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Process for preparing vinyl esters from butene oligomers

The invention relates to a process for preparing vinyl esters from butene oligomers, in particular from dibutene and tributene, and to the use of these vinyl esters.

Vinyl esters of tertiary carboxylic acids have long had a firmly established place in industry as comonomers, in particular as internal plasticizers for the production of environmentally friendly water-dispersible surface coatings and paints based on vinyl acetate. Apart from their plasticizing action, they give the copolymers further advantageous properties such as high saponification resistance which make the copolymers suitable for use under severe conditions. Examples which may be mentioned are exterior paints and thermally insulating renders on buildings.

The plasticizing properties of vinyl esters, in particular those of tertiary carboxylic acids, depend on their chain length and on the type and position of branches. One measure of the internal plasticizing action of copolymers is the glass transition temperature of the corresponding homopolymer. Comparison of the plasticizing properties of vinyl esters of various chain lengths by means of the glass transition temperature T_g of the respective homopolymer shows their dependence on the molar mass or on the degree of branching,

Chain length of the carboxylic acid	Linear vinyl ester	Glass transition temperature [°C]	Tertiary vinyl ester	Glass transition temperature [°C]
Vinyl C ₂ -ester	vinyl acetate	+ 38 (33)*		
Vinyl C ₃ -ester	vinyl propionate	- 7 (-7)*		
Vinyl C ₄ -ester	vinyl butyrate	- 5		
Vinyl C ₅ -ester		- 15 ***	2,2-dimethyl-propanoic acid	86 (70)*
Vinyl C ₆ -ester	vinyl hexanoate	- 20	2,2-dimethyl-butanoic acid	41**
Vinyl C ₁₀ -ester	vinyl decanoate	- 60		
Vinyl C ₁₂ -ester	vinyl laurate	- 75 (-53)*		

(Encyclopedia of Polymer Science and Engineering, Vol. 17, p. 439 (1989), J. Wiley & Sons. Inc.), (* Ullmann's Encyclopedia of Industrial Chemistry, Vol. A22, p. 2, 5th ed. (1993), Verlag Chemie), (** C.E.L. Feeder, Surface Coatings Austral. 228 1985), 8, pp. 11-16). (***) own measurement)

These data are suitable only for comparison with one another, since they can vary with the method of producing the test specimens and with the test method. However, it can be seen that the plasticizing properties improve with increasing chain length of the vinyl ester (in the case of linear chains, to an alkyl radical having 12 carbon atoms). In particular, the vinyl esters of linear carboxylic acids have very good plasticizing properties, but are less suitable for many applications because they are easily saponified.

In contrast, the vinyl esters of tertiary carboxylic acids can be used more widely, since they are very resistant to saponification, heat and oxidation. However, the tertiary branching drastically reduces the plasticizing action and further branches in the chain result in a further deterioration, as the following examples of homopolymers of vinyl esters of tertiary C₉-carboxylic acids show:

Tertiary C₈-carboxylic acids	Glass transition temperature [°C]
2,3-Dimethyl-2-isopropylbutanoic acid	119
2-Ethyl-2,3,3-trimethylbutanoic acid	115
2,2,3,3-Tetramethylpentanoic acid	91
(VeoVa®9, Shell)	70 (60)*
2,4,4-Tetramethylpentanoic acid	55
2,2,4-Trimethylhexanoic acid	10

(H. P. H. Scholten, J. Vermeulen, W. J. van Westrenen, Recent Development in Latices based on Vinyl Esters of branched Monocarboxylic Acids, 7th International Conference on "Water-Borne Coatings" October 26-28, 1998, Penta Hotel, London), (* W. Lau, VeoVa®, Vinyl Ester Monomer Polymers DotCom Magazine, Vol. 2., No. 2, Feb. 1996)

Nowadays, it is predominantly vinyl esters which are prepared from an isomer mixture of tertiary C₁₀-carboxylic acids and form homopolymers having a glass transition temperature of -3°C that are used in industry. This mixture is very suitable and sought-after for use in, for example, the internal plasticization of polyvinyl acetate with a simultaneous increase in the saponification resistance.

The C₁₀-carboxylic acid used for preparing the vinyl esters is in turn prepared by addition of carbon monoxide and water onto tripropene under pressure and in the presence of extremely acidic catalysts (hydrocarboxylation, in particular the KOCH reaction).

Finally, tripropene, namely a mixture of isomeric C₈-olefins, is obtained in admixture with other olefin fractions (C₆-, C₁₂-, C₁₅-olefins) by acid-catalyzed oligomerization of propene. Catalysts which can be used here are, for example, acid zeolites or phosphoric acid on a solid support.

A disadvantage of the processes for preparing vinyl esters of C₁₀-carboxylic acids is that the propene required is a comparatively expensive raw material. In this acid-catalyzed oligomerization, significant raw material losses have to be expected because of by-product formation. Finally, it should be pointed out that even in the tripropene fraction of the oligomerization products, the number of isomers is so high that analytical monitoring is difficult. The conversion into carboxylic acids lastly forms such a high number of isomers that a product mixture having properties which are difficult to define results.

Vinyl esters of tertiary carboxylic acids having more than 10 carbon atoms have been examined to some extent (e.g. WO 93/22353). They all have a plasticizing action, as can be expected from their relatively long carbon chain. However, firstly, the raw materials required are frequently not available at a sufficiently low price and, secondly, the incompatibility in the copolymer also increases with increasing chain length.

Some of the vinyl esters of tertiary carboxylic acids having less than 10 carbon atoms are likewise known and have been examined for suitability as plasticizers. Thus, the vinyl esters based on pivalic acid (a tertiary C₅-acid) and those based on tertiary C₈ acids (VeoVa®9) have some industrial importance, but both are hardening comonomers in comparison to vinyl acetate.

It would therefore be desirable to be able to use raw material sources other than propene or its oligomers for preparing vinyl esters which have the same or better plasticizing properties than the vinyl esters of, for example, the C₁₀-carboxylic acids based on tripropene.

It has surprisingly been found that tertiary carboxylic acids which have been prepared from butene oligomers are very well suited as plasticizers.

The present invention accordingly provides a process for preparing vinyl esters which comprises

- a) oligomerizing butenes,
- b) separating off the butene oligomers from the oligomerization product,
- c) converting the butene oligomers into carboxylic acids having one more carbon atom and
- d) converting the carboxylic acids into the corresponding vinyl esters.

The vinyl esters prepared by the process of the invention are very well suited as comonomers for preparing internally plasticized polymers. Examples which may be mentioned are the copolymerization of vinyl C_2 -carboxylate with vinyl chloride, and the copolymerization with vinyl acetate. Terpolymers with acrylates are also a potential field of application. The proportion of vinyl ester prepared according to the invention can vary within wide limits, depending on the desired properties. Their use as homopolymer is also included if, for example, particularly flexible films are to be produced.

In the process of the invention, butenes are firstly oligomerized, giving predominantly dibutene (C_8 -olefin). In addition, tributene (C_{12} -olefin) and tetrabutene (C_{16} -olefin) are formed by trimerization and tetramerization, respectively, of butene. It is here possible to use all industrial C_4 -olefin-containing streams as raw material, e.g. cracking C_4 , C_4 -olefins from Fischer-Tropsch processes, C_4 -olefins from dehydrogenation of butane or from other industrial processes.

It is thus possible to use dibutene, tributene, tetrabutene or even higher oligomers as butene oligomers in the process of the invention. The separation of the butene oligomers from the oligomerization product can be carried out in a technically simple manner and in high purity by distillation.

The process of the present invention can be used both for preparing vinyl C_8 -carboxylates from dibutene or from the corresponding C_8 -carboxylic acid and for preparing vinyl C_{13} -carboxylates from tributene or from the corresponding C_{13} -carboxylic acid.

To obtain vinyl esters having a low degree of branching, it is of course necessary to use largely linear C_4 streams, i.e. those having a high proportion of n-butenes, for the oligomerization.

It is usual firstly to remove butadiene from the crude cracking C_4 by extraction or to convert it into linear butenes by selective hydrogenation. In the present case, the selective hydrogenation is not absolutely necessary but is particularly useful since it considerably increases the proportion of n-butenes for the oligomerization. In both cases, the result is a butadiene-free C_4 fraction, namely raffinate I. In the next step, isobutene can be removed from the C_4 stream by, for example, preparation of methyl tert-butyl ether (MTBE) by reaction with methanol. MTBE is a sought-after fuel component. Other possibilities are reaction of the isobutene in the raffinate I with water to form TBA (tertiary butanol) or the acid-catalyzed oligomerization of isobutene to form diisobutene. The now isobutene-free C_4 fraction, namely raffinate II, comprises, as desired, only 1-butene and 2-butene. If desired, 1-butene can also be isolated by distillation, in which case the butene-free fraction is then referred to as raffinate III.

Removal of the isobutene from a C_4 fraction by simple distillation with subsequent further processing is normally not possible, since 1-butene and isobutene have virtually the same boiling point. However, the separation of 2-butene and isobutene by distillation is possible. If, therefore, 1-butene is converted into 2-butene by hydroisomerization, removal of the isobutene by simple distillation becomes a feasible route to C_4 streams which comprise only linear butenes.

The oligomerization of butene to dibutene is preferably carried out using raffinate II or III. Other industrial C_4 streams can also be used provided that they contain no further unsaturated compounds apart from the linear butenes. The particularly preferred starting material for the butene oligomerization is *n*-butene, since the resulting vinyl esters of tertiary carboxylic acids have, as evidenced by the examples, better plasticizer properties.

If, on the other hand, the plasticizing action of the vinyl esters plays a subordinate role or a hardening action is even desirable, isobutene-containing C_4 streams can be used; a preferred feedstock is then raffinate I.

The process of the invention enables industrially available C_4 streams which have hitherto frequently not been utilized at all for chemical processes to be used as economical raw materials for preparing vinyl esters.

The oligomerization of butene-containing C_4 streams to produce mixtures comprising C_6 -, C_{12} - and higher olefins is known in principle. There are three principal process variants:

The oligomerization over acid catalysts has been known for a long time; catalysts used industrially are, for example, zeolites or phosphoric acid on supports. This gives isomer mixtures of branched olefins. Even under optimized conditions, dimethylhexenes remain the main product (WO 92/13818).

As shown in the examples, the C_6 -olefins which have been separated off here can be processed to give the corresponding tertiary carboxylic acids and their vinyl esters. However, only homopolymers having a high glass

transition temperature, and thus poorly plasticizing or even hardening comonomers, are obtained.

Another process which is likewise practiced worldwide is oligomerization using soluble nickel complexes, known as the DIMERSOL process (cf. Yves Chauvin, Helene Olivier; In "Applied Homogeneous Catalysis with Organometallic Compounds"; edited by Boy Cornils, Wolfgang A. Herrmann; Verlag Chemie, 1996, 258-268). The vinyl esters of C_8 -carboxylic acids prepared from the C_8 fraction have a significantly better plasticizing action than the vinyl esters produced by the abovementioned process (see examples).

Finally, mention should also be made of the oligomerization over fixed-bed nickel catalysts by the process of OXENO GmbH. The process has become known as the OCTOL process in the literature (Hydrocarbon Process., Int. Ed. (1986) 65 (2, Sect. 1, 31-33). The tertiary carboxylic acids prepared therefrom can be converted into vinyl esters which give a particularly good internal plasticizing action in copolymers.

The use of butene oligomers, in particular dibutene and tributene, for preparing vinyl esters has a series of notable advantages: it is possible to use inexpensive industrial C_4 streams such as raffinate II, raffinate III or other C_4 -olefin-containing raw materials as starting material. The fractions containing essentially only n-butenes as oligomerizable components, e.g. raffinate II or III, are particularly suitable for preparing comonomers for internal plasticization. Particularly surprising and not to be expected was the fact that the plasticizing action of the vinyl esters prepared according to the invention and based on the tertiary C_8 -carboxylic acids obtained from dibutene was excellent and at least equal to that of the standard product based on tripropene in the copolymerization with vinyl acetate or vinyl chloride. The tributene-based vinyl esters prepared analogously can achieve a further improvement.

In the process of the invention, the butene oligomers are separated off from the oligomerization product and are in each case converted into the corresponding carboxylic acids having one more carbon atom. This can be achieved by acid-catalyzed hydrocarboxylation (KOCH reaction) or by hydroformylation and subsequent oxidation of the resulting oxo aldehydes. The KOCH synthesis, as described in Falbe, *New Synthesis with Carbon Monoxide*, Springer Verlag, Berlin 1980, p. 372 ff, will be the preferred method in practice. Here, olefins are reacted with carbon monoxide in the presence of strong acids such as sulfuric acid or boron fluoride hydrates to form tertiary carboxylic acids. Using Cu^+ as cocatalyst, the reaction proceeds even under atmospheric pressure and at ambient temperature (Y. Souma, H. Sano; *Bull. Chem. Soc. Jpn.* 1974, 47, 1717).

The carboxylic acids obtained in this way are subsequently converted into the corresponding vinyl esters. This can be achieved, for example, by reacting the carboxylic acids with acetylene, preferably in the presence of the zinc salt of the acid to be vinylated, at atmospheric pressure and 200-250 °C (e.g. as described in *Encycl. Polym. Sci. Eng.* 17, pp. 426-434).

Alternatively, the vinyl esters can be obtained by transesterification of the carboxylic acids with further vinyl esters such as vinyl acetate or vinyl propionate (e.g. as described in: *Ullmann*, 4th edition, vol. 19, p. 368 ff).

The plasticizer properties of the vinyl esters are, as mentioned above, influenced by the degree of branching. The degree of branching of the vinyl esters can in turn be influenced by the degree of branching of the starting olefins. In particular embodiments of the present invention, it is therefore possible to use dibutenes containing not more than 35% by weight, preferably 25% by weight, of multiply branched olefins, e.g. dimethylhexene.

The vinyl esters prepared by the process of the invention can be used as comonomers in polymerization reactions, for example in the preparation of polyvinyl acetate, where they effect internal plasticization together with a simultaneous increase in the hydrolysis resistance. Copolymerization with ethylene and the preparation of terpolymers with acrylates are further examples of the use of the vinyl esters prepared according to the invention as comonomers for internal plasticization.

The following examples illustrate the invention without restricting its scope.

Examples 1 to 3

The table below shows the typical composition of dibutenes formed from n-butenes in the three different oligomerization variants. The product composition is dependent essentially only on the oligomerization method. Starting materials which can be used are, for example, raffinate II or raffinate III or other n-butene-containing streams, as long as they contain no significant amounts of branched butenes. In the following examples, raffinate III was used as raw material.

Olefin A dibutene obtained by oligomerization of raffinate III over montmorillonite (acid catalysis)

Olefin B dibutene, obtained by oligomerization of raffinate III by the DIMERSOL process

Olefin C dibutene obtained by oligomerization of raffinate III by the OCTOL process

	Example 1	Example 2	Example 3
	Olefin A	Olefin B	Olefin C
n-octene	~ 0 %	~ 6 %	~ 13 %
3-Methylheptene	~ 5 %	~ 59 %	~ 62 %
3,4-Dimethylhexene	~ 70 %	~ 34 %	~ 24 %
Other C ₈ -olefins	~ 25 %	~ 1 %	~ 1 %

The proportion of linear and at most singly branched olefins is therefore about 5% in the case of olefin A, about 65% in the case of olefin B and about 75% in the case of olefin C. All figures are in % by weight.

Examples 4 to 6

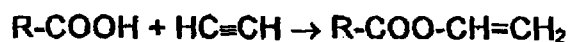
Using a method based on DE 23 39 947, tertiary carboxylic acids were prepared from the olefins A, B and C. The catalyst used was a complex of boron fluoride and water, with Cu⁺ being used as cocatalyst. The reactions were carried out in a stirring autoclave in a temperature range of 20-35°C and at a CO pressure of 30 bar. The olefin was metered in uniformly over a period of 6 hours. The pressure was kept constant by metering in further CO. The reaction was stopped as soon as no further absorption of CO was observed.

After separating off the catalyst phase, washing with water and working up the crude carboxylic acids by distillation, products having the following compositions, in each case over a number of batches, were obtained. (Figures in % by mass).

	Example 4	Example 5	Example 6
Isomeric C ₈ -carboxylic acid	Acid A	Acid B	Acid C
2,2-Dimethylheptanoic acid	0.5%	6.5%	7.4%
2-Methyl-2-ethylhexanoic acid	3.7%	48.1%	55.2%
2-Methyl-2-propylpentanoic acid	0.5%	6.3%	7.2%
2,2-Diethylpentanoic acid	0.2%	3.0%	3.5%
2,2,5-Trimethylhexanoic acid	2.1%	1.1%	0.8%
2,2,4-Trimethylhexanoic acid	2.0%	1.0%	0.8%
2,4-Dimethyl-2-ethylpentanoic acid	4.4%	2.2%	1.6%
2,2,3-Trimethylhexanoic acid	6.4%	3.2%	2.4%
2-Methyl-2-isopropylpentanoic acid	13.7%	6.9%	5.1%
2,3-Dimethyl-2-ethylpentanoic acid	37.5%	19.0%	13.8%
2-Ethyl-2-isopropylbutanoic acid	3.0%	1.5%	1.1%
Other unknown acids	25.8%	1.2%	1.3%

Examples 7 to 9

The mixtures of tertiary carboxylic acids obtained in Examples 4 to 6 were reacted with acetylene at atmospheric pressure and a temperature of 190-220°C in the presence of the zinc salt of the acid to be reacted in each case, in accordance with the equation.



The reaction was carried out as described by G. Hübner, *Fette, Seifen, Anstrichmittel*, 68 (4), pp. 290-292 (1966).

Distillation of the crude product gave vinyl esters having a purity of $\geq 99.8\%$; these have, according to gas-chromatographic analysis, a degree of branching essentially comparable to or even the same as that of the carboxylic acids. The vinyl esters obtained in this way are referred to in the following as vinyl ester A (based on acid A, Example 7), vinyl ester B

(based on acid B, Example 8) and vinyl ester C (based on acid C, Example 9).

Examples 10 to 14

The vinyl esters of Examples 7 to 9 were used to prepare homopolymers by the standard method (Examples 12-14) and their glass transition temperature was determined as a measure of their suitability as copolymers for internal plasticization.

Starting materials

Monomer	Parts by weight
Vinyl esters of the C ₈ -carboxylic acids	100.00
Aqueous phase	
Deionized water	70.00
Anionic surfactant, e.g. Marlon® A 390 (85% active content)	0.03
Nonionic surfactant, e.g. Marlophen® 820 (25% strength solution)	8.00
Potassium peroxodisulfate (K ₂ S ₂ O ₈)	0.10
Potassium carbonate	0.25
Hydroxyethylcellulose, e.g. Natrosol 250 L (or LR)	2.00
Acetic acid (100%)	0.20
Initiator solution	
Potassium peroxodisulfate	0.23
Deionized water	12.00

Procedure

The aqueous phase and about 10% of the monomer were heated while stirring to 75°C. After 15 minutes at this temperature, the remaining monomer and the initiator solution were metered in as separate streams. The addition of the monomer was carried out uniformly over a period of 120 minutes and that of the initiator solution was carried out over a period of 135 minutes. During the metered addition, the temperature was held at

from 75 to 80°C. After stirring for a further 120 minutes at the same temperature, the mixture was cooled to room temperature. Shaped bodies were produced from the resulting emulsion, if appropriate after filtration, and the glass transition temperatures of these were determined by torsional oscillation analysis (method based on DIN 53445).

In addition, two commercial vinyl esters whose glass transition temperature is known were subjected to the same procedure in order to ensure comparability of the test procedure. These were a vinyl ester of tertiary C₁₀ acids (VeoVa®10, Based on tripropene, Comparative Example 10), which is widely used as internal plasticizer for, for example, vinyl acetate, and a commercial vinyl ester of tertiary C₉ acids (VeoVa®9, Comparative Example 11), i.e. a vinyl ester having the same empirical formula as but a different degree of branching than the vinyl esters prepared as described in the above examples.

The following data were measured:

	Example 10	Example 11	Example 12	Example 13	Example 14
Starting material	(comparison)	(comparison)	from acid A	from acid B	from acid C
Glass transition temperature	-3°C	~ +60°C	~ +38°C	+1°C	-3°C

Vinyl ester A based on butene oligomerized in the presence of an acid catalyst is thus a hardening comonomer. Vinyl ester B from butene oligomerized by the Dimersol process has become a plasticizing comonomer. Vinyl ester C prepared from dibutene from the Octol process achieves an excellent plasticizing action; it is the equal of the comparative product based on tripropene (Comparative Example 10). The comparison of Example 11 with Example 14 is worthy of comment. In both cases, use was made of vinyl esters of tertiary carboxylic acids having 9 carbon

atoms, i.e. the same empirical formula. The vinyl ester of Example 14 prepared according to the invention gave an excellent plasticizing action, while Comparative Example 11 is a comonomer having a pronounced hardening action.

Example 15

Raffinate III was oligomerized by the Octol process (see Example 3). The tributene was separated off from the oligomerization product and a C₁₃-carboxylic acid mixture was prepared by the Koch synthesis (analogous to Examples 4-6). This mixture was, as described in Examples 7-9, reacted with acetylene to form the corresponding vinyl esters. The vinyl ester mixture obtained in this way was used to prepare a homopolymer by a method analogous to that of Examples 10 to 14; its glass transition temperature is -13°C. The vinyl ester of the C₁₃-carboxylic acid based on tributene thus has an extremely good plasticizing action despite its high degree of branching.

Claims:

1. A process for preparing vinyl esters from butene oligomers, which comprises
 - a) oligomerizing butenes,
 - b) separating off the butene oligomers from the oligomerization product,
 - c) converting the butene oligomers into carboxylic acids having one more carbon atom and
 - d) converting the carboxylic acids into the corresponding vinyl esters.
2. A process as claimed in claim 1,
wherein
the butene oligomers are converted into carboxylic acids having one more carbon atom by acid-catalyzed hydrocarboxylation.
3. A process as claimed in claim 1,
wherein
the butene oligomers are converted into carboxylic acids having one more carbon atom by hydroformylation and subsequent oxidation of the resulting aldehydes.
4. A process as claimed in any of claims 1 to 3,
wherein
the vinyl esters are obtained by reacting the carboxylic acids with acetylene.
5. A process as claimed in claim 4,
wherein
the vinyl esters are obtained by reacting the carboxylic acids with acetylene in the presence of a zinc salt of the carboxylic acid.



6. A process as claimed in any of claims 1 to 3,
wherein
the vinyl esters are obtained by transesterification of further vinyl
esters with the carboxylic acids.
7. A process as claimed in claim 6,
wherein
the further vinyl esters are vinyl acetate or vinyl propionate.
8. A process as claimed in any of claims 1 to 7,
wherein
the butene oligomers are dibutenes which are converted into C₈-
carboxylic acids and the corresponding vinyl esters.
9. A process as claimed in any of claims 1 to 8,
wherein
the butene oligomers are tributenes which are converted into C₁₃-
carboxylic acids and the corresponding vinyl esters.
10. A process as claimed in any of claims 1 to 8,
wherein
the dibutenes contain not more than 35% by weight of multiply
branched olefins.
11. A process as claimed in claim 10,
wherein
the dibutenes contain not more than 25% by weight of multiply
branched olefins.
12. The use of the vinyl esters prepared as claimed in any of claims 1 to
11 as comonomers in polymerization reactions.



13. The use of the vinyl esters prepared as claimed in any of claims 1 to 11 as plasticizers.

