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(54) Title: METHOD FOR THE CONTINUOUS PRODUCTION OF POLYBUTYLENE TEREPHTHALATE FROM TEREPHTHALIC ACID AND BUTANE DIOL

(54) Bezeichnung: VERFAHREN ZUR KONTINUIERLICHEN HERSTELLUNG VON POLYBUTYLEN-TEREPHTHALAT AUS TEREPHTHALSÄURE UND BUTANDIOL

(57) Abstract: The invention relates to a method for the continuous production of polybutylene terephthalate from terephthalic acid and 1,4-butane diol, comprising the following stages: a) direct esterification of terephthalic acid with 1,4-butane diol in a reactor cascade of at least two reactors b) pre-condensation of the esterification product obtained in stage a), c) polycondensation of the pre-condensate obtained in stage b), whereby the temperature of the reactor cascade in stage a) is progressively decreased during its operation.

(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur kontinuierlichen Herstellung von Polybutylenterephthalat aus Terephthalsäure und 1,4-Butandiol, umfassend d) direkte Veresterung von Terephthalsäure mit 1,4-Butandiol in einer Reaktorkaskade aus mindestens zwei Reaktoren, e) Vorkondensation des in Stufe a) erhaltenen Veresterungsproduktes, f) Polykondensation des in Stufe b) erhaltenen Vorkondensats, wobei die Reaktorkaskade in Stufe a) mit absteigender Temperaturführung betrieben wird.

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AS ORIGINALLY FILED

Continuous preparation of polybutylene terephthalate from terephthalic acid and butanediol

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The present invention relates to a process for the continuous preparation of polybutylene terephthalate (PBT) from terephthalic acid (TPA) and 1,4-butanediol (BDO).

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The preparation of polybutylene terephthalate from dimethyl terephthalate (DMT) and 1,4-butanediol is known from the prior art. A disadvantage of this process is that tetrahydrofuran (THF) formed in small amounts as by-product forms an azeotrope with the methanol liberated during the reaction and therefore can be recovered as a material of value only with great difficulty.

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The direct preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol is made difficult by the formation of relatively large amounts of THF, resulting in loss of 1,4-butanediol required for the reaction. Furthermore, not only THF but also 2,5-dihydrofuran (2,5-DHF) is formed from 1,4-butanediol. The 2,5-dihydrofuran is difficult to separate from THF and therefore contaminates and reduces the quality of the valuable product THF. A further problem in the direct preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol is that terephthalic acid is not soluble in 1,4-butanediol and goes into solution only during the esterification with 1,4-butanediol. However, to produce high quality polybutylene terephthalate, it is extremely important for this to be free of contaminants such as free acid groups from terephthalic acid. For this reason, the terephthalic acid should be completely esterified and dissolved before the actual polycondensation commences.

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Processes concerned with the direct preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol are already known from the prior art.

DD-A 269 296 relates to a continuous process for preparing polyalkylene terephthalates. Setting of appropriate reaction parameters in the esterification step of the dicarboxylic acid used with the glycol used is said to decisively favor removal of water from the esterification phase so that esterification products are
5 obtained both with a high degree of conversion and a high mean degree of polymerization. The esterification step is carried out in a reactor cascade in which the temperature is increased and the pressure is reduced from reactor to reactor. The example described relates to the preparation of polyethylene terephthalate from terephthalic acid and ethylene glycol.

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EP-A 0 431 977 describes a process for increasing the direct esterification rate of a diacid and 1,4-butanediol to esterification of > 95% of the acid groups. The process can be carried out continuously in three reactors. The process described comprises:

- 15 a) mixing 1,4-butanediol and diacid in a ratio of at least 2:1,
b) heating the reaction mixture to 180°C,
c) adding a suitable catalyst and
d) reacting the mixture at atmospheric pressure and a mean temperature in the range from 180 to 245°C for a maximum of 60 minutes.

20 In this process, less than 5% of the 1,4-butanediol is said to be cyclized to THF. However, the content of free acid groups in the end product is high.

EP-A 0 046 670 relates to a process for preparing polybutylene terephthalate by direct esterification of terephthalic acid and 1,4-butanediol. The process comprises
25 an esterification step at a temperature of up to 215°C and atmospheric pressure. After consumption of most of the terephthalic acid, at which stage, however, from 10 to 40% by weight of terephthalic acid is still present, i.e. before the clearing point, the polycondensation stage is carried out at a temperature higher than that in the esterification stage.

30

DE-A 27 11 331 describes the preparation of polyester oligomers by means of a two-stage esterification. Here, the first esterification stage is carried out at atmospheric pressure and the second esterification stage is carried out at atmospheric pressure or subatmospheric pressure, at a temperature of about 250°C
35 in both stages. However, the examples describe only the reaction of terephthalic acid with ethylene glycol.

DE-A 35 44 551 relates to the continuous preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol. The preparation is carried out in three stages. The first stage, namely the esterification, is carried out at from 225 to 260°C and a pressure of from 0.1 to 1 bar. The second stage, the precondensation, is carried out at from 230 to 260°C and a pressure of from 10 to 200 mbar, and the third stage, the polycondensation, is carried out at from 240 to 265°C and a pressure of from 0.25 to 25 mbar.

It is an object of the present invention to provide a process for preparing polybutylene terephthalate which is improved compared to the prior art. In particular, formation of THF from the 1,4-butanediol used should be as low as possible and the polybutylene terephthalate obtained should have a very low content of free acid groups.

The achievement of this object starts out from a process for the continuous preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol, comprising:

- a) direct esterification of terephthalic acid with 1,4-butanediol in a reactor cascade comprising at least two reactors,
- b) precondensation of the esterification product obtained in stage a), and
- c) polycondensation of the precondensate obtained in stage b).

In the process of the present invention, the temperature decreases along the reactor cascade in stage a).

The polybutylene terephthalate prepared according to the present invention is of excellent quality. It has a low content of acid and alcohol groups. The formation of THF and 2,5-DHF from 1,4-butanediol is low. As a result, only little 1,4-butanediol is lost, so that the yield of polybutylene terephthalate based on 1,4-butanediol is high.

a) Esterification stage

The stage a) is carried out in a reactor cascade comprising at least two reactors, preferably from two to five reactors, particularly preferably three reactors. The reactors used are generally stirred vessels.

The temperature range for the overall esterification stage is generally from 170 to 250°C, preferably from 180 to 240°C, particularly preferably from 190 to 230°C. According to the present invention, the temperature decreases along the reactor cascade, i.e. the esterification temperature drops from reactor to reactor. The temperature in an esterification reactor is generally from 2 to 30°C lower than that in the preceding reactor. The temperature preferably drops by from > 5 to 30°C from reactor to reactor. In a preferred embodiment, the reactor cascade comprises three reactors, and the temperature in reactor 1 (T1) is generally from 200 to 250°C, preferably from 210 to 240°C, particularly preferably from 218 to 230°C. The temperature in reactor 2 (T2) is generally from 190 to 230°C, preferably from 200 to 225°C, particularly preferably from 205 to 220°C, and the temperature in reactor 3 (T3) is generally from 170 to 220°C, preferably from 180 to 215°C, particularly preferably from 190 to 210°C, with the temperature dropping from reactor to reactor.

The residence times for the overall esterification stage are generally from 140 to 430 minutes, preferably from 160 to 420 minutes, particularly preferably from 170 to 390 minutes. In the case of a reactor cascade made up of three reactors, the residence time in the first reactor (V1) is generally from 100 to 250 minutes, preferably from 110 to 250 minutes, particularly preferably from 120 to 240 minutes, in the second reactor (V2) generally from 20 to 105 minutes, preferably from 30 to 100 minutes, particularly preferably from 30 to 90 minutes, and in the third reactor (V3) generally from 20 to 75 minutes, preferably from 20 to 70 minutes, particularly preferably from 20 to 60 minutes.

The esterification stage is generally carried out at a reaction pressure of not more than 1 bar. Preference is given to a pressure of < 1 bar. The experimental parameters pressure (p) and temperature (T) in the respective reactor particularly preferably lie within a plane defined by

$$p(\text{lower limit}) = 0.348 \times (T/^{\circ}\text{C})^2 - 124.12 \times (T/^{\circ}\text{C}) + 11121 \text{ and} \\ p(\text{upper limit}) = 0.0802 \times e^{(0.0405 \times (T/^{\circ}\text{C}))},$$

where the pressure does not increase from reactor to reactor. Very particularly preferably, the pressure drops continuously from reactor to reactor. In the case of a reactor cascade made up of three reactors, the pressure in the first reactor (p1) is

preferably from 650 to 900 mbar, in the second reactor (p2) preferably from 500 to 600 mbar and in the third reactor (p3) preferably from 350 to 500 mbar. The pressure difference between the individual reactors is generally at least 50 mbar, preferably from 50 to 400 mbar, particularly preferably from 100 to 300 mbar.

5

The preferred process conditions with a pressure of less than 1 bar suppress the formation of THF from 1,4-butanediol even more effectively. Furthermore, only very small amounts of 2,5-dihydrofuran (2,5-DHF), which arises as a further product from 1,4-butanediol, are formed. The 2,5-dihydrofuran is difficult to
10 separate from THF by distillation and therefore contaminates the valuable product THF and reduces its quality.

The esterification is generally carried out using a molar excess of 1,4-butanediol in order to push the ester equilibrium in the desired direction. The molar ratios of 1,4-
15 butanediol to terephthalic acid are generally from 1.1:1 to 3.5:1, preferably from 1.5:1 to 2.8:1, particularly preferably from 1.9:1 to 2.5:1.

In a preferred embodiment, a suspension comprising 1,4-butanediol and terephthalic acid in a molar ratio of generally $< 2:1$, preferably $< 1.5:1$, is placed in
20 a reservoir and diluted with hot 1,4-butanediol so as to heat it to from 50 to 100°C, preferably from 60 to 100°C, particularly preferably from 70 to 90°C, and give a ratio of 1,4-butanediol to terephthalic acid corresponding to the abovementioned final ratio.

25 An esterification catalyst, generally a Lewis acid metal compound, preferably of titanium or tin, is added to this BDO/TPA mixture. Particularly preferred esterification catalysts are tetrabutyl orthotitanate (TBOT), triisopropyl titanate and tin dioctoate, with very particular preference being given to tetrabutyl orthotitanate. The catalyst is generally used in the esterification stage in an amount
30 of < 200 ppm, preferably from 65 to 150 ppm, particularly preferably from 75 to 100 ppm, calculated as the metal of the esterification catalyst used and based on polybutylene terephthalate. All of the catalyst can be added to the first reactor. However, in a preferred embodiment only part of the catalyst, preferably
35 < 50 ppm, particularly preferably < 25 ppm, calculated as the metal and based on polybutylene terephthalate, is introduced into the first reactor and the remainder of the catalyst is introduced into the subsequent reactors, preferably into the second

reactor. The esterification catalyst is preferably introduced into the reactor as a mixture with 1,4-butanediol.

5 The reaction mixture comprising terephthalic acid, 1,4-butanediol and an esterification catalyst is reacted in a reactor cascade to a conversion of generally > 97%, preferably from 97 to 99%, based on terephthalic acid. If the esterification stage is carried out in a reactor cascade having three reactors, the esterification in the first reactor generally proceeds to a conversion (C1) of > 89%. The THF/water mixture formed is separated off and the reaction mixture is transferred to the
10 second reactor in which it is esterified to a conversion (C2) of generally > 95%. At this point in time, all of the terephthalic acid has generally reacted or gone into solution, which can be seen from a clear reaction mixture (clearing point). The reaction mixture is, to be safe, preferably transferred to a third reactor and esterified to a conversion (C3) of generally > 97%.

15 The reaction mixture obtained is subsequently fractionated continuously into the esterification product and a THF/BDO/water mixture. The THF/BDO/water mixture is fractionated in a column system and recovered 1,4-butanediol is returned to the first esterification reactor. The esterification product is transferred
20 continuously to the precondensation stage.

b) Precondensation stage

25 The precondensation stage generally has at least two, preferably at least three, particularly preferably at least four, temperature zones. The temperature of a zone is generally from 1 to 25°C, preferably from 1 to 15°C, particularly preferably from 1 to 10°C, higher than the temperature of the preceding zone. The temperature range for the overall precondensation is generally from 220 to 300°C, preferably from 225 to 290°C, particularly preferably from 230 to 260°C.

30 In general, the precondensation is carried out in a pressure range from 0.05 bar to the esterification pressure in the last reactor of the reactor cascade of the esterification stage. It is preferably carried out so that the pressure in the first zone corresponds to the reaction pressure in the last esterification reactor, and in the
35 following zones is generally from 20 to 500 mbar, preferably from 25 to 450 mbar, particularly preferably from 30 to 400 mbar, with the pressure preferably dropping from one zone to the following zone.

The precondensation stage is preferably carried out in an ascending tube reactor.

5 The residence times for the overall stage b) of the process are generally from 10 to 80 minutes, preferably from 15 to 70 minutes, particularly preferably from 30 to 60 minutes. In a particularly preferred embodiment, the precondensation is carried out in four temperature zones, with the temperature rising slightly from zone to zone in the above-described ratios and the pressure being reduced from the first to the fourth zone within the limits described. In this preferred embodiment, the fourth
10 zone comprises an apparatus for separating vapor and liquid phases. In this zone, excess 1,4-butanediol, THF and water are separated from the precondensate.

The catalysts mentioned for the esterification stage of the process of the present invention can likewise be introduced in the amounts specified into the precondensation stage.
15

After the precondensation b), the precondensate has a viscosity number of generally from 5 to 50 ml/g, preferably from 20 to 50 ml/g, measured as a 0.5% strength by weight solution in phenol/o-dichlorobenzene (1:1) in accordance with
20 DIN 53728, Part 3 (1985), at 25°C.

The precondensate is subsequently transferred to the polycondensation reactor (stage c)).

25 **c) Polycondensation stage**

Stage c) is generally carried out in a single zone at temperatures of generally from 240 to 290°C, preferably from 240 to 270°C, particularly preferably from 240 to 265°C. The pressure is generally from 0.2 to 20 mbar, preferably from 0.3 to 10
30 mbar.

The residence times are usually from 30 to 180 minutes, preferably from 35 to 150 minutes.

35 During the polycondensation, a renewal of the surface of the product is preferably carried out. Renewal of the surface means that new polymer is continually brought to the surface of the melt so as to aid exit of the diol. This is preferably from 1 to

20 m²/kg of product and minute, particularly preferably from 1.5 to 6 m²/kg of product and minute.

5 In general, no further catalyst is added in the polycondensation stage, but it is also possible to add a catalyst, for example a catalyst as described above, in this stage of the process, too.

10 After the continuous polycondensation, the polyester generally has a viscosity number of from 60 to 180 ml/g, preferably from 90 to 160 ml/g, determined in a 0.5% strength by weight solution in a phenol/o-dichlorobenzene mixture (weight ratio = 1:1, at 25°C) in accordance with DIN 53728, Part 3 (1985).

15 In the polycondensation stage of the process of the present invention, lubricants and nucleating agents are preferably added together to the polymer melt when the viscosity number has reached at least 80%, preferably at least 95%, particularly preferably 100%, of the desired final viscosity number of the polyester, and the melt is, if desired, post-condensed and subsequently discharged, cooled and granulated. The lubricant is preferably added in an amount of generally from 0.01 to 3% by weight, preferably from 0.1 to 1% by weight, particularly preferably from 20 0.2 to 0.8% by weight, and the nucleating agent is added in an amount of generally from 0.001 to 2% by weight, preferably from 0.01 to 1% by weight, particularly preferably from 0.03 to 0.5% by weight, in each case based on 100% by weight of polybutylene terephthalate.

25 The addition is particularly preferably in the form of a suspension, with the nucleating agent being suspended in the lubricant, if desired at elevated temperature, prior to addition to the melt. Depending on the type of lubricant used, it may be necessary to heat the mixture of lubricant and nucleating agent to generally from 30 to 150°C, preferably from 60 to 130°C, in order to prepare a 30 suspension and subsequently add it to the polymer melt.

Examples of suitable lubricants are low molecular weight polyethylene waxes which are solid at room temperature and have to be heated to prepare a suspension of the nucleating agent.

35 Such lubricants are low molecular weight polyethylene waxes which may advantageously contain functional groups such as glycidyl and/or carboxyl groups

and have a mean molecular weight M_n (number average) of generally from 500 to 20,000 g/mol, preferably from 1000 to 10,000 g/mol, particularly preferably from 1000 to 5000 g/mol and very particularly preferably from 1000 to 3000 g/mol.

- 5 The molecular weight is usually determined by gel permeation chromatography (GPC) using an LDPE standard (low density polyethylene). The melt viscosity is preferably from 100 to 5000 mm²/g, particularly preferably from 100 to 3000 mm²/g and very particularly preferably from 100 to 2000 mm²/g, (in accordance with DIN 51 562) at 120°C.

10

Suitable nucleating agents are, in particular, minerals selected from the group consisting of alkali metal (alumino)silicates and/or alkaline earth metal (alumino)silicates, preferably selected from the group consisting of island silicates or sheet silicates. All possible compounds such as hydroxides, carbonates, 15 hydroxycarbonates, sulfates, silicates and phosphates and phosphonates can be used. Further suitable nucleating agents which may be mentioned are alkali metal or alkaline earth metal salts of organic or inorganic acids, for example sodium antimonate, calcium stearate, sodium terephthalate, calcium citrate and metal acids (basic acids) of titanium or tungsten.

20

Suitable derivatives of inorganic acids are preferably phosphoric acid derivatives, with particular preference being given to sodium phenylphosphinate, zinc phosphate, calcium bis(3,5-di-tert-butylethylphosphonate) (Irganox[®] 1425 from Ciba Geigy AG) and tetrakis(2,4-di-tert-butylphenyl) 4,4-biphenylenedi- 25 phosphonite.

Suitable polycondensation apparatus are known to those skilled in the art. In a particularly preferred embodiment, it is possible to discharge the melt from the polycondensation reactor, to add the mixture of lubricant and nucleating agent by 30 means of suitable devices, e.g. a metering pump with heating, and subsequently to homogenize the polymer melt in a static mixer and then discharge, cool and granulate it.

The polybutylene terephthalate obtained generally has an acid number of 35 < 50 meq/kg, preferably < 35 meq/kg, particularly preferably < 30 meq/kg. The acid number was determined by titration with aqueous sodium hydroxide.

The process of the present invention has the advantage that only small amounts of THF are formed from 1,4-butanediol, and thus only little 1,4-butanediol is lost. In general, the amount of THF formed, based on the amount of polybutylene terephthalate obtained, is < 5% by weight, preferably < 4% by weight, particularly preferably < 3.5% by weight. Likewise, only little 2,5-dihydrofuran is formed from 1,4-butanediol. The amount of 2,5-dihydrofuran formed is preferably < 150 ppm, particularly preferably < 100 ppm, based on the amount of polybutylene terephthalate obtained.

The following examples illustrate the invention.

EXAMPLES

Experimental procedure 1: *Esterification stage with decreasing temperature and constant pressure of 1 bar*

Terephthalic acid is premixed with 1,4-butanediol in a molar ratio of terephthalic acid to 1,4-butanediol of 1:1.2, placed in a reaction vessel R1 and made up with 1,4-butanediol. TBOT (1), i.e. part of the esterification catalyst, is mixed into the 1,4-butanediol. The mixture runs through a total of 8 reaction zones (3 reaction vessels R1 to R3 (esterification stage a)), 4 reaction zones in an upright tube R4 to R7 (precondensation stage b)) and the polycondensation reactor R8 (polycondensation stage c))) to the final polybutylene terephthalate, at temperatures T1 to T8, pressures p1 to p8 and residence times V1 to V8, with only the temperatures T1 to T3 being varied in the reaction zones R1 to R3. In R2, an additional amount of TBOT (2) was metered in. The distillates from R1 to R3 were fractionated continuously in a column system and 1,4-butanediol was returned to R1 and the remainder (essentially water and THF) was condensed in a collection vessel and analyzed. The collection vessel for the distillates was cooled to -20°C by means of a cryostat so that the volatile THF did not vaporize. In addition, a sample was taken at the overflow from R1 to R2, from R2 to R3 and from R3 to R4, and the conversions C1 to C3 were determined by determination of the acid number. The clearing point was determined visually. THF was determined quantitatively by means of gas chromatography and its ratio to the amount of polybutylene terephthalate obtained was calculated, i.e. at a THF formation of 5%, 50 g of THF are formed per kilogram of polybutylene terephthalate. The end groups of the polybutylene terephthalate products obtained were determined by

titration. The viscosity measurement (VN measurement) was carried out in accordance with ISO 1628 in phenol/o-dichlorobenzene.

5 The esterification product was passed to an upright tube divided into four heating zones.

The temperature in the fourth reaction zone was 247°C at a pressure of 700 mbar and a mean residence time of 22 minutes.

10 The temperature in the fifth reaction zone was 252°C at a pressure of 400 mbar and a mean residence time of 11 minutes.

The temperature in the sixth reaction zone was 256°C at a pressure of 30 mbar and a mean residence time of 18 minutes.

15 The excess 1,4-butanediol and the reaction products such as THF and water were separated off at the upper end of the reaction tube. The precondensate was transferred without further addition of catalysts to a polycondensation reactor (zone 8).

20 The temperature in the eighth reaction zone was 257°C at a pressure of 0.4 mbar, a mean residence time of 115 minutes and a surface renewal of 4 m²/h*kg of polybutylene terephthalate.

25 Table 1 shows the results obtained using the experimental procedure 1 and also the results of the comparative experiments Comp. 1 to Comp. 4.

Experimental parameters which were not varied:

30 p1, p2, p3 = 1 bar
V1, V2, V3 = 182 minutes, 63 minutes, 40 minutes (mean residence time)

T4, T5, T6, T7, T8 = 247°C, 252°C, 255°C, 256°C and 257°C

p4, p5, p6, p7, p8 = 700 mbar, 400 mbar, 150 mbar, 30 mbar and 0.4 mbar

35 V4, V5, V6, V7, V8 = 22 minutes, 11 minutes, 5 minutes, 18 minutes and 115 minutes

Throughput: BDO:TPA = 450 g/h:690 g/h

Yield of PBT: 910 g/h

Table 1:

	1	2	3	4	5	Comp. 1	Comp. 2	Comp. 3 (*)	Comp. 4 (**)
TBOT (1)	15	20	25	40	15	15	15	200	75
TBOT (2)	90	100	90	75	85	90	85	0	-
BDO (g/h)	370	370	370	370	370	370	370	370	420
T1	225	220	225	225	230	220	230	-	-
T2	217	215	215	215	215	220	230	-	-
T3	209	203	200	200	200	220	230	-	-
C1	91.3	91.1	93.2	94.8	93.6	90.7	93.3	91.2	90.5
C2	96.2	96.0	97.6	98.1	97.1	96.9	98.5	-	-
C3	97.5	97.4	98.4	98.7	98.2	98.7	99.1	-	-
Clearing point	yes	yes	yes	yes	Yes	yes	yes	no	no
THF(%)	3.25	3.29	3.32	3.83	3.41	6.22	8.35	3.71	7.32
OH	23	25	24	24	25	25	25	25	52
COOH	24	25	25	24	25	24	25	132	143
VN	123	121	125	122	125	122	124	120	95

(*)=Method analogous to EP-A 0 431 977, Ex. 1, continuous operation is not possible without R2 and R3 since, owing to the continual addition of fresh TPA/BDO, terephthalic acid is also always carried over into the upright reactor R4 and is no longer completely converted in the further condensation and thus leads to high acid numbers in the polybutylene terephthalate. As a result, the clearing point is also not reached.

(**)=Method analogous to DE-A 35 445 51, Ex. 9; unlike the preceding experiments, the esterification was carried out at a pressure of 0.65 bar. Since the boiling point of 1,4-butanediol at 0.65 bar is about 210°C, the reaction temperature described in Ex. 9 (245°C) could not be reached. When the temperature of the heating bath was increased, 1,4-butanediol distilled off, as a result of which the temperature of the reaction mixture settled down to 217°C.

Experimental procedure 2: *Esterification stage at decreasing temperature and decreasing pressure (decreasing subatmospheric pressure)*

The experimental procedure 2 corresponds to experimental procedure 1 except that not only the temperatures T1 to T3 but also the pressures p1 to p3 were varied in the reaction vessels R1 to R3. The pressure in the fourth reaction zone corresponds to the pressure in the third reactor of the esterification zone.

Table 2 shows the results obtained using experimental procedure 2 and also the results of the comparative experiments Comp. 1 to Comp. 5.

Experimental parameters which were not varied:

T4 to T8 = see experimental procedure 1

V4 to V8 = see experimental procedure 1

p4 = p3

p5, p6, p7, p8 = 400 mbar, 150 mbar, 30 mbar and 0.4 mbar

Throughput: BDO:TPA = see experimental procedure 1

Yield of PBT: see experimental procedure 1

Table 2:

	1	2	3	4	5	6	Comp.1	Comp.2	Comp.3 (**)	Comp.4	Comp.5 (***)
TBOT (1)	15	15	15	20	20	20	15	15	15	15	75
TBOT (2)	100	100	100	100	100	100	100	100	100	100	-
BDO (g/h)	370	370	370	370	370	370	370	370	370	370	420
p1	900	800	900	750	650	650	900	850	800	800	650
p2	600	600	600	500	500	500	700	650	700	800	
p3	500	400	400	350	350	350	600	500	600	800	
T1	225	225	230	220	210	210	225	220	215	215	217
T2	215	220	220	215	205	205	225	220	225	215	-
T3	210	215	215	200	200	200	225	220	230	215	-
V1	182	182	182	182	182	212	182	182	182	182	182
V2	63	63	63	63	63	78	63	63	63	63	-
V3	40	40	40	40	40	65	40	40	40	40	-
C1	90.9	91.0	93.4	90.6	87.3	89.2	91.1	90.8	90.4	90.2	90.5
C2	92.6	93.5	95.2	92.8	91.2	92.7	93.9	93.5	94.1	91.7	-
C3	96.8	97.8	98.1	95.1	94.5	95.3	98.2	98.1	98.5	96.3	-

	1	2	3	4	5	6	Comp.1	Comp.2	Comp.3 (**)	Comp.4	Comp.5 (***)
Clearing point	yes	yes	yes	yes	yes(*)	Yes	yes	yes	yes	yes	no
THF (%)	1.78	1.89	1.97	1.62	2.01	2.21	2.37	2.11	3.89	3.15	7.32
2,5-DHF (ppm)	47	52	67	34	94	147	134	103	361	276	43
OH	24	23	23	24	24	23	23	25	23	24	52
COOH	24	24	23	23	42	24	25	25	24	25	143
VN	130	131	131	128	130	128	126	122	125	127	95

(*) In the experiments under these conditions, the reaction solution was still very slightly turbid.

- 5 (**)= Method analogous to DD-A 269 296, decreasing pressure and increasing temperature.

10 (***)= Method analogous to DE-A 35 445 51, Ex. 9; unlike the preceding experiments, the esterification was carried out at a pressure of 0.65 bar. Since the boiling point of 1,4-butanediol at 0.65 bar is about 210°C, the reaction temperature described in Ex. 9 (245°C) could not be reached. When the temperature of the heating bath was increased, 1,4-butanediol distilled off, as a result of which the temperature of the reaction mixture settled down to 217°C.

We claim:

- 5 1. A process for the continuous preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol, comprising:
- 10 a) direct esterification of terephthalic acid with 1,4-butanediol in a reactor cascade comprising at least two reactors,
- b) precondensation of the esterification product obtained in stage a), and
- c) polycondensation of the precondensate obtained in stage b),
- wherein the temperature decreases along the reactor cascade in stage a).
- 15 2. A process as claimed in claim 1, wherein the temperature in the reactors of the reactor cascade in stage a) is set to a value in the range from 180°C to 240°C, preferably from 190°C to 230°C.
- 20 3. A process as claimed in claim 1 or 2, wherein the temperature in the reactors of the reactor cascade in stage a) drops by from 2 to 30°C from reactor to reactor.
4. A process as claimed in any of claims 1 to 3, wherein the esterification in stage a) is carried out at pressures of < 1 bar.
- 25 5. A process as claimed in claim 4, wherein the experimental parameters pressure and temperature in each reactor of the reactor cascade in stage a) lie within a plane defined by
- 30 $p(\text{lower limit}) = 0.348 \times (T/^{\circ}\text{C})^2 - 124.12 \times (T/^{\circ}\text{C}) + 11121$ and
 $p(\text{upper limit}) = 0.0802 \times e^{0.0405 \times (T/^{\circ}\text{C})}$,
- where the pressure does not increase from reactor to reactor.
- 35 6. A process as claimed in any of claims 1 to 5, wherein the pressure in the reactors of the reactor cascade in stage a) drops by at least 50 mbar from reactor to reactor.

7. A process as claimed in any of claims 1 to 6, wherein the molar ratio of 1,4-butanediol to terephthalic acid at the beginning of the esterification in stage a) is from 1.1:1 to 3.5:1.
- 5 8. A process as claimed in any of claims 1 to 7, wherein the conversion after the last reactor of stage a) is $> 97\%$, based on terephthalic acid, before the precondensation in stage b) commences.
- 10 9. A process as claimed in any of claims 1 to 8, wherein stage a) is carried out in the presence of a catalyst, preferably tetrabutyl orthotitanate.
10. A process as claimed in any of claims 1 to 9, wherein stage b) is carried out at temperatures from 220 to 300°C and pressures in the range from 0.05 bar to the esterification pressure in the last reactor of the reactor cascade of stage a).
- 15 11. A process as claimed in any of claims 1 to 10, wherein the precondensate obtained in stage b) is polycondensed in stage c) at from 240 to 290°C and pressures of from 0.2 to 20 mbar.
- 20 12. A process as claimed in claim 11, wherein the polycondensation is continued until the polycondensate obtained has an acid number of < 50 meq/kg.

Abstract

In a process for the continuous preparation of polybutylene terephthalate from terephthalic acid and 1,4-butanediol comprising:

- d) direct esterification of terephthalic acid with 1,4-butanediol in a reactor cascade comprising at least two reactors,
- e) precondensation of the esterification product obtained in stage a), and
- f) polycondensation of the precondensate obtained in stage b),

the temperature decreases along the reactor cascade in stage a).