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(54) Synthesis of acrylic or methacrylic acid/acrylate or methacrylate ester polymers using pervaporation

Synthese von Acryl- oder Methacrylsäure bzw. Acrylat- oder Methacrylatesterpolymeren mithilfe von Pervaporation

Synthèse d'acide/acrylate méthacrylique ou acrylique ou polymères d'ester méthacrylate utilisant la pervaporation

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Description

[0001] The present invention relates to the synthesis of copolymers or terpolymers of acrylic or methacrylic acid and acrylate or methacrylate ester by esterification of polyacrylic or polymethacrylic acid with various alcohols assisted by the pervaporation technique.

Background of the invention

[0002] Acrylic and methacrylic acid and their esters are perhaps some of the most versatile monomers for improving performance characteristics of thousands of polymer and copolymer formulations. Major markets for copolymers of acrylic or methacrylic acid with acrylic or methacrylic esters include the fields of surface coatings, dispersions, textiles, adhesives, paper and plastics. Acrylic acid/acrylate ester copolymers are considered as non-toxic.

[0003] The copolymerization of acrylic or methacrylic acid is generally known. The formation of copolymers from monomers is known to be a non-economic method. This is due to the cost of acrylic and methacrylic esters. On the other hand, the production of these copolymers by usual methods, such as esterification of polyacrylic or polymethacrylic acid with alcohol, is known to be based on an equilibrium reaction.

[0004] A major problem in the esterification of polyacrylic or methacrylic acid is removing water from the reaction mixture during its production due to the presence of an azeotropic water-alcohol mixture. Sometimes the boiling points of alcohol and water are very close and sometimes some crosslinking reaction occurs at high temperature. The extraction of water from the reaction mixture using a traditional technique such as distillation is a non-economical method.

[0005] The synthesis of acrylic or methacrylic acid/acrylate or methacrylate ester copolymers directly from their corresponding monomer acids after esterification shows several problems.

[0006] A major problem in the esterification of acrylic or methacrylic acid is the high tendency of these monomers to polymerize owing to their reactive double bonds. This is true in particular, if the acrylic or methacrylic acid is exposed to relatively high temperatures, *cf.* for example WO 97/37962. In their preparation purified ester compounds are exposed to temperatures which can readily trigger polymerization and can lead to polymer formation. This results in soiling the apparatus, pump, coating of column trays and heat exchanger surfaces (fouling). Cleaning is complicated, expensive and presents environmental problems, *cf.* DE 10 67 806 A. In addition, availability is greatly reduced thereby.

[0007] As a rule, polymerization inhibitors (phenothiazine or *p*-methoxyphenol) [1], i.e. compounds which are capable of substantially suppressing radical polymerization, are therefore added for stabilization. For using acrylates or methacrylates, however, the polymerization inhibitors have to be separated off. In the preparation of high-boiling point compounds which cannot be purified by distillation, it is possible to use only inhibitors which can be extracted by another method, for example by extraction, filtration or adsorption, or which do not interfere with processing. Thus, DE 28 38 691 A describes the use of Cu(I) oxide as an inhibitor. The Cu(I) can be removed by extraction. WO 90/07487 describes the use of hydroquinone addition with the active esterification mixture. The active carbon, which is filtered off after the esterification, is added in order to avoid discoloration of the ester due to the hydroquinone. US Patent 6,726,854 discloses the use of phosphites, such as triethyl phosphate, as a polymerization inhibitor.

[0008] EP-71239 describes one pot preparation of an alcoholic soln. of a copolymer of an unsatd. monocarboxylic acid (I) and ester from a reaction mixture. containing. (I), the ester and a lower aliphatic monohydric alcohol comprises (a) concurrently forming the ester and copolymer in the presence of water in the lower alcohol containing. an acid esterification catalyst and a free radical polymerisation initiator at the reflux temp. of the reaction mixt., (b) removing water until a predetermined amount of ester is formed by distillation and (c) recovering an alcoholic soln. of the copolymer.

[0009] US-2006/0009589 describes a process of preparing partial (meth)acrylic esters of dihydric polyalcohols (C) containing different hydroxyl groups comprising subjecting alternatively polyalcohols having primary hydroxyl group(s) and/or secondary hydroxyl group(s) and/or tertiary hydroxyl group to esterification with (meth)acrylic acid or to transesterification with (meth)acrylic ester(s) in the presence of enzyme(s).

[0010] Various acrylic esters are useful chemicals [2]. Esterification of acrylic acid with alcohol has commercially been performed by using liquid catalysts such as sulfuric acid, hydrofluoric acid, and para-toluenesulfonic acid; but these are toxic, corrosive and often hard to remove from the reaction solution [3-5].

[0011] The esterification of acrylic or methacrylic acid is generally effected in a reactor to which a distillation condenser is attached. The said column serves to remove water from the reactor in form of a mixture with the solvent. Mostly used reactors are stirred reactors with double-wall. Their disadvantage here is that the stirrers frequently need to be repaired and polymer is readily accumulated. Moreover, the reactor size is subject to limits because of the specific wall area available for heating with increasing reactor size.

[0012] Thus, it is an object of the present invention to provide an improved method for the synthesis of acrylic or methacrylic acid/acrylate or methacrylate ester copolymers or terpolymers.

Summary of the invention

[0013] The object of the present invention is solved by a process for the production of a copolymer, preferably a poly(acrylic acid-co-acrylate ester) or a poly(methacrylic acid-co-methacrylate ester), or a terpolymer, preferably a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)) comprising:

(a) esterifying a polyacrylic or polymethacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst; and
(b) extracting water produced in (a) through a membrane.

[0014] In one embodiment, the process is a process for the production of a poly(acrylic acid-co-acrylate ester) copolymer or a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) terpolymer comprising:

(a) esterifying a polyacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst; and
(b) extracting water produced in (a) through a membrane.

[0015] In one embodiment, the process is a process for the production of a poly(methacrylic acid-co-methacrylate ester) copolymer or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)) terpolymer comprising:

(a) esterifying a polymethacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst; and
(b) extracting water produced in (a) through a membrane.

[0016] In one embodiment, the process for the production of a poly(acrylic acid-co-acrylate ester) copolymer or a poly(methacrylic acid-co-methacrylate ester) copolymer comprises esterifying with one alcohol.

[0017] In one embodiment, the process for the production of a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) terpolymer or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)) terpolymer comprises esterifying with two alcohols.

[0018] In one embodiment, polyacrylic acid is esterified with benzylacohol resulting in a copolymer.

[0019] In one embodiment, polyacrylic acid is esterified with benzylalcohol and cyclohexanol resulting in a terpolymer.

[0020] In one embodiment, the acid, preferably sulfuric acid, is used in excess.

[0021] In one embodiment, the membrane is water selective.

[0022] In one embodiment, the water extracted through the membrane is trapped under liquid nitrogen.

[0023] In one embodiment, the membrane is a non-porous, dense membrane.

[0024] In one embodiment, the membrane is used in a pervaporation technique, i.e. the process comprises the step of extracting water produced during the esterification reaction using a pervaporation technique.

[0025] In one embodiment, the polyacrylic or polymethacrylic acid consists of more than three monomers, i.e. the molecular weight of polyacrylic or polymethacrylic acid is above trimer.

[0026] In one embodiment, the polyacrylic acid and the polymethacrylic acid which constitute the principal reactive components in this invention have a low molecular weight. This hydrosoluble polymer dissolves in appropriate amounts of alcohol employed as solvent and reactant simultaneously.

[0027] In one embodiment, the molecular weight of the polyacrylic or polymethacrylic acid is in the range of 400-10,000 g/mol.

[0028] In one embodiment, the alcohol used in this invention is liquid, little viscous and dehydrated to more than 98 %.

[0029] In one embodiment, the alcohol is selected from the group comprising an aliphatic and aromatic alcohol, preferably comprising methanol, ethanol, propanol, butanol, pentanol, *iso*-butanol, *tert*-butanol, cyclohexanol, and benzylalcohol.

[0030] In one embodiment, the polyacrylic or polymethacrylic acid/alcohol solutions include molar fractions which depend on comonomers ratio in copolymers or terpolymers.

[0031] In one embodiment, the membrane comprises or is made of polyvinylalcohol modified and crosslinked with a crosslinking agent at 2-6 weight-%, preferably at 2-5 weight-%, using dif ferent techniques.

[0032] In one embodiment, the membrane has a thickness of about 5-200 μm, preferably of about 22-55 μm, most preferably of about 25 μm.

[0033] In one embodiment, the copolymer or terpolymer is produced by esterifying an acidic site (i.e. a carboxyl group) of the polyacrylic acid with one or more alcohols.

[0034] In one embodiment, the copolymer or terpolymer is produced by esterifying an acidic site (i.e. a carboxyl group) of the polymethacrylic acid with one or more alkanols.

[0035] In one embodiment, the step of esterifying is carried out at a temperature in the range of about 30°C to about 80°C.

[0036] In one embodiment, the alcohol is used both as the reaction partner in the esterification reaction and as a solvent of the polyacrylic or polymethacrylic acid.

[0037] In one embodiment, the conversion of esterification is controlled during removing water from the reaction, e.g. for the production of copolymers or terpolymers at controlled compositions.

[0038] In one embodiment, the copolymer or terpolymer is isolated from the alcohol by precipitation, preferably in petroleum ether.

[0039] In one embodiment, the copolymer is a poly(acrylic acid-co-alkyl acrylic ester) or a poly(methacrylic acid-co-alkyl methacrylic ester).

[0040] In one embodiment, the terpolymer is a poly(acrylic acid-co-alkyl acrylate(I)-co-alkyl acrylate(II)) or a poly(methacrylic acid-co-alkyl acrylate(I)-co-alkyl methacrylate(II)).

[0041] The object of the present invention is further solved by a use of a membrane in the production of a copolymer, preferably a poly(acrylic acid-co-acrylate ester) or a poly(methacrylic acid-co-methacrylate ester), or a terpolymer, preferably a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)), for extracting water produced during esterification of polyacrylic or polymethacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst.

[0042] In one embodiment, the use is a use of a membrane in the production of a poly(acrylic acid-co-acrylate ester) copolymer or a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) terpolymer for extracting water produced during esterification of polyacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst.

[0043] In one embodiment, the use is a use of a membrane in the production of a poly(methacrylic acid-co-methacrylate ester) copolymer or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)) terpolymer for extracting water produced during esterification of polymethacrylic acid with one or two alcohols in the presence of an acid as a catalyst, preferably of a least amount of an acid as a catalyst.

[0044] In one embodiment of the use, the membrane is a non-porous, dense membrane.

[0045] In one embodiment of the use, the membrane is used in a pervaporation technique, i.e. the use is a use of a pervaporation technique in the production of the copolymer or terpolymer.

[0046] In one embodiment of the use, the membrane comprises or is made of polyvinylalcohol modified and crosslinked with a crosslinking agent at 2-6 weight-%, preferably at 2-5 weight-%, using different techniques.

[0047] In one embodiment of the use, the membrane has a thickness of about 5-200 μm, preferably of about 22-55 μm, most preferably of about 25 μm.

[0048] The present invention relates to a method for producing acrylic or methacrylic acid/acrylate or methacrylate ester copolymers or terpolymers by esterification of polyacrylic acid or polymethacrylic acid with several alcohols (aliphatics and aromatics) using the pervaporation technique. The reaction mixtures were fixed at their optimum temperature by circulation of water via an external thermostat. The water produced by the reaction is extracted selectively during its formation through an adequate membrane. The method according to the invention allows for the production of copolymers or terpolymers at controlled compositions (0-87 mol-%). The pervaporation apparatus employed in this invention is similar to that used by different authors, such as Bing Cao et al. [6].

[0049] The starting material in the process for the production of a copolymer or terpolymer is polyacrylic or polymethacrylic acid which is reacted with a variety of alcohols in order to manipulate the type of alkyl group and also the type of ester.

[0050] As an example, the process is a modification of polyacrylic or polymethacrylic acid to convert them to a copolymer of one of the following:

(1) category of copoly(acrylic acid - alkyl acrylate), where the alkyl group is changeable; or
(2) category of copoly(methacrylic acid - methacrylic esters), where the ester can be varied.

[0051] Pervaporation is an energy efficient and highly selective extraction process for the extraction of volatile products and for the dehydratation of organic chemicals [7]. The productivity and conversion rate can be significantly increased when the reaction is coupled with pervaporation, i. e., a pervaporation reactor. Techno-economic studies revealed that pervaporation reactors have good market potential in process industries.

[0052] The combination of an esterification reaction of polyacrylic or polymethacrylic acid with a pervaporation process increases the conversion of reversible reactions, such as esterification, by removing selectively the water formed from the reacting mixture. Thus, the yield of the conversion is greatly enhanced.

[0053] An esterification reaction between an alcanol and a carboxylic acid in the presence of a catalyst is a reversible reaction, and a high industrial conversion can be achieved by adding a large excess of acid. A water selective pervaporation membrane can be used in the esterification reactor. This can shift the equilibrium to the right, thus reducing excess reactants.

[0054] The composition of acrylic or methacrylic ester comonomers can be easily controlled during the removal of water from the reaction by a kinetic of extraction. The high rate of comonomer ester in the copolymers (87 %) is favored by the selective extraction of water during its production.

[0055] Thus, the production of copolymers (acrylic or methacrylic acid/acrylate or methacrylate ester) at different compositions by esterification assisted by a pervaporation technique can be a competitive method. This method is economic (energy saving) and clean (without addition of a tiers component or catalysts to the reaction mixture).

Detailed description of the invention

[0056] The present invention will now be described more specifically with reference to the following examples. It is to be noted that the following explanations are presented herein for the purposes of illustration and description only; they are not intended to be exhaustive or to limit the invention to the precise form disclosed or claimed.

[0057] A reaction of copolymerization is shown below:

$$\text{-}[CH_2\text{-}CHOH]_n\text{-} + mR\text{-}OH \rightarrow \text{-}[CH_2\text{-}CHOH]_{n'}\text{-}[CH_2\text{-}CHOOR]_{m'}\text{-} + m'H_2O + m''R\text{-}OH$$

$n=n'+m'$ and $m=m'+m''$

[0058] A reaction of terpolymerization is shown below:

$$\text{-}[CH_2\text{-}CHCO_2H]_n\text{-} + mR\text{-}OH + pR'\text{-}OH \rightarrow \text{-}[CH_2\text{-}CHCO_2H]_{n'}\text{-}[CH_2\text{-}CHOOR]_{m'}\text{-}[CH_2\text{-}CHOOR']_{p'}\text{-} + (m'+p')H_2O + m''R\text{-}OH + p''R'\text{-}OH$$

$N = n' + m'$, $m = m' + m''$ and $p = p' + p''$

[0059] The preferred process embodied in this invention utilizes the polyacrylic or polymethacrylic acid with low molecular weights (400-10,000 g/mol) which may be esterfied using one or more of the series of liquid alcohols. It is preferable to add to the reaction mixture some drops of sulfuric acid as a catalyst.

[0060] Concerning the lower alcanol such as methanol, ethanol, propanol, pentanol, isopropanol, and butanol, it is preferable to add this reactant in excess to compensate for the amount of risk which accompanies the water during its extraction in addition to its role as a solvent in which esterification is carried out.

[0061] Concerning viscous or higher alcohols a raising of temperature is necessary for increasing the kinetics of the reaction.

[0062] For example, the conditions of exemplary reactions are illustrated in Tables 1 to 3 below.

Table 1. Conditions of poly(acrylic acid-co-acrylic ester) synthesis

Alcohol* (mol)	Polyacrylic acid (mol)	Time (hr)	Copolymer (acrylic acid/alkylacrylate) composition (mol-%)
0.20 - 0.30	0.012 - 0.01	1 - 1.3	15 - 28
0.20 - 0.30	0.012 - 0.01	3 - 3.5	22 - 37
0.20 - 0.30	0.012 - 0.01	5 - 6	37 - 54
0.20 - 0.30	0.012 - 0.01	7 - 8	64 - 72
0.20 - 0.30	0.012 - 0.01	18 - 20	82 - 87
* Alcohol: methanol; ethanol; propanol; *iso*-propanol; butanol; *iso*-butanol; cyclohexanol; benzylalcohol			

Table 2. Condition of poly(methacrylic acid-co-alkylmethacrylic ester) synthesis

Alcohol* (mol)	Polymethacrylic acid (mol)	Time (hr)	Copolymer (methacrylic acid/alkylmethacrylate) composition (mol-%)
0.13 - 0.20	0.012 - 0.010	1 - 1.3	12 - 25
0.13 - 0.20	0.012 - 0.010	3 - 3.5	18 - 29
0.13 - 0.20	0.012 - 0.010	5 - 6	32 - 44
0.13 - 0.20	0.012 - 0.010	7 - 8	58 - 63

(continued)

Alcohol* (mol)	Polymethacrylic acid (mol)	Time (hr)	Copolymer (methacrylic acid/alkylmethacrylate) composition (mol-%)
0.13 - 0.20	0.012 - 0.010	18 - 20	72 - 82
* Alcohol: methanol; ethanol; propanol; *iso*-propanol; butanol; *iso*-butanol; cycloheaxanol; benzylalcohol			

Table 3. Conditions of poly(acrylic acid-co-alkylacrylate(I)-co-alkylacrylate(II)) synthesis

Alcohol* (I)/ alcohol(II) (mol/mol)	Polyacrylic acid (mol)	Time (hr)	Terpolymer (acrylic acid/alkylacrylate(I)/alkylacrylate(II)) composition (mol-%)
0.07/0.07	0.01 - 0.008	1 - 1.3	(57/34/05) - 42/28/30
0.07/0.07	0.01 - 0.008	3 - 3.5	(41/38/21) - 34/32/34
0.07/0.07	0.01 - 0.008	5 - 6	(32/45/23) - 28/47/25
0.07/0.07	0.01 - 0.008	7 - 8	(27/52/21) - 19/67/14
0.07/0.07	0.01 - 0.008	18 - 20	(14/62/24) - 12/72/16
* Alcohol: methanol; ethanol; propanol; *iso*-propanol; butanol; *iso*-butanol; cyclohexanol; benzylalcohol			

[0063] The copolymers or terpolymers obtained at the end of the reaction were isolated by precipitation in excess of petroleum ether.

[0064] The membrane used in this process is confectioned in polyvinylalcohol (PVA), physically crosslinked. The crosslinked film produced was dried under vacuum at 30-70 °C for several hours. The thickness of each membrane was about 5-200 μm.

[0065] The pervaporation apparatus used in this work is similar to that reported in the literature and comprises the following parts: stainless steel pervaporation cell; pervaporation pyrex-made receiving set filled with vapor traps; primary vacuum pump.

[0066] The different runs were carried out at a temperature in the range of 30-80 °C. The reaction mixture was in contact with the membrane for over 24 hr to reach a steady state before starting the experiment. Different runs were at least in duplicate and the results were quite reproducible.

[0067] In addition to the previous parameters of the PVA, its crystallinity degree was found to be 20-30%.

[0068] The swelling performance of PVA membrane with different constituents of the esterification reaction can be deduced from the curves (swelling degree versus time at temperatures of 30-50 °C). The result shows a strong affinity between water and PVA, whereas swelling in alcohol is very weak for the lower alcohol and very weak or nil for the higher alcohol.

[0069] The conversion of the reaction varies with time and temperature, for example is 80-87% after 6-7 hr at 40-50 °C.

EXAMPLE 1: Preparation of a copolymer of acrylic acid and acrylate ester having an acid number 15 and benzylalcohol as raw materials.

[0070] About 0.10 mol (100 g) of polyacrylic acid containing 1.5 mol of acrylic acid units corresponds to 1.5 mol (162 g) of benzylalcohol for esterifying 100% of acrylic acid in main chains. Thus, after 18 hr of reaction assisted by pervaporation a maximum of 87% acid units in main chains have been esterified.

[0071] The pervaporation apparatus employed in the present invention was previously described by Bing Cao et al. [6].

[0072] Accordingly, 100 g of polyacrylic acid is introduced into the pervaporation cell containing initially 162 g of benzylalcohol and 3 drops of 10^{-1} N aqueous solution of sulfuric acid. It is preferable to add the benzylalcohol in excess to compensate the amount which risk to be accompanied by water during its extraction. The reaction mixture was fixed at 50 °C and stirred using a magnetic stirrer. The thickness of the membrane was estimated to be 25 μm.

[0073] The structure of copo(acrylic acid/benzylacrylate) at different compositions is confirmed by IR, NMR and DSC analysis.

EXAMPLE 2: Preparation of a terpolymer of acrylic acid, cyclohexylacrylate and benzylacrylate esters from polyacrylic acid, cyclohexylalcohol and benzylalcohol.

[0074] A solution containing about 100 g of polyacrylic acid, 162 g of benzylalcohol and 150 g of cyclohexanol is introduced into the pervaporation cell. 3 or 4 drops of an aqueous solution of sulfuric acid were added to the mixture. An alcohol was added in excess to compensate for the amount which risk accompanies the water during its extraction and is also considered as solvent in which the esterification is carried out. The mixture was stirred using a magnetic stirrer. Thus, after 18 hr of reaction assisted by pervaporation we achieved a maximum of 82% esterification of acid units in main chains distributed statistically. The composition of terpolymers obtained in different units depends on the composition of the initial mixture, the reaction time and the temperature of the reaction.

[0075] The structure of terpolymers is confirmed by IR, NMR and DSC analysis.

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[0076]

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Claims

1. A process for the production of a copolymer, preferably a poly(acrylic acid-co-acrylate ester) or a poly(methacrylic acid-co-methacrylate ester), or a terpolymer, preferably a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)) comprising:

(a) esterifying a polyacrylic or polymethacrylic acid with one or two alcohols in the presence of a least amount of an acid as a catalyst; and
(b) extracting water produced in (a) through a membrane.

2. The process according to claim 1, further comprising:

(c) trapping the water extracted in (b) under liquid nitrogen.

3. The process according to claim 1 or 2, wherein the membrane is a non-porous, dense membrane.

4. The process according to any of claims 1 to 3, wherein the membrane is used in a pervaporation technique.

5. The process according to any of the preceding claims, wherein the polyacrylic or polymethacrylic acid consists of more than three monomers.

6. The process according to any of the preceding claims, wherein the molecular weight of the polyacrylic or polymethacrylic acid is in the range of 400-10,000 g/mol.

7. The process according to any of the preceding claims, wherein the alcohol is selected from the group comprising an aliphatic and aromatic alcohol, preferably comprising methanol, ethanol, propanol, butanol, pentanol, *iso*-butanol, *tert*-butanol, cyclohexanol, and benzylalcohol.

8. The process according to any of the preceding claims, wherein the membrane comprises polyvinylalcohol modified and crosslinked with a crosslinking agent at 2-6 weight-%, preferably at 2-5 weight-%.

9. The process according to any of the preceding claims, wherein the membrane has a thickness of 5-200 μm, preferably of 22-55 μm, most preferably of 25 μm.

10. The process according to any of the preceding claims, wherein the esterification in (a) is carried out at a temperature in the range of 30°C to 80°C.

11. The process according to any of the preceding claims, wherein the conversion of esterification is controlled during removing water from the reaction.

12. The process according to any of the preceding claims, wherein the copolymer or terpolymer is isolated from the alcohol by precipitation.

13. A use of a membrane in the production of a copolymer, preferably a poly(acrylic acid-co-acrylate ester) or a poly(methacrylic acid-co-methacrylate ester), or a terpolymer, preferably a poly(acrylic acid-co-acrylate ester(I)-co-acrylate ester(II)) or a poly(methacrylic acid-co-methacrylate ester(I)-co-methacrylate ester(II)), for extracting water produced during esterification of polyacrylic or polymethacrylic acid with one or two alcohols in the presence of a least amount of an acid as a catalyst.

14. The use according to claim 13, wherein the membrane is a non-porous, dense membrane.

15. The use according to claim 13 or 14, wherein the membrane is used in a pervaporation technique.

16. The use according to any of claims 13 to 15, wherein the membrane comprises polyvinylalcohol modified and crosslinked with a crosslinking agent at 2-6 weight-%, preferably at 2-5 weight-%.

17. The use according to any of claims 13 to 16, wherein the membrane has a thickness of 5-200 μm, preferably of 22-55 μm, most preferably of 25 μm.

Patentansprüche

1. Verfahren für die Herstellung eines Copolymers, bevorzugt eines Poly(acrylsäure-co-acrylatesters) oder eines Poly(methacrylsäure-co-methacrylatesters), oder eines Terpolymer, bevorzugt eines Poly(acrylsäure-co-acrylatesters(I)-co-acrylatester(II)) oder eines Poly(methacrylsäure-co-methacrylatester(I)-co-methacrylatesters(II)), welches umfasst:

(a) Veresterung einer Polyacryl- oder Polymethacrylsäure mit einem oder zwei Alkoholen in der Gegenwart einer geringsten Menge einer Säure als einen Katalysator; und
(b) Extrahieren von in (a) erzeugtem Wasser durch eine Membran.

2. Verfahren nach Anspruch 1, weiter umfassend:

(c) Einfangen des in (b) extrahierten Wassers unter flüssigem Stickstoff.

3. Verfahren nach Anspruch 1 oder 2, wobei die Membran eine nicht-poröse, dichte Membran ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, wobei die Membran in einer Pervaporationsmethode verwendet wird.

5. Verfahren nach einem der vorangehenden Ansprüche, wobei die Polyacryl- oder Polymethyacrylsäure aus mehr als drei Monomeren besteht.

6. Verfahren nach einem der vorangehenden Ansprüche, wobei das Molekulargewicht der Polyacryl- oder Polymethacrylsäure in einem Bereich von 400-10.000 g/Mol ist.

7. Verfahren nach einem der vorangehenden Ansprüche, wobei der Alkohol ausgewählt wird aus der Gruppe umfassend einen aliphatischen und aromatischen Alkohol, bevorzugt umfassend Methanol, Ethanol, Propanol, Butanol, Pentanol, iso-Butanol, tert-Butanol, Cyclohexanol und Benzylalkohol.

8. Verfahren nach einem der vorangehenden Ansprüche, wobei die Membran Polyvinylalkohol umfasst, der modifiziert ist und mit einem Vernetzungsmittel bei 2-6 Gewichtsprozent, bevorzugt 2-5 Gewichtsprozent, vernetzt ist.

9. Verfahren nach einem der vorangehenden Ansprüche, wobei die Membran eine Dicke von 5-200 µm, bevorzugt 22-55 µm, noch bevorzugter 25 µm aufweist.

10. Verfahren nach einem der vorangehenden Ansprüche, wobei die Veresterung in (a) bei einer Temperatur im Bereich von 30°C bis 80°C durchgeführt wird.

11. Verfahren nach einem der vorangehenden Ansprüche, wobei die Umsetzung der Veresterung während eines Entfernens von Wasser aus der Reaktion gesteuert wird.

12. Verfahren nach einem der vorangehenden Ansprüche, wobei das Copolymer oder Terpolymer von dem Alkohol durch Ausfällung isoliert wird.

13. Verwendung einer Membran in der Herstellung eines Copolymers, bevorzugt eines Poly(acrylsäure-co-acrylatesters) oder eines Poly(methacrylsäure-co-methacrylatesters), oder eines Terpolymers, bevorzugt eines Poly(acrylsäure-co-acrylatester(I)-co-acrylatcsters(II)) oder eines Poly(methacrylsäure-co-methacrylatester(I)-co-methaerylatester(II)), zum Extrahieren von Wasser, das während einer Veresterung von Polyacryl- oder Polymethacrylsäure mit einem oder zwei Alkoholen in der Gegenwart einer geringsten Menge einer Säure als einen Katalysator erzeugt wird.

14. Verwendung nach Anspruch 13, wobei Membran eine nicht-poröse, dichte Membran ist.

15. Verwendung nach Anspruch 13 oder 14, wobei die Membran in einer Pervaporationsmethode verwendet wird.

16. Verwendung nach einem der Ansprüche 13 bis 15, wobei die Membran Polyvinylalkohol umfasst, der modifiziert ist und mit einem Vernetzungsmittel bei 2-6 Gewichtsprozent, bevorzugt 2-5 Gewichtsprozent, vernetzt ist.

17. Verwendung nach einem der Ansprüche 13 bis 16, wobei die Membran eine Dicke von 5-200 µm, bevorzugt 22-55 µm, am bevorzugtesten 25 µm, aufweist.

Revendications

1. Procédé de production d’un copolymère, préférablement d’un poly(acide acrylique-co-ester d’acrylate) ou d’un poly(acide méthacrylique-co-ester de méthacrylate), ou d’un terpolymère, préférablement d’un polylacide acrylique-co-ester d’acrylate (I)-co-ester d’acrylate (II)] ou d’un poly[acide méthacrylique-co-ester de méthacrylate (I)-co-ester de méthacrylate (II)], comprenant :

(a) l’estérification d’un acide polyacrylique ou polyméthacrylique avec un ou deux alcools en la présence d’une quantité minimale d’un acide servant de catalyseur ; et
(b) l’extraction de l’eau produite en (a) au travers d’une membrane.

2. Procédé selon la revendication 1, qui comprend également ;

(c) le piégeage de l’eau extraite en (b) sous azote liquide.

3. Procédé selon la revendication 1 ou 2, dans lequel la membrane est une membrane dense non poreuse.

4. Procédé selon l’une quelconque des revendications 1 à 3, dans lequel la membrane est utilisée dans une technique de pervaporation.

5. Procédé selon l’une quelconque des revendications précédentes, dans lequel l’acide polyacrylique ou polyméthacrylique consiste en plus de trois monomères.

6. Procédé selon l’une quelconque des revendications précédentes, dans lequel le poids moléculaire de l’acide polyacrylique ou polyméthacrylique est dans la plage de 400-10 000 g/mol.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'alcool est sélectionné dans le groupe comprenant un alcool aliphatique et aromatique, et comprenant préférablement le méthanol, l'éthanol, le propanol, le butanol, le pentanol, l'*iso*-butanol, le *tert*-butanol, le cyclohexanol et l'alcool benzylique.

8. Procédé selon l'une quelconque des revendications précédentes, dans lequel la membrane comprend un alcool polyvinylique modifié et réticulé avec un agent de réticulation à un taux de 2-6 % en poids, préférablement de 2-5 % en poids.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel la membrane a une épaisseur de 5-200 μm, préférablement de 22-55 μm et plus préférablement de 25 μm.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'estérification de l'étape (a) est effectuée à une température dans la plage de 30 °C à 80 °C.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel la conversion par estérificatian est contrôlée durant l'élimination de l'eau de la réaction.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le copolymère ou le terpolymère est isolé de l'alcool par précipitation.

13. Utilisation d'une membrane dans la production d'un copolymère, préférablement d'un poly(acide acrylique-co-ester d'acrylate) ou d'un poly(acide méthacrylique-co-ester de méthacrylate), ou d'un terpolymère, préférablement d'un poly[acide acrylique-co-ester d'acrylate (I)-co-ester d'acrylate (II)] ou d'un poly[acide méthacrylique-co-ester de méthacrylate (I)-co-ester de méthacrylate (II)], pour l'extraction de l'eau produite durant l'estérification de l'acide polyacrylique ou polyméthacrylique avec un ou deux alcools en la présence d'une quantité minimale d'un acide servant de catalyseur.

14. Utilisation selon la revendication 13, dans laquelle la membrane est une membrane dense non poreuse.

15. Utilisation selon la revendication 13 ou 14, dans laquelle la membrane est utilisée dans une technique de pervaporation.

16. Utilisation selon l'une quelconque des revendications 13 à 15, dans laquelle la membrane comprend un alcool polyvinylique modifié et réticulé avec un agent de réticulation à un taux de 2-6 % en poids, préférablement de 2-5 % en poids.

17. Utilisation selon l'une quelconque des revendications 13 à 16, dans laquelle la membrane a une épaisseur de 5-200 μm, préférablement de 22-55 μm et plus préférablement de 25 μm.

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