

Process for the Production of Polycarbonate

5 The present invention relates to a process for the isolation of polycarbonate produced by the phase interface process, by evaporating and degassing a solution of polycarbonate in an organic solvent.

10 The process for synthesising polycarbonate by the phase interface process is described variously in the literature, for example inter alia in Schnell, "Chemistry and Physics of Polycarbonates", Polymer Reviews, Volume 9, Interscience Publishers, New York, London, Sydney 1964, pp. 33-70.

15 In the phase interface process the phosgenation of a disodium salt of a bisphenol (or a mixture of various bisphenols) in aqueous-alcoholic solution (or suspension) is carried out in the presence of an inert organic solvent or solvent mixture that forms a second phase. The oligocarbonates that are formed, and that are present mainly in the organic phase, undergo condensation by means of suitable catalysts to form high molecular weight polycarbonates dissolved in the organic phase. The organic phase is finally separated.

20 The polycarbonate must then be isolated from the organic phase. The current methods for concentrating the polycarbonate solution and for isolating the polycarbonate are described in the patent literature and in text books and are known to the person skilled in the art. The isolation of the polycarbonate from the solution is preferably carried out by evaporating the solvent by heating or applying a vacuum. This process requires the use of a high boiling point ($> 100^{\circ}\text{C}$) solvent, for
25 example chlorobenzene, in order directly to obtain the melt phase after the evaporation of the solvent. In order to improve the solubility of the polymer in the solvent during the reaction, a mixture of one or more high boiling point solvents and the low boiling point compound dichloromethane is also used. Typically the weight
30 ratio of dichloromethane to the high boiling point solvent is about 1:1.

Another possibility is to inject a heated gas, in particular steam, in order to expel the volatile constituents. In this case the polycarbonate solution is sprayed together with the carrier gas and polycarbonate is formed as a solid, especially as a water-wet suspension. Other isolation methods include crystallisation and precipitation as well
5 as heating the residues of the solvent in the solid phase. The last method requires the use of dichloromethane as solvent, whereby residual contents of volatile constituents of about 2 ppm dichloromethane can be achieved. Residual contents of dichloromethane particularly interfere in the polycarbonate since dichloromethane in the working-up process with residual moisture together split off hydrogen chloride
10 and can thus cause discolourations of the polycarbonate and lead to corrosion of the equipment.

In the known methods for evaporation, or also flash evaporation, polycarbonate solutions are repeatedly heated under slight excess pressure to temperatures above
15 the boiling point and these superheated solutions are then flashed into a vessel at a lower pressure than the vapour pressure in the solution. The evaporation or flash evaporation of the solvent may be carried out using various methods, equipment and machinery, e.g. stripping extruders, thin-film evaporators or friction-compaction devices. Conventional methods for the apparatus-based evaporation of
20 polycarbonate solutions are known to the person skilled in the art. For example the superheated solution can be flashed into a heated coil evaporator that terminates in a separator. In this connection it may be advantageous to carry out the process in several stages. In addition processes are known in which in some cases a multistage concentration of the solution is carried out in vertical shell-and-tube heat
25 exchangers.

In order to achieve particularly low residual contents extrusion evaporators may be used for the last degassing stage. In this case the polymer melt is formed in a separator under a vacuum and elevated temperature into fine strands and thereby
30 freed from the solvent. The disadvantage of the extrusion evaporation technique is that an effective degassing is ensured only by stable strands, i.e. strands that do not break off in the equipment. The stability of the strands is influenced by the viscosity

of the polymer solution. Too low a viscosity can lead to strand breakages, which in turn means a restriction of the operating parameters in terms of temperature and entry content of residual volatile constituents. Apart from the negative influence on the viscosity, too high an entry concentration of volatile constituents has direct deleterious effects on the degree of degassing that can be achieved, since the mass transfer is determined purely by diffusion. The surface available for the mass transfer is however fixed by the strand geometry. The necessary large area of the melt distributor that is needed to produce the strands requires in turn large expensive equipment.

It is also known from the prior art to carry out the last degassing step in the working-up of polymers under foaming (expansion) with or without entrainment agents. Methods for the apparatus-based degassing of thermoplastic polymers that are based on the principle of foam degassing exist in the prior art. However, these methods often have the disadvantage that either very large amounts of gas have to be suctioned off, or that sufficiently low residual contents cannot be achieved. Furthermore, the methods described in the literature are often inflexible as regards throughput and polymer type and viscosity, and as regards the entry concentration of volatile components at the inlet to the respective degassing stage.

EP-A 200 368 describes the foam degassing of styrene polymers in a two-stage process. The method is based on the fact that the amount of solvent in the polymer solution is adjusted to be sufficiently large so as to initiate a foaming.

EP-A 914 355 describes mixing a sparingly soluble separating agent in a polymer solution followed by flashing, with foaming, into a separator under low pressure. The process described there is used to separate readily volatile solvents with the aid of foaming agents. The readily volatile separating agent is not completely dissolved, but is dispersed.

DE-A 100 15 862 describes a multistage process for removing volatile constituents from polyamides. Before the last degassing stage foaming agents for this, e.g.

nitrogen, carbon dioxide or water, are dispersed using a static mixer and thereby partially dissolved. The polyamide melt is then flashed in a vertical shell-and-tube heat exchanger or in a loop evaporator or in a combination thereof into a degassing vessel under low pressure. Wire loops onto which the melt flows from above ensure
5 an extended residence time and thus a better degassing result.

The object of the present invention is to provide a process for the isolation of polycarbonate produced by the phase interface process, in which the polycarbonate is obtained dissolved in an organic solvent. By means of the process low residual
10 contents of volatile components totalling less than 250 ppm, preferably less than 100 ppm and particularly preferably less than 25 ppm, referred to the total mass, should be achieved. Volatile components are understood to include solvents such as monochlorobenzene and dichloromethane, the corresponding unreacted monomers, e.g. BPA, and their volatile oligomers such as dimers, trimers and tetramers. In
15 particular the process should be capable of removing dichloromethane employed in the reaction to levels of below 2 ppm and to yield preferably dichloromethane-free product containing less than 0.5 ppm of dichloromethane.

The process should have a high flexibility in terms of throughput and polycarbonate
20 type and viscosity and as regards the entry concentration of volatile components at the inlet to the respective degassing stage. Flexibility means in this connection that the aforementioned parameters and product properties can be altered in a plant while maintaining the quality, without complicated changeover of equipment or downtimes. In other words, a constant quality should be achieved independently of
25 the entry conditions.

The present invention provides a process for the isolation of polycarbonate produced by the phase interface process from a solution in an organic solvent, said process comprising the following steps:

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- (a) evaporation of the organic solvent to obtain a content of polycarbonate of 90 to 99.95 wt.%,

(b) optionally mixing the melt obtained in step (a) with a foaming agent,

(c) degassing the melt obtained from (a) and optionally (b) by feeding the melt
5 through inlet openings into a separating vessel,

characterised in that

10 in the degassing according to step (c) the melt is subdivided by the inlet openings
into partial streams of 0.1 to 20 kg/hr and on entry into the inlet openings has a
supersaturation with volatile constituents of at least 1 bar as well as a temperature of
250° to 340°C, wherein the pressure in the separating vessel is 0.1 to 20 mbar.

15 According to step (a) of the process according to the invention the solution of
polycarbonate in an organic solvent (hereinafter simply referred to as polycarbonate
solution) is first of all evaporated to such an extent that the content of polycarbonate
is 90 to 99.95 wt.%. The polycarbonate solution thereby obtained is also
synonymously referred to as polycarbonate melt. Step (a) may be carried out as a
one-stage or multistage process, preferably a multistage process.

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Conventional methods for evaporating polymer solutions according to step (a) are
known to the person skilled in the art. For example, the superheated solution can be
flashed into a heated coil evaporator that terminates in a separator. An example of
such a process is described for example in DE 1 921 045 A. In this connection it
25 may be advantageous not to allow the concentration stages, or in other words the
temperature stages of the superheating, to become too large, but instead choose a
two-stage to four-stage process, as described for example in EP 1 094 873 A. In
addition processes are known in which a pre-concentration of the polycarbonate
solution is carried out in vertical shell-and-tube heat exchangers. Such processes, in
30 some cases multistage processes, are described for example in DE 19 835 744 A.
Polymer concentrations of 90 to 99.95 wt.% or above can be achieved by such

processes. Combinations of coil evaporators and shell-and-tube heat exchangers are also conceivable.

Starting from the polycarbonate melt obtained according to step (a), a polycarbonate
5 with a low content of volatile constituents is optionally obtained according to step
(b) by adding a foaming agent and according to step (c) in at least one foam
degassing step by splitting up the polycarbonate melt into partial streams and also by
reducing the pressure. A low content of volatile constituents is understood within
the context of the present invention to mean a concentration of the volatile
10 constituents of less than 250 ppm, preferably less than 100 ppm and particularly
preferably less than 25 ppm, in each case referred to the total mass.

The volatile constituents to be removed according to step (c) include the solvents of
the polymerisation reaction according to the phase interface process, in particular
15 monochlorobenzene and residual amounts of dichloromethane. The mass fraction of
monochlorobenzene before the foam degassing (step (c)), i.e. on entry into the inlet
nozzles of the separating vessel, is for example less than 10%. The entry content of
dichloromethane, referred to the mass, is for example less than 5%. Further possible
solvents for the polycarbonate production are known to the person skilled in the art,
20 for example ethylbenzene, toluene or xylene, which if present also have to be
removed to low residual contents. In addition the polycarbonate melt contains
residues of monomers or volatile oligomers whose proportion is likewise reduced by
the process according to the invention.

25 In order to initiate a foaming of the polycarbonate melt in step (c) and thereby
achieve a particularly effective degassing, sufficient solvent must be present in the
polycarbonate melt. The supersaturation of the polycarbonate melt with volatile
constituents on entry into the inlet openings is correspondingly at least 0.1 bar,
preferably at least 0.5 bar and particularly preferably at least 1 bar. The
30 supersaturation is defined as the difference between the vapour pressure of all
volatile components on entry into the inlet openings and the pressure in the
separating vessel (hereinafter also referred to as separator or degassing vessel). The

vapour pressure is the sum of the partial pressures of all components present in the polymer melt and depends on the temperature and the concentration of the volatile constituents.

- 5 The success of the degassing is largely independent of whether the supersaturation is generated only by the solvents present in the melt or whether in addition a foaming agent is added. The temperature and the concentration of the volatile components is decisive as regards the vapour pressure. If the required vapour pressure is generated simply by residues of solvents in the polycarbonate melt, then the use of foaming
10 agents can be dispensed with.

- If a sufficient amount of solvent is not present in the polycarbonate melt, i.e. if the vapour pressure of the solvent alone is too low, a foaming agent is added in order to create the necessary vapour pressure in the polycarbonate melt. Accordingly, in one
15 embodiment of the process according to the invention the melt obtained from step (a) is mixed with a foaming agent according to step (b) before the degassing according to step (c).

- The foaming agent is as a rule a readily volatile substance with a high vapour
20 pressure. The foaming of the polycarbonate melt is initiated by the high vapour pressure of the foaming agent. The foam produces a large increase in surface area, which is advantageous for the degassing. In addition the partial pressure of the residues of solvents or other volatile constituents in the gaseous phase of the separator that are present in the polymer is reduced, whereby in principle lower
25 residual contents of volatile constituents should be achieved.

- As foaming agent there is preferably used an inert gas or an inert liquid or a mixture of inert gases and/or liquids. Examples of suitable foaming agents are nitrogen, carbon dioxide, water, methane and helium. Particularly preferably water, carbon
30 dioxide or nitrogen is used as foaming agent, and most particularly preferably nitrogen is used.

Within the scope of the present invention it was also found that the success of the degassing is significantly improved if the foam degassing, with or without the addition of a foaming agent, is carried out several times in succession. In this connection the necessary supersaturation must be ensured in each degassing stage.

5 If necessary a foaming agent according to step (b) may be added before each foam degassing step (c). If the degassing is carried out in several stages care should be taken to ensure that the overall residence time remains small in order to prevent undesirable discolouration or degradation. A short residence time can be achieved by a suitable design of the apparatus. If the foam degassing is carried out in several
10 stages, the individual stages need not necessarily be carried out in exactly the same way. Depending on the particular application, i.e. depending on throughput, viscosity of the product and temperature, the stages may be carried out differently as regards their execution or splitting of the partial streams, amount of foaming agent, temperature, and diameter of the inlet openings.

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The foaming agent is distributed in step (b) in the polycarbonate melt. A static mixer is preferably used for the distribution and dissolution of the foaming agent. Conventional modifications of static mixers for mixing highly viscous polycarbonate melts have been known for a long time from the prior art. Static
20 mixers preferably have the structure of an SMX mixer, which is described in detail for example in Arno Signer, Statisches Mischen in der Kunststoffverarbeitung und -herstellung, Plastverarbeiter 11(43), 1992. Static mixers according to EP 947 239 A or US 6 394 644 B may also preferably be used. Particularly preferred is an SMX mixer whose free internal diameter varies along the length of the mixer as a
25 result of various mixing elements, in which particularly preferably the free internal diameter decreases for example in a cascade manner or in stages in the direction in which the material flows through the mixer.

In order to improve the dispersion and dissolution of the foaming agent in the
30 polycarbonate melt, the pressure in the static mixer can be increased by means of a suitable device, for example a pressure retention valve or a throttle. It is known to

the person skilled in the art that a larger amount of a volatile substance can be dissolved in a melt by increasing the pressure.

5 The state of the polycarbonate melt on entry into inlet openings according to step (c) before the flashing, namely the existence of one or more phases, is decisive for the success of the degassing and for the process stability. A particularly good degassing result is achieved if all volatile components, including foaming agents, are completely dissolved before the flashing. Completely dissolved within the context of the present invention means that the polycarbonate melt with the solvent
10 contained therein and added foaming agent forms a single-phase mixture. No bubbles or droplets are then present in the polycarbonate melt on entry into the inlet openings.

In particular the mixed-in foaming agent should be completely dissolved. The
15 amount of foaming agent, the pressure and the temperature are in this connection chosen so that the foaming agent is completely dissolved in the polycarbonate melt. The pressure and temperature that are necessary for the complete dissolution of a specific amount of foaming agent depend on the nature of the said foaming agent. It is known to the person skilled in the art that, for a given temperature of a
20 polycarbonate melt, the maximum amount of a foaming agent that can be dissolved is increased by raising the pressure. The same is also true for the other volatile components contained in the polycarbonate melt.

The foaming agent should be chosen so that even small amounts are sufficient in
25 order, after a pressure release, to produce a vigorous foaming of the polycarbonate melt on entry into the inlet openings. Within the scope of the process according to the invention a small amount means the addition to the polycarbonate melt of 0.01 to 1 wt.% of foaming agent, preferably 0.02 to 0.5 wt.% and particularly preferably 0.05 to 0.3 wt.%, referred to the polymer mass. Despite this small amount of
30 foaming agent the flashing successfully takes place accompanied by foaming of the polycarbonate melt.

The vapour pressure of the foaming agent for the temperature prevailing at the entry to the inlet openings of the degassing stage (c) at the adjusted concentration of foaming agent in the melt is 0.1 to 100 bar, preferably 0.5 to 60 bar and particularly preferably 1 to 40 bar.

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The polycarbonate melt may be heated or cooled, preferably heated, before, during or after the mixing in of the foaming agent. An increased temperature means a higher vapour pressure of the volatile components, with the result that the foam formation is assisted in the subsequent degassing and the separation of the volatile constituents successfully takes place more easily. Suitable apparatus and equipment for heating or cooling a polymer melt, for example shell-and-tube heat exchangers, plate heat exchangers or heat exchangers with static mixers, are known to the person skilled in the art.

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Preferably the temperature change in the melt from the point of addition of the foaming agent up to the entry into the inlet openings according to step (c) is not more than 100°C, preferably not more than 90°C. The temperature of the polycarbonate melt at the entry to the inlet openings is preferably 250°C to 340°C, particularly preferably 260°C to 320°C. A further heating of the polycarbonate melt is also possible after the entry to the inlet openings up to the entry to the degassing vessel, if for example heatable tubes are used as inlet openings and flashing devices. Preferably the temperature difference between the entry to the inlet openings and the entry to the separating vessel is not more than 100°C, particularly preferably not more than 80°C.

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According to step (c) the polycarbonate melt is introduced via inlet openings into a separating vessel in the form of partial streams of 0.1 to 20 kg/hr, preferably 0.125 to 10 kg/hr and particularly preferably 0.15 to 5 kg/hr.

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The polycarbonate melt is flashed in a separating vessel at a low pressure of 0.1 to 20 mbar, preferably 0.3 to 10 mbar, particularly preferably 0.5 to 5 mbar. The temperature of the polycarbonate melt on entry into the degassing vessel is

according to the invention 250° to 360°C, preferably 260° to 340°C and particularly preferably 270° to 320°C.

- 5 The polycarbonate melt is introduced from above through the inlet openings into the separating vessel. The inlet openings are accordingly located in the upper region of the separating vessel. The inlet openings are in particular arranged in one level, though they may also be arranged at different levels in the upper region of the separating vessel.
- 10 The inlet openings perform the function of flashing devices. An essential design criterion for these flashing devices is the pressure loss that is generated by them. The pressure loss is calculated from the viscosity of the polymer melt, which in turn depends on the type of product, temperature and concentration of volatile constituents and foaming agent, and the throughput and geometry of the flashing
- 15 devices. The connection between the diameter of the bores, mass flow, viscosity of the polycarbonate melt and pressure loss is known to the person skilled in the art. When calculating the pressure loss the person skilled in the art can disregard the influence of the entraining agent, so that a design according to known rules of the technology is possible. The pressure loss should be adjusted so that the absolute
- 20 pressure before the entry to the inlet openings is sufficiently high in order to prevent a foaming before the entry to the inlet openings. The foaming takes place only after the entry into the inlet openings.

- 25 Suitable inlet openings are for example bores or slits, hereinafter termed nozzles, in a plate (also termed nozzle plate). Nozzles are preferably designed as bores in a nozzle plate. The plate may in principle be of any suitable thickness.

- 30 In a preferred implementation of the process according to the invention the partial streams of the polycarbonate melt are in each case guided through nozzles in a horizontally arranged plate. The bores terminate directly in the separating vessel, in which a low pressure exists. Preferred diameters of the nozzles are 0.8 to 5 mm, particularly preferably 1 to 4 mm.

Tubes also may be used as inlet openings. Preferably the tubes are arranged vertically and polycarbonate melt flows through the tubes from the top downwardly. Preferred tube diameters are 4 to 20 mm, particularly preferably 5 to 15 mm.

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In a further preferred execution of the process according to the invention the tubes are used as a heat interchanger or heat exchanger. For this purpose they are arranged in particular in the form of a parallel bundle and are surrounded by a heat transfer medium, preferably a liquid heat transfer oil or condensing steam or heat transfer oil vapour. The length of the tubes is preferably 300 to 2500 mm, particularly preferably 500 to 2000 mm.

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The tubes of the shell-and-tube heat exchanger thus terminate directly in the separating vessel. The individual tubes are designed so that the polycarbonate melt does not yet foam on entry into the shell-and-tube heat exchanger. The tubes may be made narrower by nozzles in order to maintain a predetermined pressure loss. The pressure loss in an individual tube is in this connection dependent on the state of the polycarbonate, the temperature at the inlet and outlet of the tube, the throughput, and the proportion of volatile constituents at both the inlet and outlet of the tube. The polymer foam is formed only at the outlet side of the tubes to the separator, i.e. at the inlet openings of the separating vessel. The diameters of the tubes are in this connection preferably 4 to 20 mm, particularly preferably 5 to 15 mm. Nozzles that are used to increase the pressure loss have diameters of 0.8 to 5 mm, preferably 1 to 4 mm. The mass flow per tube is 0.1 to 20 kg/hr.

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The execution of the process according to the invention with a shell-and-tube heat exchanger provides a preferred method for heating or cooling the polymer melt, as discussed further hereinbefore.

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The interspacings of the inlet openings, measured from midpoint to midpoint, and thus the interspacings of the partial streams on entry into the separating vessel, are 5 to 50 mm, preferably 10 to 40 mm and particularly preferably 15 to 25 mm.

5 The residence time of the polycarbonate melt in the separating vessel must on the one hand be sufficiently long to permit a sufficient degassing. The residence time must on the other hand not be too large, so that it does not affect the product quality of the polycarbonate. The residence time of the polycarbonate melt in the separating vessel in step (c) is preferably at most 10 minutes, particularly preferably at most 5 minutes.

10 In a further modification of the process according to the invention the residence time may be influenced by guide elements. The guide elements have the function of extending the residence time and at the same time increasing the surface of the polycarbonate melt.

15 The guide elements may consist for example of perforated metal sheets, profiled metal sheets, wires, wire meshes, link chains, narrow metal strips of arbitrary cross-section, etc., and are preferably arranged substantially horizontally. Examples of such guide elements are described for example in DE-A 10 144 233 or in EP-A 1 095 960. Particularly preferably the guide elements are formed as wires, which are arranged substantially horizontally in the separating vessel. The degassing of the polycarbonate melt is thereby significantly improved, without a harmful back-cleavage of the polycarbonate occurring.

25 The wires may be arranged in virtually any desired manner so long as the wires do not contact one another and are arranged substantially horizontally. Within the context of the present invention substantially horizontally means a maximum deviation from the horizontal of 20°. In particular, two or more wires should not contact one another, for example by crossing over. A plurality of wires may for example be provided in several levels, in which neither the wires of one level nor the wires of different levels contact one another. If a plurality of wires are provided in one level, then these may be arranged substantially parallel to one another. The wires of one level should in particular have an angle of at most 20°. If furthermore
30 several levels of wires are provided, the wires of different levels may be arranged at

any arbitrary angle to one another. Preferably the wires of different levels form an angle of at most 180° , particularly preferably 30° to 150° and most particularly preferably 70° to 110° . If the individual wires of a level are not clamped parallel, then the angle of rotation of the wires of different levels is fixed according to the angle bisecting lines.

Preferred are wires with a diameter of 1 mm to 5 mm, particularly preferably 2 mm to 4 mm.

The advantage of substantially horizontally arranged wires, which are preferably clamped between opposite walls of the separating vessel, is that an effective surface regeneration and thus a good mass transfer between the gas space and polycarbonate melt can take place with a minimum contact area between the metal material of the wire and the polycarbonate melt. In the most unfavourable cases a large accumulation (hold-up) of highly viscous polycarbonate melt can form on vertically arranged wires, i.e. the polycarbonate melt forms blockages on the wires. This leads to unfavourable residence time distributions or to degradation of the polymer. Both may be deleterious as regards the quality of the product. Also, it has been found experimentally that a network, mesh, fabric or the like made of wires, as described for example in EP-A 1 095 960, tends to form a large blockage of polycarbonate melt at the nodal points of the wires and leads to polymer degradation. Horizontally clamped wires produce in addition a good distribution of the foam strands and thus an effectively enlarged surface for mass transfer compared to metal sheets, etc.

A higher viscosity of the polycarbonate melt leads, with otherwise identical guide elements, to a larger blockage, to greater layer thicknesses and to longer residence times.

The polycarbonate melt falls downwardly in the separating vessel into a sump and is removed therefrom by a suitable discharge device, for example a gear-type pump or a discharge extruder. The discharge is preferably effected with a gear-type pump. The floor of the separating vessel is preferably designed conically with the tip

pointing downwards. The angle of the cone with respect to the horizontal is preferably 20° to 60°, particularly preferably 30° to 45°. In the case of very large throughputs (for example more than 12 tonnes per hour) a design may be chosen in which the floor of the separating vessel consists of several cones, each of which has
5 a discharge device at its lowest point.

The volatile constituents separated in step (c) may be freed from the foaming agent that is possibly present and passed to a working-up stage. In this, the volatile constituents that are separated, which consist to a considerable extent of the solvents
10 used in the process, may be recycled to the process for the production of the polycarbonate.

Advantageously the separated volatile components are not recycled to the process for the production of polycarbonate if only minor amounts of volatile components
15 are separated from the polycarbonate melt in the process according to step (c), for example amounts of 0.1% to 0.5%. The effort and expenditure involved in working up the volatile components must be weighed against the economic benefit of recycling. Also, the quality of the polycarbonate that is formed, for example as regards colour, may be adversely affected if impurities are introduced into the
20 process due to the worked-up solvents. A working-up and recycling of the monomers and oligomers separated in the process according to step (c) is not economical on account of their very small amount and may also affect the quality as regards colour.

25 A recycling and working-up of the foaming agent is as a rule not economical on account of the small amounts that are employed.

The thermoplastic polycarbonates that are obtained by the process according to the invention are also covered by the present invention. These polycarbonates have a
30 residual content of volatile substances (in particular monochlorobenzene) of at most 500 ppm, preferably at most 100 ppm and particularly preferably at most 25 ppm, referred to the polymer mass. The residual content of dichloromethane is at most

5 ppm, preferably at most 2 ppm and particularly preferably less than 0.5 ppm (free of dichloromethane).

For the process according to the invention, suitable diphenols for the production of polycarbonate are described in many places in the prior art.

Suitable diphenols are for example hydroquinone, resorcinol, dihydroxydiphenyl, bis-(hydroxyphenyl)-alkanes, bis-(hydroxyphenyl)-cycloalkanes, bis-(hydroxyphenyl) sulfides, bis-(hydroxyphenyl) ethers, bis-(hydroxyphenyl) ketones, bis-(hydroxyphenyl) sulfones, bis-(hydroxyphenyl) sulfoxides, α,α' -bis-(hydroxyphenyl)-diisopropylbenzenes, as well as their alkylated, nuclear-alkylated and nuclear-halogenated compounds.

Preferred diphenols are 4,4'-dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-1-phenylpropane, 1,1-bis-(4-hydroxyphenyl)-phenylethane, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,3-bis-[2-(4-hydroxyphenyl)-2-propyl]-benzene (bisphenol M), 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, bis-(3,5-dimethyl-4-hydroxyphenyl)-sulfone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methylbutane, 1,3-bis-[2-(3,5-dimethyl-4-hydroxyphenyl)-2-propyl]-benzene and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC).

Particularly preferred diphenols are 4,4'-dihydroxydiphenyl, 1,1-bis-(4-hydroxyphenyl)-phenylethane, 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC).

In the case of homopolycarbonates only one diphenol is used, whereas in the case of copolycarbonates several diphenols are used, in which obviously the diphenols used, like also all the other chemicals and auxiliary substances employed in the synthesis, may be contaminated with impurities derived from their specific synthesis, handling

and storage, although of course it is desirable to use raw materials that are as pure as possible.

5 The monofunctional chain terminators required to regulate the molecular weight, such as phenol or alkylphenols, in particular phenol, p-tert.-butylphenol, iso-octylphenol, cumylphenol, their chlorocarbonic acid esters or acid chlorides of monocarboxylic acids or mixtures of these chain terminators, are either added together with the bisphenolate or the bisphenolates to the reaction, or alternatively are added at any suitable time to the synthesis so long as phosgene or chlorinated carbonic acid terminal groups are still present in the reaction mixture or, in the case of acid chlorides and chlorinated carbonic acid esters as chain terminators, so long as sufficient phenolic terminal groups of the polymer being formed are available. Preferably however the chain terminator or terminators is/are added after the phosgenation at a site or at a time at which phosgene is no longer present but the catalyst has not yet been metered in. Alternatively the chain terminators may also be metered in together or in parallel before the catalyst or with the catalyst.

20 In the same way optionally branching agents or mixtures of branching agents are added to the synthesis. Normally however branching agents are added before the chain terminators. As a rule trisphenols, quaternary phenols or acid chlorides of tricarboxylic acids or tetracarboxylic acids or mixtures of the polyphenols or acid chlorides are used. Some of the compounds suitable as branching agents and containing three or more than three phenolic hydroxyl groups are for example phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptene-2, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-heptane, 1,3,5-tri-(4-hydroxyphenyl)-benzene, 1,1,1-tri-(4-hydroxyphenyl)-ethane, tri-(4-hydroxyphenyl)-phenylmethane, 2,2-bis-[4,4-bis-(4-hydroxyphenyl)-cyclohexyl]-propane, 2,4-bis-(4-hydroxyphenylisopropyl)-phenol, tetra-(4-hydroxyphenyl)-methane.

30 Some of the other trifunctional compounds are 2,4-dihydroxybenzoic acid, trimesic acid, cyanuric chloride and 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

Preferred branching agents are 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole and 1,1,1-tri-(4-hydroxyphenyl)-ethane.

5 The catalysts used in the phase interface synthesis of polycarbonates include tertiary amines, in particular triethylamine, tributylamine, trioctylamine, N-ethylpiperidine, N-methylpiperidine, N-i/n-propylpiperidine, quaternary ammonium salts such as tetrabutylammonium, tributylbenzylammonium, tetraethylammonium hydroxide, chloride, bromide, hydrogen sulfate and tetrafluoroborate, as well as the
10 phosphonium compounds corresponding to the ammonium compounds. These compounds are described in the literature as typical phase interface catalysts, are commercially obtainable, and are commonly known to the person skilled in the art. The catalysts may be added individually, as a mixture, or also side by side and in succession to the synthesis, optionally also before the phosgenation, but preferably
15 metered in after the addition of phosgene, unless an onium compound or a mixture of onium compounds are used as catalysts. In this case an addition before phosgene is metered in is preferred. The metering in of the catalyst or catalysts may take place in bulk, in an inert solvent, preferably the solvent used for the polycarbonate synthesis, or also as aqueous solution, and in the case of tertiary amines then as their
20 ammonium salts with acids, preferably mineral acids, in particular hydrochloric acid. When using several catalysts or when metering in partial amounts of the total catalyst amount, different metering procedures may of course also be employed at different sites or at different times. The total amount of the catalysts that are used is 0.001 to 10 mole % referred to moles of bisphenols used, preferably 0.01 to 8 mole
25 %, particularly preferably 0.05 to 5 mole %.

The polycarbonate synthesis may be carried out continuously or batchwise. The reaction may therefore take place in stirred vessels, tubular reactors, circulating pump reactors or stirred vessel cascades or combinations thereof. In this connection
30 it should be ensured by using the previously mentioned mixing devices that aqueous and organic phases as far as possible undergo demixing only when the synthesis

mixture has fully reacted, i.e. when it no longer contains saponifiable chlorine from phosgene or chlorinated carbonic acid esters.

5 After addition of the phosgene it may be advantageous thoroughly to mix the organic phase and the aqueous phase for a certain time before optionally branching agent, insofar as this has not been metered in together with the bisphenolate, and chain terminator and catalyst are added. Such a post-reaction time may be advantageous after each metering step. These post-stirring times are from 10 seconds to 60 minutes, preferably 30 seconds to 40 minutes, particularly preferably 10 1 to 15 minutes.

The organic phase may consist of a solvent or mixtures of several solvents. Suitable solvents are chlorinated hydrocarbons (aliphatic and/or aromatic), preferably dichloromethane, trichloroethylene, 1,1,1-trichloroethane, 1,1,2-trichloroethane and 15 chlorobenzene, and their mixtures. There may however also be used aromatic hydrocarbons such as benzene, toluene, m/p/o-xylene or aromatic ethers such as anisole, alone or as a mixture with or in addition to chlorinated hydrocarbons. Another modification of the synthesis uses solvents that do not dissolve but only swell polycarbonate. Non-solvents for polycarbonate may therefore also be used in 20 combination with solvents. In this connection solvents such as tetrahydrofuran, 1,3-/1,4-dioxane or 1,3-dioxolane that are also soluble in the aqueous phase may be used as solvent if the solvent partner forms the second organic phase.

25 The fully reacted, at least two-phase reaction mixture containing at most only traces (<2 ppm) of chlorinated carbonic acid esters is allowed to settle for the phase separation. The aqueous alkaline phase is recycled, possibly in whole or in part, as aqueous phase to the polycarbonate synthesis or alternatively is passed to the effluent working-up stage, where solvent and catalyst fractions are separated and recycled. In another variant of the working-up stage, after separating the organic 30 impurities, in particular solvents and polymer residues, and optionally after the adjustment of a specific pH value, for example by adding sodium hydroxide, the salt

is separated and may for example be passed to a chlorine-alkali electrolysis plant, while the aqueous phase is possibly recycled to the synthesis.

5 The organic phase containing the polycarbonate must now be purified to remove all contaminations of an alkaline, ionic or catalytic nature. The organic phase still also contains, after one or more settling procedures, fractions of the aqueous alkaline phase in the form of fine droplets as well as the catalyst, as a rule a tertiary amine. The settling procedures may optionally be assisted by passing the organic phase through settling vessels, stirred vessels, coalescers or separators or combinations
10 thereof, in which connection water may optionally be metered in in each or some of the separating steps, if necessary using active or passive mixing devices.

After this coarse separation of the alkaline, aqueous phase, the organic phase is washed once or several times with dilute acids, mineral acids, carboxylic acids,
15 hydroxycarboxylic acids and/or sulfonic acids. Preferred are aqueous mineral acids, in particular hydrochloric acid, phosphorous acid and phosphoric acid or mixtures of these acids. The concentration of these acids should be in the range 0.001 to 50 wt.%, preferably 0.01 to 5 wt.%.

20 In addition the organic phase is repeatedly washed with deionised or distilled water. The separation of the organic phase, possibly dispersed with some of the aqueous phase, after the individual wash stages is carried out by means of settling vessels, stirred vessels, coalescers or separators or combinations thereof, wherein the wash water may be metered in between the wash stages, optionally using active or passive
25 mixing devices.

Acids, preferably dissolved in the solvent used to form the polymer solution, may optionally be added between these wash stages or also after the washing procedure. Hydrogen chloride gas and phosphoric acid or phosphorous acid are preferably used
30 for this purpose, and may optionally also be used as mixtures.

Conventional additives (e.g. auxiliary substances and reinforcing agents) may be added to the polycarbonates obtained by the process according to the invention in order to alter the properties. The addition of additives and auxiliary substances serves to prolong the service life (e.g. hydrolysis stabilisers or decomposition
5 stabilisers), to improve the colour stability (e.g. thermal stabilisers and UV stabilisers), to simplify the processing (e.g. mould release agents, antiblocking agents), to improve the use properties (e.g. antistatics), to improve the flameproofing effect, to influence the optical impression (e.g. organic colourants, pigments), or to match the polymer properties to specific stresses (impact strength modifiers, finely
10 comminuted minerals, fibrous substances, quartz flour, glass fibres and carbon fibres).

The invention is discussed in more detail hereinafter with the aid of the accompanying drawings, in which

15

Fig. 1 shows diagrammatically a first embodiment of the separating vessel for carrying out the process according to the invention,

Fig. 2 shows diagrammatically a second embodiment of the separating vessel.

20

In Fig. 1 a separating vessel 9 is shown that has in its upper region a horizontally arranged plate 7 with inlet openings 8. The separating vessel 9 has an outlet 10 for the volatile constituents as well as a downwardly directed conical outlet 13 in the lower region, which is provided with a discharge device 11. Guide elements in the
25 form of wires 12 are provided in the interior of the separating vessel 9. The wires 12 are arranged substantially horizontally, wherein in each case several wires 12 form a level. The wires of a level are arranged substantially parallel to one another. Several levels of such parallel arranged wires 12 are provided (3 levels in Fig. 1), in which the wires of two superimposed levels are arranged at substantially right angles
30 with respect to one another.

The polycarbonate melt is added through a feed line 1 to the separating vessel 9. With the aid of a feed line 2 foaming agent is mixed into the polycarbonate melt through a metering device 3. The polycarbonate/foaming agent mixture is first of all led through a static mixer 4 and then through a heat exchanger 6. The polycarbonate melt flows through a pressure retention valve 5 onto the plate 7 provided with the inlet openings 8. The melt is thereby divided into partial streams. The partial streams of the polycarbonate melt pass through the inlet openings 8 and enter the separating vessel 9. On the floor 13 of the separating vessel 9 the degassed polycarbonate melt is removed via the discharge device 11.

10

Fig. 2 shows, in contrast to the embodiment illustrated in Fig. 1, in the upper region of the separating vessel 9 a vertically arranged heat exchanger 6' in the form of a shell-and-tube heat exchanger. The downwardly directed tubes constitute the inlet openings 8'.

15

According to Fig. 2 the polycarbonate melt is fed through a feed line 1 to the separating vessel 9. With the aid of a feed line 2 foaming agent is mixed through a metering device 3 into the polycarbonate melt. The polycarbonate/foaming agent mixture is first of all passed through a static mixer 4. The polycarbonate melt then flows through a pressure retention valve 5 into the inlet openings 8' of a shell-and-tube heat exchanger 6', whereby the polycarbonate melt is subdivided into a plurality of partial streams. The inlet openings 8' terminate in the separating vessel 9. At the floor 13 of the separating vessel 9 the degassed polycarbonate melt is removed via the discharge device 11.

20

Examples

5 The experiments described hereinafter were carried out on polycarbonates that were produced based on bisphenol A in the phase interface process. The volatile component to be removed was in all experiments monochlorobenzene, and in one experiment was in addition dichloromethane. The results of the experiments are summarised in Table 1.

10 The entry concentrations of the solvents before the foam degassing step and optionally before the mixing in of a foaming agent are given in Table 1. Nitrogen was used as foaming agent in all experiments in which in general a foaming agent was employed. The dispersion of the foaming agent was carried out in a static mixer of the SMX type.

15 The state of the melt is likewise specified in the table: "one-phase" means that all volatile components, including foaming agent, were completely dissolved in the melt; "two-phase" means that, on entry into the inlet openings, a two-phase mixture existed and bubbles or droplets were already present in the melt. The pressure in the static mixer could be raised by means of a pressure retention valve.

20 The pressure before the inlet opening is specified, as is the estimated vapour pressure in the melt on entry into the inlet openings, the estimated value being obtained from the temperature and concentration of volatile constituents on entry into the inlet openings. From this the supersaturation can be calculated as the
25 difference between the vapour pressure and pressure in the separator.

The relative viscosity is calculated from the ratio of the viscosity of a polymer solution to the viscosity of the pure solvent. The relative viscosity is generally determined at 25°C in dichloromethane at a concentration of 5 g of polymer per
30 1 litre of solvent.

The temperature after the static mixer, i.e. after the mixing in of the foaming agent, before entry into the inlet openings and on entry into the separator are specified in each case. From this it can be determined whether any heating has occurred between the individual process steps.

5

The specified throughput refers to the throughput per inlet opening. The inlet openings are characterised by their diameter and length.

10

The internal fittings, or guide elements, consisted of horizontally arranged wires that were clamped underneath the inlet opening in the separator at a vertical distance of 10 cm between one another. The number in the table denotes the number of wires clamped horizontally under one another. In each case two wires arranged under one another were rotated with respect to one another by 90° in the horizontal plane. The diameter of the wires was 4 mm.

15

In the experiments 1-3, 5-13 and 16 heatable tubes were used as inlet openings. In the examples the melt in these tubes was heated before the entry to the separator relative to the temperature at the entry to the inlet opening.

20

Experiment 4 was carried out with a nozzle at the end of a heatable tube. The melt was in this case heated between the mixing in of the foaming agent and the inlet opening. In Example 4 the melt was no longer further heated in the inlet opening, i.e. in the nozzle itself.

25

Experiments 14 and 15 were also carried out with heated tubes as inlet openings, though in this case the diameters were significantly smaller (4 mm) in order to generate a higher pressure loss and thus maintain the melt as a one-phase melt before the inlet opening.

30

Experiments 17 and 18 were carried out with a nozzle plate, in which the melt was no longer heated after the mixing in of the foaming agent.

The supersaturation corresponds in all examples approximately to the pressure at the inlet opening, since the pressure in the separator is 1 mbar in all experiments.

5 The influence of the supersaturation on the degassing becomes clear on the basis of experiments 1 and 2. In experiment 1, on account of the MCB concentration of 1% the supersaturation of 0.8 bar is too low to produce an effective foam degassing. 5% MCB entry concentration as in experiment 2 is sufficient however to cause the melt to foam. The melt is in both cases still a single phase melt before the inlet opening. In experiment 3, in contrast to experiment 1 0.2% nitrogen is additionally added as
10 foaming agent. The supersaturation consequently rises further, though the vapour pressure becomes so large that the melt is no longer present as a single phase. Compared to experiment 2 the degassing in experiment 3 is therefore less effective. In experiment 4 the pressure before the inlet opening was increased to such an extent by an altered geometry of the inlet opening that again a single phase flow is present
15 before the inlet opening. The degassing is even better compared to experiment 3.

The experiments 5-7 were carried out with a very low MCB entry concentration of 0.1%. The supersaturation without foaming agent is only 0.1 bar. The supersaturation is increased only by the addition of foaming agent, whereupon the
20 melt foams and the degassing proceeds down to a residual content of 17 ppm MCB. The degassing result is also slightly improved by internal fittings, as shown in experiment 7.

25 The experiments 8-10 illustrate the same effects as already discussed for experiments 5-6, though with an entry concentration of MCB of 0.5%. The foaming agent causes foaming and thus an effective degassing, while internal fittings improve the result slightly.

30 In the experiments 5-10 the flow at the entry to the degassing openings was a single phase flow, and the pressure loss in the inlet opening was also sufficiently large.

The experiments 11-13 illustrate the effect of the single phasedness on the degassing result. In experiment 12, 0.1% of foaming agent was added. The melt was still single phase before the inlet opening. In experiment 13 the amount of foaming agent was increased to 0.5%, whereby the vapour pressure rose to such an extent
5 that the melt was two-phase before the inlet opening. The residual content is accordingly slightly increased in experiment 13 compared to experiment 12. However, the degassing with foaming agent in experiments 12 and 13 is also clearly more effective than without foaming agent under otherwise identical conditions, as demonstrated in experiment 11. The experiments 11-13 were carried out with four
10 horizontal wires as internal fitting.

The experiments 14 and 15 were carried out with a heatable tube of 4 mm diameter. As shown in the table, the pressure before the inlet opening, i.e. in front of the tube, is accordingly significantly higher than in the case of the 10 mm diameter tubes,
15 despite the relatively high temperature and smaller throughput of only 2 kg/hr. The degassing with foaming agents is very effective in experiment 15, and on account of the high pressure before the inlet opening the melt is in each case single phase.

Experiment 16 is an example showing that also dichloromethane (DCM) can be
20 removed to extremely low residual contents by means of foam degassing. The DCM residual content is less than 2 ppm.

The experiments 17 and 18 were carried out with a nozzle plate without intermediate heating of the melt. The throughput per bore was 0.15 kg/hr. Due to the use of
25 foaming agents an effective removal of volatile constituents can be achieved also by using a nozzle plate.

The experiments show that a removal of volatile constituents from a polycarbonate melt down to very low residual contents is possible by foam degassing. By a
30 suitable choice of the process parameters an optimal adjustment as regards temperature, amounts of foaming agent and solvent, and pressure loss can be found for different apparatus configurations.

Table 1:

Expm.	Entry Solvent		Entrainment Agent		State of Melt	Through-put PC*** [kg/hr]	Relative Viscosity	Inlet Opening		Temperatures			Vapour press. at entry to sepr. [bar]	Press. at inlet opening [bar]	Press. of separator [mbar]	Intnl. fitting horiz. wires	Residual Content	
	MCB* [wt.%]	DCM** [wt.%]	Type [wt.%]	Amount [wt.%]				Diam. [mm]	Length [mm]	After mixer [°C]	Inlet opening [°C]	Sep- arator [°C]					MCB* [ppm]	DCM** [ppm]
1	1.0	-	-	-	sngl-phs	3	1.288	10	1150	280	280	300	0.8	10.4	1	-	126	****
2	5.0	-	-	-	sngl-phs	3	1.288	10	1150	280	280	300	3.7	4.9	1	-	10	****
3	1.0	-	N2	0.2	two-phs	3	1.288	10	1150	280	280	300	>10	2.6	1	-	45	****
4	1.0	-	N2	0.2	sngl-phs	3	1.31	3.5	50	280	300	300	>10	20.6	1	-	<20	****
5	0.1	-	-	-	sngl-phs	5	1.288	10	1150	295	295	315	0.1	23.5	1	-	934	****
6	0.1	-	N2	0.3	sngl-phs	5	1.288	10	1150	295	295	315	>15	23	1	-	17	****
7	0.1	-	N2	0.3	sngl-phs	5	1.288	10	1150	295	295	315	>15	22	1	10	7	****
8	0.5	-	-	-	sngl-phs	5	1.288	10	1150	295	295	315	0.4	20.6	1	-	1600	****
9	0.5	-	N2	0.3	sngl-phs	5	1.288	10	1150	295	295	315	>15	21.8	1	-	20	****
10	0.5	-	N2	0.3	sngl-phs	5	1.288	10	1150	295	295	315	>15	19.3	1	10	13	****
11	0.5	-	-	-	sngl-phs	3	1.288	10	1150	280	280	330	0.6	9.4	1	4	340	****
12	0.5	-	N2	0.1	sngl-phs	3	1.288	10	1150	280	280	330	>10	10.1	1	4	11	****
13	0.5	-	N2	0.5	two-phs	3	1.288	10	1150	280	280	330	>20	11.2	1	4	18	****
14	0.5	-	-	-	sngl-phs	2	1.288	4	300	310	310	315	0.5	42.9	1	-	955	****
15	0.5	-	N2	0.2	sngl-phs	2	1.288	4	300	310	310	315	>15	40	1	-	10	****
16	9.6	0.4	-	-	sngl-phs	5	1.288	10	1150	280	280	295	6.1	6.5	1	-	60	<2
17	0.5	-	-	-	sngl-phs	0.15	1.288	1	10	315	315	315	0.5	63	1	-	235	****
18	0.5	-	N2	0.2	sngl-phs	0.15	1.288	1	10	315	315	315	>15	51	1	-	30	****

* Monochlorobenzene

** Dichloromethane

*** Polycarbonate per partial stream in a pressure release device

**** not measured

Patent Claims

1. Process for the isolation of polycarbonate produced by the phase interface process, from a solution in an organic solvent, comprising the following steps:

5

 - (a) evaporation of the organic solvent to obtain a content of polycarbonate of 90 to 99.95 wt.%,
 - 10 (b) optionally mixing the melt obtained in step (a) with a foaming agent,
 - (c) degassing of the melt obtained from (a) or optionally (b) by feeding the melt through inlet openings into a separating vessel,
 - 15 characterised in that

in the degassing according to step (c) the melt is subdivided by the inlet openings into partial streams of 0.1 to 20 kg/hr and on entry into the inlet openings has a supersaturation with volatile constituents of at least 1 bar as well as a temperature of 250° to 340°C, wherein the pressure in the

20 separating vessel is 0.1 to 20 mbar.
2. Process according to claim 1, characterised in that before the degassing according to step (c) the melt obtained from (a) is mixed with a foaming agent in a step (b).

25
3. Process according to claim 2, characterised in that the foaming agent is completely dissolved on entry into the inlet openings according to step (c).
- 30 4. Process according to one of claims 1 to 3, characterised in that the residence time in the separating vessel according to step (c) is at most 10 minutes.

5. Process according to one of claims 1 to 4, characterised in that substantially horizontally arranged guide elements, in particular wires, are provided in the separating vessel.
- 5 6. Process according to one of claims 1 to 5, characterised in that the melt is heated or cooled between the steps (a) and (b) and/or (b) and (c).
7. Process according to one of claims 1 to 6, characterised in that the melt is heated after entry into the inlet openings.
- 10 8. Polycarbonate produced according to one of claims 1 to 7.