, for example, to reduce monomer evaporation and to reduce the hardening shrinkage of resin. The oligomers of hydrocarbons which contain a non-aromatic olefinic group, such as cyclohexane and vinyl cyclohexene, can be used, for example, in polyester and vinyl ester resins as inhibitors of shrinkage during hardening, as so-called Low Profile agents, and in part to replace the monomer. By means of such non-aromatic monomers it is possible to reduce the absorption of UV light by the products prepared and thereby to reduce their yellowing and discoloration.

Examples

For a detailed illustration of the present invention, the oligomerization of alicyclic or aromatic hydrocarbons containing an olefinic pendant group is described in several examples.

The oligomerization reactions were carried out, unless otherwise stated, in a steel reactor having a volume of 300 ml. It was cooled internally with a cooling coil and was heated, when necessary, by using an electric bath. The reactor was equipped with a mixer. The temperature of the reaction mixture was monitored by using a thermocouple. The aim was to maintain the temperature of the reaction mixture at the set value with a precision of ± 1 . The reagents used and their amounts are given in the examples.

The reactor was first charged with a solvent, if necessary, and the cocatalyst, as well as the aromatic or cyclic hydrocarbon containing a vinylic or aromatic pendant group, mentioned in the examples, as the reactor liquid phase. Thereafter the reactor was pressurized with BF_3 gas, whereupon the catalyst com-

plex formed in situ and the reaction started immediately.

The reactor pressure was maintained constant by means of BF_3 gas. The pressure was sufficient to keep the monomers in the liquid phase. The reaction parameters used were as follows: pressure 0...10 bar, indicated as overpressure; reaction temperature 10...70 °C; and reaction time 1...4 hours. The reaction was terminated by adding into the reactor an excess of either an NaOH solution or water. The product fraction was washed with an NaOH solution and was neutralized with water after the wash.

The examples illustrate the various possibilities of the process to produce oligomer fractions with different monomers. All of the examples describe the present invention. It should be borne in mind that with the process being disclosed it is possible to produce highly varied product fractions, and so the examples are only indicative of the possibilities of the process.

Example 1.

α -Methyl styrene was oligomerized for $\frac{1}{2}$ h at a BF_3 pressure of 3.2 bar at 20 °C in toluene solvent. The feed of monomer was 46.2 g, the feed of toluene as a solvent was 100 ml, and the feed of n-valerianic acid as a cocatalyst was 2.8 g. The monomer conversion was 92.4 %. The composition of the product distribution, from which the monomer residue had been removed by vacuum distillation, was as follows: dimer 79.8 %, trimer 13.3 %, tetramer 2.5 %, and pentamer and heavier oligomers 4.4 %. For this product fraction, from which the monomer residue had been removed, kinematic viscosities were measured, which were $\text{KV}_{40} = 155$ cSt and $\text{KV}_{100} = 8.30$ cSt. The number-average molar mass of the product was 273 and its degree of polymerization was 2.3.

Example 2.

4-Vinyl-1-cyclohexene was oligomerized for $\frac{1}{2}$ h at a BF_3 pressure of 2.0 bar at 20 °C in toluene solvent. The feed of monomer was 41.3 g, the feed of toluene solvent was 100 ml and the feed of n-valerianic acid as a cocatalyst was 2.7 g. The monomer conversion was approx. 95 %, and the yield of heavy fractions, i.e. trimers and heavier, was 79.2 %. For the total product, i.e. dimers and heavier fractions, number-average and weight-average molar masses were determined by the GPC method; they were $M_n = 320$ g/mol (degree of polymerization is approx. 3) and $M_w = 1020$ g/mol. The molar mass distribution ranged up to a molar mass of 10,000 g/mol.

Example 3.

4-Vinyl-1-cyclohexene was oligomerized for 2 h at a BF_3 pressure of 3.0 bar at 20 °C in n-heptane solvent. The feed of monomer was 82.3 g, the feed of n-heptane solvent was 50 ml and the feed of n-valerianic acid as a cocatalyst was 2.8 g. The monomer conversion was approx. 95 %. For the total product, i.e. dimers and heavier fractions, number-average and weight-average molar masses were determined by the GPC method; they were $M_n = 410$ g/mol (degree of polymerization approx. 3.8) and $M_w = 4090$ g/mol. The molar mass distribution ranged up to a molar mass of 100,000 g/mol.

Examples 4-14.

Various monomers were oligomerized using the parameters given in Tables 1 and 2. The results obtained were oligomers, for which certain values are determined in Table 2.

Table 1 shows the starting materials used in the various examples, the solvent medium and the cocatalyst, as well as their amounts.

Table 1

Ex.No.	Monomer, g	Cocatalyst, g	Solvent/mixture, ml
1	STY, 90.3	val.acid, 2.8	toluene 50
2	STY, 90.5	pentanol, 2.85	toluene 50
3	STY, 90.1	val.acid, 2.6	toluene 70/heptane 30
4	AMS, 91.3	val.acid, 2.8	toluene 50/heptane 50
5	AMS, 89.8	val.acid, 2.4	toluene 70/heptane 30
6	VCHE, 82.1	pentanol, 2.0	toluene 70/heptane 30
7	VCHA, 80.1	pentanol, 2.0	toluene 70/heptane 30
8	VCHA, 80.0	val.acid, 2.8	toluene 100
9	VCHA, 79.6	val.acid, 2.35	toluene 70/heptane 30
10	VCHA, 80.8	pentanol, 2.0	toluene 100
11	VCHE, 82.3	pentanol, 2.1	toluene 70/heptane 30

Abbreviations and acronyms: AMS = alpha-methyl styrene, STY = styrene, VCHA = vinyl cyclohexane, VCHE = 4-vinyl-1-cyclohexene, val.acid = n-valerianic acid. Pentanol stands for 1-pentanol and heptane stands for n-heptane.

Table 2 shows the reaction conditions in the various examples. The table shows the reaction temperature (T, C), reaction pressure (p, bar) indicated as overpressure, and the reaction time (t, h). Of the results, the monomer conversion (conv. %), number- and weight-average molar masses (Mn and Mw, g/mol) and the degree of polymerization (DP) calculated from the number-average molar mass are given.

Table 2

Ex.No.	t,h	T,C	p,bar	conv.%	Mn,g/mol	Mw,g/mol	DP
1	0.35	30	2.6	abt. 100	940	3800	9
2	0.53	30	2.6	abt. 100	860	4400	8.3
3	0.28	50	2.2	abt. 100	860	2700	8.3
4	0.42	40	2.0	abt. 99	270	1500	2.3
5	0.33	30	2.0	abt. 100	280	1300	2.4
6	0.38	40	1.8	abt. 90	410	730	3.8
7	0.25	40	2.2	abt. 96	310	330	2.8
8	0.25	30	2.0	abt. 94	310	330	2.8
9	0.33	40	2.0	abt. 99	300	330	2.7
10	0.33	40	2.0	abt. 100	310	340	2.8
11	0.33	55	1.7	abt. 89	420	730	3.9

Claims

1. A process for the oligomerization of aromatic or alicyclic hydrocarbons which contain an olefinic pendant group, or their derivatives which contain a heteroatom, to a macromolecule having a number-average molar mass of 200 - 1000 and a weight-average molar mass of 500 - 5000, characterized in that the oligomerization reaction is performed by means of a complex made up of BF_3 and a cocatalyst, with or without a medium, at a temperature above 0 °C and a pressure of 1 - 10 bar.
2. A process according to Claim 1, characterized in that the aromatic hydrocarbon is styrene or α -methyl styrene.
3. A process according to Claim 1, characterized in that vinyl cyclohexane, vinyl cyclohexene, allyl cyclohexane or allyl cyclohexene is oligomerized.
4. A process according to any of Claims 1 - 3, characterized in that the cocatalyst is an aliphatic alcohol, carboxylic acid, or inorganic acid.
5. A process according to Claim 4, characterized in that the cocatalyst is n-valerianic acid.
6. A process according to any of Claims 1 - 5, characterized in that the medium in the oligomerization reaction is an inert solvent, preferably an aromatic C_6 - C_8 hydrocarbon or a C_4 - C_8 alkane.
7. A process according to Claim 6, characterized in that the medium is benzene, toluene, pentane, hexane, heptane, or a mixture thereof.
8. The use of an oligomer prepared by the process according to any of Claims 1 - 7 as a solvent, an additive in fuels or lub-

ricants, in surfactants, in white oils and cosmetic oils requiring extra purity, and in polyvinyl chloride or polyolefin plastics.

9. The use of an oligomer prepared by a process according to any of Claims 1 - 7 in polyester resins and vinyl ester resins to replace in part the monomer to reduce monomer evaporation and to inhibit shrinkage at the hardening stage, and to improve optical properties.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 95/00105

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C07C 2/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C07C, C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CHEMICAL ABSTRACTS, EPODOC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Chemical Abstracts, Volume 90, No 20, 14 May 1979 (14.05.79), (Columbus, Ohio, USA), Higashimura, T. et al, "Catalytic difference between oxo acids and metal halides in the cationic oligomerization of styrene", page 2, THE ABSTRACT No 152660m, Macromolecules 1979, 12 (2), 217-222 --	1-2
X	US 3385905 A (JAMES G. SMITH ET AL), 28 May 1968 (28.05.68), column 1, line 28 - line 30; column 2, line 1 - line 14 --	1-2
A	WO 9415895 A1 (NESTE OY), 21 July 1994 (21.07.94), abstract --	1-9

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 95/00105

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>Chemical Abstracts, Volume 84, No 6, 9 February 1976 (09.02.76), (Columbus, Ohio, USA), Heublein, Guenther et al, "Cationic polymerization of vinylcyclohexane", page 31585, THE ABSTRACT No 31585h, Faserforsch. Textiltech. 1975, 26 (9), 441-444</p> <p style="text-align: center;">-- -----</p>	1,3

INTERNATIONAL SEARCH REPORT
Information on patent family members

28/08/95

International application No.
PCT/FI 95/00105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3385905	28/05/68	NONE	
WO-A1- 9415895	21/07/94	NONE	