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(71) Applicants: **ROHM AND HAAS COMPANY** [US/US]; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US). **DOW GLOBAL TECHNOLOGIES LLC** [US/US]; 2211 H.H. Dow Way, Midland, Michigan 48674 (US).

(72) Inventors: **SATHIOSATHAM, Muhunthan**; 400 Arcola Road, Collegeville, Pennsylvania 19426 (US). **MENDOZA, Joy L.**; 1900 Tidal Road, Deer Park, Texas 77536 (US). **DAUGS, Edward D.**; 2788 N. Tupelo Drive, Midland, Michigan 48642 (US).

(74) Agent: **MUTSCHLER, Brian**; The Dow Chemical Company, P.O. Box 1967, Midland, Michigan 48674 (US).

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(54) Title: TRANSESTERIFICATION CATALYSIS BY UNNEUTRALIZED POLY ALKOXYLATES

(57) Abstract: A process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprises providing an unneutralized poly alkoxylated alcohol, wherein the unneutralized poly alkoxylated alcohol was produced by base-catalyzed alkoxylation. An alkyl (meth)acrylate is transesterified with the unneutralized poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol. No transesterification catalyst is added during the step of transesterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol.

TRANSESTERIFICATION CATALYSIS BY UNNEUTRALIZED POLY ALKOXYLATES

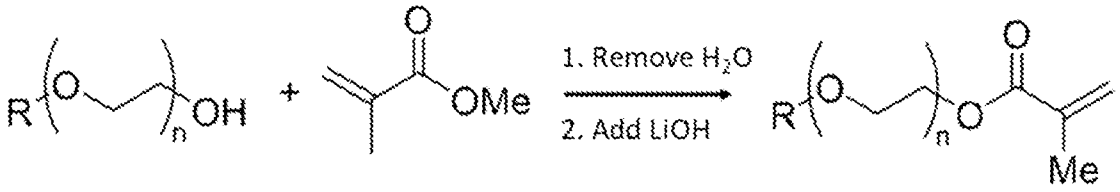
FIELD OF THE INVENTION

This invention relates generally to transesterification catalysis by unneutralized poly alkoxylates.

BACKGROUND

(Meth)acrylate monomers of polyethoxylated or poly alkoxylated alcohols are typically synthesized via either direct esterification or transesterification.

A common method for producing (meth)acrylate monomers of polyethoxylated or poly alkoxylated alcohols is transesterification of the polyethoxylated or poly alkoxylated alcohols with an alkyl (meth)acrylate using a transesterification catalyst such as lithium hydroxide (LiOH) or tetraethylhexyl titanate. Typically, the poly alkoxylated alcohol is mixed with the alkyl (meth)acrylate and then dehydrated, after which a transesterification catalyst (e.g., LiOH)is added to form the (meth)acrylate monomer of the poly alkoxylated alcohol.



Polyethoxylated or poly alkoxylated alcohols are typically synthesized by base-catalyzed ethoxylation of fatty alcohols. Commonly used base catalysts include sodium hydroxide (NaOH) and potassium hydroxide (KOH). These ethoxylation or alkoxylation reactions are terminated by neutralization by acids such as acetic acid or phosphoric acid.

It has been discovered that acid neutralization of polyethoxylated or poly alkoxylated alcohols can quench the transesterification catalyst LiOH and result in production irregularities. Other hydroxides such as NaOH and KOH have not been found to provide any appreciable conversions under similar transesterification conditions used for LiOH-catalyzed transesterification reactions to produce (meth)acrylate monomers of polyethoxylated or poly alkoxylated alcohols.

With the rapidly increasing costs of lithium-based catalysts, there is a need for an improved process for producing (meth)acrylate monomers of polyethoxylated or poly alkoxylated alcohols. The present invention solves one or more of the problems associated with conventional processes for producing (meth)acrylate monomers of polyethoxylated or poly alkoxylated alcohols.

SUMMARY OF THE INVENTION

One aspect of the invention provides a process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol. The process comprises providing an unneutralized poly alkoxylated alcohol, wherein the unneutralized poly alkoxylated alcohol was produced by base-catalyzed alkoxylation, and transesterifying an alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol. No transesterification catalyst is added during the step of esterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol.

Another aspect of the invention provides a process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprising reacting an alkyl alcohol with an epoxide in the presence of a base catalyst to form a poly alkoxylated alcohol of formula (I)

$$R(OR^1)_nOH \qquad (I)$$

wherein R is an alkyl group comprising 8 to 24 carbon atom, R^1 is an alkenyl group comprising 2 to 4 carbon atoms, and n ranges from 10 to 30. An alkyl (meth)acrylate is transesterified with the poly alkoxylated alcohol to produce the (meth)acrylate monomer of the poly alkoxylated alcohol. The poly alkoxylated alcohol is not neutralized prior to transesterifying the alkyl (meth)acrylate with the poly alkoxylated alcohol.

DETAILED DESCRIPTION

The inventors have surprisingly found that (meth)acrylate monomers of poly alkoxylated alcohols can be prepared by directly transesterifying an alkyl (meth)acrylate with an unneutralized poly alkoxylated alcohol that has been prepared by base-catalyzed alkoxylation. This discovery is significant because it allows the transesterification to be performed without adding any additional transesterification catalyst, without the use of expensive lithium hydroxide catalyst, and/or at a faster rate than traditional lithium hydroxide-catalyzed transesterification reactions.

As used herein, the term "(meth)acrylate" refers to either acrylate or methacrylate or combinations thereof. As used herein, the term "substituted" refers to having at least one attached chemical group, for example, alkyl group, alkenyl group, vinyl group, hydroxyl group, carboxylic acid group, other functional groups, and combinations thereof.

The present invention relates to processes for producing a (meth)acrylate monomer of a poly alkoxylated alcohol.

On aspect of the invention relates to a process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprising providing an unneutralized poly alkoxylated alcohol,

wherein the unneutralized poly alkoxylated alcohol was produced by base-catalyzed alkoxylation, and transesterifying an alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol.

The base-catalyzed alkoxylation reaction preferably uses a base catalyst selected from sodium hydroxide (NaOH) and potassium hydroxide (KOH). The base catalyst is still present in the unneutralized poly alkoxylated alcohol when the alkyl (meth)acrylate is transesterified with the poly alkoxylated alcohol. The inventors have surprisingly discovered that the base catalyst remaining from the alkoxylation reaction is sufficient to catalyze the subsequent transesterification reaction. This outcome is particularly surprising because NaOH and KOH do not typically produce appreciable conversions when used according to conventional transesterification reactions of alkyl (meth)acrylates and poly alkoxylated alcohols catalyzed by lithium hydroxide (LiOH). Other transesterification reactions, such as the production of biodiesel, may use sodium hydroxide or potassium hydroxide as a transesterification catalyst. However, these transesterifications use a solvent, such as methanol, that increases the solubility of the catalyst and allows them to effectively catalyze the reaction. Preferably, no additional solvent, such as methanol or other solvent that increases the solubility of the transesterification catalyst, is added to the reaction in the inventive process.

No transesterification catalyst is added during the step of transesterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol. The transesterification reaction is catalyzed solely by the residual base catalyst used for the alkoxylation reaction.

Preferably, the unneutralized poly alkoxylated alcohol comprises a compound of formula (I):

$$R(OR^1)_nOH \qquad (I)$$

in which R is an alkyl group comprising 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms. R^1 is an alkenyl group comprising 2 to 4 carbon atoms, preferably 2 or 3 carbon atoms (i.e., an ethylenyl or propenyl group), and more preferably 2 carbon atoms (i.e., an ethylenyl group). The variable n ranges from 10 to 30, preferably from 15 to 25.

Examples of poly alkoxylated alcohols include cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, lauryl alcohol ethoxylate, and combinations thereof (e.g., cetyl stearyl alcohol ethoxylate).

The alkyl (meth)acrylate is preferably methyl methacrylate or methyl acrylate. More preferably, the alkyl (meth)acrylate is methyl methacrylate.

The alkyl (meth)acrylate is preferably added to the reaction mixture in a molar excess with respect to the poly alkoxylated alcohol. Preferably, the molar ratio of alkyl (meth)acrylate to the poly alkoxylated alcohol is at greater than 1:1, more preferably at least 1.5:1, and even more preferably at least 2:1.

A polymerization inhibitor may be added with the alkyl (meth)acrylate to prevent unwanted polymerization. Suitable polymerization inhibitors are known in the art. For example, 4-hydroxy-TEMPO (4-HT), monomethyl ether hydroquinone (MeHQ), or phenothiazine (PTZ) may be used as a polymerization inhibitor.

The transesterification reaction may take place at a temperature ranging from 100 to 140 °C, preferably from 110 to 130 °C. The transesterification reaction is preferably conducted at sub-atmospheric pressure.

When the poly alkoxylated alcohol is prepared at a different site or substantially before the transesterification reaction occurs (e.g., at least an hour prior to the transesterification reaction), the poly alkoxylated alcohol can be maintained at an elevated temperature.

Another aspect of the present invention relates to a process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprising reacting an alkyl alcohol with an epoxide in the presence of a base catalyst to form a poly alkoxylated alcohol. An alkyl (meth)acrylate is transesterified with the poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol. The poly alkoxylated alcohol is not neutralized prior to transesterifying an alkyl (meth)acrylate with the poly alkoxylated alcohol.

Preferably, the poly alkoxylated alcohol is a compound of formula (I):

$$R(OR^1)_nOH \qquad (I)$$

in which R is an alkyl group comprising 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms; R^1 is an alkenyl group comprising 2 to 4 carbon atoms, preferably 2 or 3 carbon atoms, and more preferably 2 carbon atoms; and n ranges from 10 to 30, preferably from 15 to 25.

Some embodiments of the invention will now be described in detail in the following Examples.

EXAMPLES

Inventive Example

To a 1000 ml four-necked flask fitted with a stirrer, thermometer, 10-tray distillation head, and a reflux splitter was added unneutralized cetyl stearyl alcohol ethoxylate (CSA-20, 277.9 g, 0.224 mol), methyl methacrylate (MMA, 149.7 g, 1.49 mol), and polymerization inhibitor 4-HT (0.1 g 0.6 mmol). The reaction mixture was heated to the setpoint of 120 °C under reduced pressure (550 mmHg). The vapor temperature varied between 57 °C and 63 °C. The reflux/distillation splitter was set at 70/30 and the distillate was collected over 2 hours. The amount of MMA/MeOH distillate collected was 13 ml/8.9 g. The ^{1}H-NMR analysis of the

reaction mixture after 1h and 2 h revealed 90 and 99% conversion of the cetyl stearyl alcohol ethoxylate.

Excess MMA was distilled off at 200 mmHg to 1 mmHg and the resulting mixture was diluted with 85 g of GMAA and 43 g of water.

Comparative Example #1

To a 1000 ml four-necked flask fitted with a stirrer, thermometer, 10-tray distillation head, and a reflux splitter was added neutralized cetyl stearyl alcohol ethoxylate (CSA-20 acquired from BASF, 278.1 g, 0.224 mol), methyl methacrylate (MMA, 149.5 g, 1.49 mol), and polymerization inhibitor 4-HT (0.25 g). The resulting mixture was dehydrated by distilling off 30 g of MMA under a 550 mmHg vacuum and 105 °C reactor temperature. After the dehydration contents were cooled down and NaOH (0.2 g, 0.005 mol) was added. The resulting mixture was heated to the setpoint of 115 °C under reduced pressure of 550 mm Hg.

After 1 hour of heating at 109 °C, the vapor temperature remained above 90 °C indicating no MeOH generation. The lack of MeOH generation indicates that no transesterification occurred.

Comparative Example #2

To a 1000 ml four-necked flask fitted with a stirrer, thermometer, 10-tray distillation head, and a reflux splitter was added neutralized cetyl stearyl alcohol ethoxylate (CSA-20 from BASF, 278.1 g, 0.224 mol), methyl methacrylate (MMA, 180 g, 1.8 mol), and polymerization inhibitor 4-HT (0.25 g). The resulting mixture was dehydrated by distilling off 29 g of MMA under a 550 mmHg vacuum and 105 °C reactor temperature. After the dehydration contents were

cooled down and LiOH (0.205 g, 0.005 mol) was added. The resulting mixture was heated to the setpoint of 115 °C under reduced pressure of 550 mm Hg. The vapor temperature varied between 57 °C and 60 °C. The reflux/distillation splitter was set at 70/30 and the distillate was collected over three hours, at this point vapor temperature started to rise and reached 65 °C. The amount of MMA/MeOH distillate collected was 14 ml/11.1 g. The ^{1}H-NMR analysis of the reaction mixture revealed a 99% conversion of MACOL alcohol.

Excess MMA was distilled off at 200 mmHg to 1 mmHg and the resulting mixture was diluted with 85 g of GMAA and 43 g of water.

A comparison of the Inventive Example and Comparative Example #1 surprisingly shows that the no additional catalyst was required to conduct the transesterification reaction. The examples further shows that NaOH was incapable of catalyzing the transesterification reaction (Comparative Example #1) using the same reaction conditions as Comparative Example #2, which used LiOH as the transesterification catalyst. A comparison of the Inventive Example and Comparative Example #2 surprisingly shows that even without adding a separate transesterification catalyst, the Inventive Example was able to complete the transesterification reaction faster than using the convention LiOH transesterification catalyst.

WHAT IS CLAIMED IS:

1. A process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprising:

providing an unneutralized poly alkoxylated alcohol, wherein the unneutralized poly alkoxylated alcohol was produced by base-catalyzed alkoxylation; and

transesterifying an alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol;

wherein no transesterification catalyst is added during the step of transesterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol.

2. The process of claim 1, wherein the step of transesterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol is catalyzed by residual base catalyst present in the unneutralized poly alkoxylated alcohol.

3. The process of claim 2, wherein the residual base catalyst present in the unneutralized poly alkoxylated alcohol is selected from sodium hydroxide and potassium hydroxide.

4. The process of any one of the preceding claims, the unneutralized poly alkoxylated alcohol comprises a compound of formula (I)

$$R(OR^1)_nOH \qquad (I)$$

wherein:

R is an alkyl group comprising 8 to 24 carbon atoms;

R^1 is an alkenyl group comprising 2 to 4 carbon atoms; and

n ranges from 10 to 30.

5. The process of claim 4, wherein R is an alkyl group comprising 10 to 20 carbon atoms.

6. The process of claim 5, wherein R is an alkyl group comprising 12 to 16 carbon atoms.

7. The process of claim 4, wherein R^1 is an ethylenyl or propenyl group.

8. The process of claim 7, wherein R^1 is an ethylenyl group.

9. The process of claim 4, wherein n ranges from 15 to 25.

10. The process of claim 1, wherein the unneutralized poly alkoxylated alcohol is selected from cetyl alcohol ethoxylate, stearyl alcohol ethoxylate, lauryl alcohol ethoxylate, and combinations thereof.

11. The process of any one of the preceding claims, wherein the unneutralized poly alkoxylated alcohol comprises base catalyst from the base-catalyzed alkoxylation.

12. The process of claim 11, wherein the base catalyst comprises sodium hydroxide or potassium hydroxide.

13. The process of any one of the preceding claims, wherein the alkyl (meth)acrylate is methyl methacrylate.

14. The process of any one of the preceding claims, wherein a polymerization inhibitor is added during the step of transesterifying the alkyl (meth)acrylate with the unneutralized poly alkoxylated alcohol.

15. A process for producing a (meth)acrylate monomer of a poly alkoxylated alcohol comprising:

reacting an alkyl alcohol with an epoxide in the presence of a base catalyst to form a poly alkoxylated alcohol of formula (I)

$$R(OR^1)_nOH \qquad (I)$$

wherein:

R is an alkyl group comprising 8 to 24 carbon atoms;

R^1 is an alkenyl group comprising 2 to 4 carbon atoms; and

n ranges from 10 to 30; and

transesterifying an alkyl (meth)acrylate with the poly alkoxylated alcohol to produce the (meth)acrylate monomer of a poly alkoxylated alcohol.

wherein the poly alkoxylated alcohol is not neutralized prior to transesterifying an alkyl (meth)acrylate with the poly alkoxylated alcohol.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/054867

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G65/332
ADD.

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)
C08G

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 902 017 A1 (ROHM & HAAS [US]) 17 March 1999 (1999-03-17) claims 1-4 example 6	1-15
A	US 2015/232409 A1 (MISSKE ANDREA [DE] ET AL) 20 August 2015 (2015-08-20) claims 1-19 examples 5-6	1-15
A	US 7 687 596 B2 (BASF AG) 30 March 2010 (2010-03-30) examples 1,4 claims 1-4	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 February 2025	25/02/2025

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Mensah, Laure

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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