Claims

1. A controlled process for the preparation of polymers comprising at least the steps of

a) preparing an active first liquid medium comprising at least one polymerisation catalyst or at least one polymerisation initiator

b) contacting in a polymerization reactor

- a volume of a feed stream of said active first liquid medium comprising V1 at least one polymerisation catalyst or at least one polymerisation initiator

with

- a volume of a feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer V2

to form a reaction medium and polymerizing the at least one polymerizable monomer within the reaction medium to form a product medium comprising a polymer,

whereby

- the feed streams V1 and V2 employed in step b)

are controlled by at least the steps

i) measuring at least one spectrum of the active first liquid medium

ii) determining the specific activity ($a_{specific}$) of the active first liquid medium using a predictive model

iii) determining a desired volume ratio of the active first liquid medium V1 and the second liquid medium V2 necessary to obtain a desired ratio of total activity a_{Total} (= $a_{specific}$ x V1) and the amount of monomer M contained in V2, said ratio hereinafter being referred to as $R_{desired}$

iv) controlling

either

- the volume V1 of a active first liquid medium or
- the volume V2 of the feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer
- or both volumes V1 and V2 of the feed streams

entering the polymerization reactior in such a manner, that the volume ratio of V1 and V2 at least converges to $R_{desired}$

or

- the volume V1 of a active first liquid medium or
- the volume V2 of the feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer
- or both volumes V1 and V2 of the feed streams

and

- the preparation conditions of the active first liquid medium

and optionally

- the amount of monomer M within the second liquid medium

or alternatively

- the preparation conditions of the active first liquid medium

or alternatively

- the amount of monomer M within the second liquid medium

and whereby the predictive model was generated by a process comprising at least the steps of

A) measuring spectra for a plurality of active liquid media having different activity

B) determining the specific activity ($a_{specific}$) for said plurality of active liquid media by their employment in a polymerisation reaction with known volumes V1 and V2 and a known amount of the at least one monomer M and analysis of the polymer formed thereby, whereby said polymerisation reaction proceeds substantially via the same mechanism as the polymerisation in step b)

C) correlating the spectra of the active liquid media measured in step A) with their specific activity ($a_{specific}$) determined in step B).

2. A method to control the feed streams of a process for the production of polymers comprising the contacting of a feed stream of an active liquid medium comprising an polymerization initiator or catalyst and a second liquid medium comprising an amount M of at least one polymerizable monomer within a polymerization reactor, the process comprising at least the steps of

1) measuring at least one spectrum of an active liquid medium comprising an initiator or catalyst to be employed in the polymerization process

2) determining the specific activity ($a_{specific}$) of the active liquid medium using a predictive model

3) controlling the volume or the volume flow rate of the feed stream of the active liquid medium or of a second liquid medium comprising an amount M of at least one polymerizable monomer and optionally or alternatively, preferably optionally, the preparation conditions of the active first liquid medium or optionally or alternatively, preferably optionally, the amount M of monomer present in the second liquid medium

whereby the predictive model was generated by a process comprising at least the steps of

A) measuring spectra for a plurality of active liquid media having different activity

B) determining the specific activity ($a_{specific}$) for said plurality of active liquid media by their employment in a polymerisation and analysis of the polymer formed thereby, whereby said polymerisation reaction proceeds substantially via the same mechanism as the polymerisation for which the feed stream of the active liquid medium is intended to be used

C) correlating the spectra of the active liquid media measured in step A) with their specific activity ($a_{specific}$) determined in step B).

3. The process according to claim 1 or the method according to claim 2, wherein the active liquid medium comprises at least one polymerisation initiator or polymerisation catalyst and an organic solvent.

4. The process or method according to claim 3, wherein the polymerisation initiator is selected from cationic initiators.

5. The process or method according to claim 4, wherein the cationic initiators are selected from

- reaction products of
  - at least one lewis acid or at least one organometal compound or a mixture of lewis acids and organometal compounds and
  - at least one proton source
- carbocationic compounds of formula (I)

$[CR^1R^2R^3]^+ An^-$ (I)

wherein R^1, R^2 and R^3 are independently hydrogen, C_1-C_{20}-alkyl or C_5-C_{20}-aryl with the proviso that either one or none of R^1, R^2 and R^3 is hydrogen and

An^- denotes a monoanion or 1/p equivalent of a p-valent anion

or

- silylium compounds of formula (II)

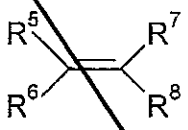
$[SiR^1R^2R^3]^+ An^-$ (II)

wherein R^1, R^2 and R^3 and An^- have the same meaning as set forth above for formula (I)

- or mixtures of the aforementioned compounds and reaction products

6. The process or method according to claim 3 or 4, wherein the organic solvent is selected from C_2-C_{20} alkanes and C_1-C_{20} haloalkanes and mixtures thereof.

7. The process according to one of the claims 1 or 3 to 6 or the method according to one of the claims 2 to 6 wherein the polymerizable monomers are those of formula (IV):



(IV)

wherein

R^5, R^6, R^7 and R^8 are independently of one another selected from the group consisting of:

C_1-C_{18}-alkoxy, C_1-C_{18}-alkyl, C_2-C_{18}-alkenyl, C_2-C_{18}-alkinyl,

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting of:

-O-, -CO-, -OCO-, -O(CO)O-, $NR^4(CO)$-, $-NR^9(CO)O$-, $-O(CO)NR^9$, $-(CO)NR^9$-, $-NR^9(CO)NR^9$-, $-Si(R^{10})_2$-, $-OSi(R^{10})_2$-, $-OSi(R^{10})_2O$-, $-Si(R^{10})_2O$-

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{15}-heterocyclo-diyl and C_6-C_{14}-aryldiyl,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, epoxy, C_6-C_{14}-aryl; C_3-C_{15}-heterocyclyl, C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, C_2-C_8-alkenyl, C_4-C_{15}-arylalkyl, hydroxy, $-SO_2N(R^9)_2$, NR^4SO_2-R^{10}, $-N(R^9)_2$, $-CO_2N(R^{10})_2$,

$-COR^9$, $-OCOR^9$, $-O(CO)OR^9$, $NR^9(CO)R^{10}$, $-NR^9(CO)OR^{10}$, $O(CO)N(R^9)_2$, $-NR^4(CO)N(R^9)_2$, $-OSi(OR^{10})_{y-3}(R^{10})_y$, $-Si(OR^{10})_{(y-3)}(R^{10})_y$ where y is 1, 2 or 3.

8. The process according to one of the claims 1 or 3 to 7 or the method according to one of the claims 2 to 7 wherein the second liquid media comprises a mixture of from 70.0 to 99.5 wt.-% of a C_4-C_{16} monoolefin and of from 0.5 to 30.0 wt.-% of a C_4-C_{16} monoolefin of at least one conjugated C_4-C_{16} multiolefin.

9. The process according to one of the claims 1 or 3 to 8 or the method according to one of the claims 2 to 8 wherein the second liquid media comprises a mixture of from 92.0 to 99.0 wt.-% of a C_4-C_{16} monoolefin and of from 1.0 to 8.0 of a C_4-C_{16} monoolefin of at least one conjugated C_4-C_{16} multiolefin.

10. The process according to one of the claims 1 or 3 to 9 or the method according to one of the claims 2 to 9 wherein the second liquid media comprises a mixture of from 90.0 to 98.5 wt.-% of isobutene and of from 1.0 to 8.0 of isoprene and of from 0.5 to 9 wt.-% of a monomer selected from the group consisting of 2-, 3- or 4-methylstyrene, styrene, 2-, 3- or 4-chlorostyrene, p-methoxystyrene, cyclopentadiene, methylcyclopentadiene, indene.

11. The process according to one of the claims 1 or 3 to 10 or the method according to one of the claims 2 to 10 wherein the second liquid media comprises a mixture of from 91.0 to 98.5 wt.-% of isobutene and of from 1.0 to 8.0 of isoprene and of from 0.5 to 3 wt.-% of at least one non-conjugated C_4-C_{16} multiolefin.

12. The process according to one of the claims 1 or 3 to 11 or the method according to one of the claims 2 to 11 wherein the second liquid media comprising an amount M of at least one polymerizable monomer comprises of from 0,1 to 100,0 wt.-% of at least one polymerizable monomer.

13. The process according to one of the claims 1 or 3 to 12 wherein step b) is carried out continuously.

14. The process according to one of the claims 1 or 3 to 13 wherein V1 and V2 refer to volume flow rates.

15. The process according to one of the claims 1 or 3 to 14 or the method according to one of the claims 2 to 12 wherein the measurement is made at-line or in-line.

16. The process according to one of the claims 1 or 3 to 15 or the method according to one of the claims 2 to 12 or 15 wherein the spectrum is a infrared spectrum.

17. The process according to one of the claims 1 or 3 to 16 or the method according to one of the claims 2 to 12 or 15 to 16 wherein the spectrum is measured using a fourier transform-infrared spectrometer (FT-IR).

18. The process according to one of the claims 1 or 3 to 17 or the method according to one of the claims 2 to 12 or 15 to 17 wherein the control the feed stream is effected by a valve or pump.

19. The process according to one of the claims 1 or 3 to 18 or the method according to one of the claims 2 to 12 or 15 to 18 wherein the correlation according to step C) includes either correlation of the whole spectrum measured for the active liquid media with their specific activity or the correlation of at least one part of the spectrum.

20. The process according to one of the claims 1 or 3 to 19 or the method according to one of the claims 2 to 12 and 15 to 19 wherein the predictive model is generated using Bruker Optics' OPUS software or GRAMS suite spectroscopy software of Thermo Scientific.

21. Use of the following IR-absorbances:

Al-Cl absorbance, Al-ethyl absorbances and absorbances of Al-O modes

in a controlled process for or a method to control the preparation of polymers, wherein reaction products of dialkylaluminum halides alkylaluminum dihalides or a mixture of the aforementioned organoaluminium compounds and a proton source are used as polymerization initiator.

22. A chemical plant comprising at least:

- a line (6a, 6b, 12a, 12b, 12c) equipped with a feed stream controller (7a, 7b,

7d, 7e, 12a, 12b, 12c) which is in communication with

- a polymerization reactor (9) which is in communication with said line
- a device, in particular a flow-through spectrometer (3) arranged to measure a spectrum of a feed stream in a loop (2) bypassing line (6a) or inline of line (6a)
- a computer (5) adapted to:
  - applying a predictive model to said spectrum or parts thereof in order to determine the specific activity of said feed stream of an active liquid medium and to
  - controlling the volume or the volume flow rate a feed stream intended to finally enter the polymerization reactor by controlling the feed stream controller (7a, 7b, 7c, 12a, 12b, 12c)
- a data link (4a) connecting said computer (5) with said device (3) to allow data transfer of the device (3) to the computer (5)
- a data link (4b, 4c, 4d, 4e, 4g, 4h, 4i) connecting said computer (5) with a feed stream controller (7a, 7b, 7d, 7e, 12a, 12b, 12c) to allow the control of said feed stream controller by said computer

and whereby the predictive model was generated by a process comprising at least the steps of

A) measuring spectra for a plurality of active liquid media having different activity

B) determining the specific activity ($a_{specific}$) for said plurality of active liquid media by their employment in a polymerisation reaction with known volumes V1 and V2 and a known amount of the at least one monomer M and analysis of the polymer formed thereby, whereby said polymerisation reaction proceeds substantially via the same mechanism as the polymerisation in step b)

C) correlating the spectra of the active liquid media measured in step A) with their specific activity ($a_{specific}$) determined in step B).

Claims

1. A controlled process for the preparation of polymers comprising at least the steps of

a) preparing an active first liquid medium comprising at least one polymerisation catalyst or at least one polymerisation initiator,

whereby the active first liquid medium comprises at least one polymerisation initiator and an organic solvent wherein the polymerisation initiator is selected from reaction products of

- at least one lewis acid or at least one organometal compound or a mixture of lewis acids and organometal compounds and

- at least one proton source

b) contacting in a polymerization reactor

- a volume of a feed stream of said active first liquid medium comprising V1 at least one polymerisation catalyst or at least one polymerisation initiator

with

- a volume of a feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer V2

to form a reaction medium and polymerizing the at least one polymerizable monomer within the reaction medium to form a product medium comprising a polymer,

whereby

- the feed streams V1 and V2 employed in step b)

are controlled by at least the steps

i) measuring at least one spectrum of the active first liquid medium wherein the spectrum is measured using a fourier-transform-infrared spectrometer (FT-IR)

ii) determining the specific activity ($a_{specific}$) of the active first liquid medium using a predictive model

iii) determining a desired volume ratio of the active first liquid medium V1 and the second liquid medium V2 necessary to obtain a desired ratio of total activity a_{Total} (= $a_{specific}$ x V1) and the amount of monomer M contained in V2, said ratio hereinafter being referred to as $R_{desired}$,

iv) controlling

either

- the volume V1 of the feed stream of a catalytically active first liquid medium or
- the volume V2 of the feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer
- or both volumes V1 and V2 of the feed streams

entering the polymerization reactor in such a manner, that the volume ratio of V1 and V2 at least converges to $R_{desired}$.

or

- the volume V1 of the feed stream of a catalytically active first liquid medium or
- the volume V2 of the feed stream of a second liquid medium comprising an amount M of at least one polymerizable monomer

and

- the preparation conditions of the active first liquid medium

and optionally

- the amount of monomer M within the second liquid medium

or alternatively

- the preparation conditions of the active first liquid medium

or alternatively

- the amount of monomer M within the second liquid medium

and whereby the predictive model was generated by a process comprising at least the steps of

A) measuring spectra for a plurality of active liquid media having different activity

B) determining the specific activity ($a_{specific}$) for said plurality of active liquid media by their employment in a polymerisation reaction with known volumes V1 and V2 and a known amount of the at least one monomer M and analysis of the polymer formed thereby, whereby said polymerisation reaction proceeds substantially via the same mechanism as the polymerisation in step b)

C) correlating the spectra of the active liquid media measured in step A) with their specific activity ($a_{specific}$) determined in step B).

2. A method to control the feed streams of a process for the production of polymers comprising the contacting of a feed stream of an active liquid medium comprising an polymerization initiator or catalyst and a second liquid medium comprising an amount M of at least one polymerizable monomer within a polymerization reactor, the process comprising at least the steps of

1) measuring at least one spectrum of an active liquid medium comprising an initiator or catalyst to be employed in the polymerization process

2) determining the specific activity ($a_{specific}$) of the active liquid medium using a predictive model

3) controlling the volume or the volume flow rate of the feed stream of the active liquid medium or of a second liquid medium comprising an amount M of at least one polymerizable monomer and optionally or alternatively,

preferably optionally, the preparation conditions of the active first liquid medium or optionally or alternatively, preferably optionally, the amount M of monomer present in the second liquid medium

whereby the predictive model was generated by a process comprising at least the steps of

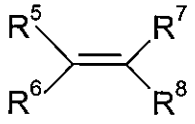
A) measuring spectra for a plurality of active liquid media having different activity

B) determining the specific activity ($a_{specific}$) for said plurality of active liquid media by their employment in a polymerisation and analysis of the polymer formed thereby, whereby said polymerisation reaction proceeds substantially via the same mechanism as the polymerisation for which the feed stream of the active liquid medium is intended to be used

C) correlating the spectra of the active liquid media measured in step A) with their specific activity ($a_{specific}$) determined in step B).

3. The process or method according to claim 1 or 2, wherein the organic solvent is selected from C_2-C_{20} alkanes and C_1-C_{20} haloalkanes and mixtures thereof.

4. The process according to one of the claims 1 or 3 or the method according to one of the claims 2 to 3 wherein the polymerizable monomers are those of formula (IV):



(IV)

wherein

R^5, R^6, R^7 and R^8 are independently of one another selected from the group consisting of:

C_1-C_{18}-alkoxy, C_1-C_{18}-alkyl, C_2-C_{18}-alkenyl, C_2-C_{18}-alkinyl,

which is either not, once, twice or more than twice interrupted by non-successive functional groups selected from the group consisting

of:

-O-, -CO-, -OCO-, -O(CO)O-, $NR^4(CO)$-, $-NR^9(CO)O$-, $-O(CO)NR^9$, $-(CO)NR^9$-, $-NR^9(CO)NR^9$-, $-Si(R^{10})_2$-, $-OSi(R^{10})_2$-, $-OSi(R^{10})_2O$-, $-Si(R^{10})_2O$-

and which is either not, once, twice or more than twice interrupted by bivalent residues selected from the group consisting of C_3-C_{15}-heterocyclo-diyl and C_6-C_{14}-aryldiyl,

and which is not, additionally or alternatively either once, twice or more than twice substituted by substituents selected from the group consisting of:

halogen, cyano, epoxy, C_6-C_{14}-aryl; C_3-C_{15}-heterocyclyl, C_1-C_8-alkyl, C_1-C_8-alkoxy, C_1-C_8-alkylthio, C_2-C_8-alkenyl, C_4-C_{15}-arylalkyl, hydroxy, $-SO_2N(R^9)_2$, NR^4SO_2-R^{10}, $-N(R^9)_2$, $-CO_2N(R^{10})_2$, $-COR^9$, $-OCOR^9$, $-O(CO)OR^9$, $NR^9(CO)R^{10}$, $-NR^9(CO)OR^{10}$, $O(CO)N(R^9)_2$, $-NR^4(CO)N(R^9)_2$, $-OSi(OR^{10})_{y-3}(R^{10})_y$, $-Si(OR^{10})_{(y-3)}(R^{10})_y$ where y is 1, 2 or 3.

5. The process according to one of the claims 1 or 3 to 4 or the method according to one of the claims 2 to 4 wherein the second liquid media comprises a mixture of from 70.0 to 99.5 wt.-% of a C_4-C_{16} monoolefin and of from 0.5 to 30.0 wt.-% of a C_4-C_{16} monoolefin of at least one conjugated C_4-C_{16} multiolefin.

6. The process according to one of the claims 1 or 3 to 5 or the method according to one of the claims 2 to 5 wherein the second liquid media comprises a mixture of from 92.0 to 99.0 wt.-% of a C_4-C_{16} monoolefin and of from 1.0 to 8.0 wt.-% of a C_4-C_{16} monoolefin of at least one conjugated C_4-C_{16} multiolefin.

7. The process according to one of the claims 1 or 3 to 6 or the method according to one of the claims 2 to 6 wherein the second liquid media comprises a mixture of from 90.0 to 98.5 wt.-% of isobutene and of from 1.0 to 8.0 wt.-% of isoprene and of from 0.5 to 9 wt.-% of a monomer selected from the group consisting of 2-, 3- or 4-methylstyrene, styrene, 2-, 3- or 4-chlorostyrene, p-methoxystyrene, cyclopentadiene, methylcyclopentadiene, indene.

8. The process according to one of the claims 1 or 3 to 7 or the method according to one of the claims 2 to 7 wherein the second liquid media comprises a mixture of from 91.0 to 98.5 wt.-% of isobutene and of from 1.0 to 8.0 wt.-% of isoprene and of from 0.5 to 3 wt.-% of at least one non-conjugated C_4-C_{16} multiolefin.

9. The process according to one of the claims 1 or 3 to 8 or the method according to one of the claims 2 to 8 wherein the second liquid media comprising an amount M of at least one polymerizable monomer comprises of from 0,1 to 100,0 wt.-% of at least one polymerizable monomer.

10. The process according to one of the claims 1 or 3 to 9 wherein step b) is carried out continuously.

11. The process according to claim 10 wherein V1 and V2 refer to volume flow rates.

12. The process according to one of the claims 1 or 3 to 11 or the method according to one of the claims 2 to 9 wherein the measurement is made at-line or in-line.

13. The process according to one of the claims 1 or 3 to 12 or the method according to one of the claims 2 to 9 or 12 wherein the control the feed stream is effected by a valve or pump.

14. The process according to one of the claims 1 or 3 to 13 or the method according to one of the claims 2 to 9 or 12 to 13 wherein the correlation according to step C) includes either correlation of the whole spectrum measured for the active liquid media with their specific activity or the correlation of at least one part of the spectrum.

15. The process according to one of the claims 1 or 3 to 14 or the method according to one of the claims 2 to 9 and 12 to 14 wherein the predictive model is generated using Bruker Optics' OPUS software or GRAMS suite spectroscopy software of Thermo Scientific.