

- 1 -

Preparation of polycarbonate which is damaged to a particularly small extent by oxygen

The present invention relates to a process for the
5 preparation or processing of polycarbonate using apparatus or equipment in which the leakage rate is $< 10^{-3}$ litre He x mbar/sec, as well as the polycarbonates obtainable therewith.

10 Polycarbonate that is prepared by the phase interface process is subjected in some cases to extreme temperatures ($>200^{\circ}\text{C}$) in order to evaporate the solvent. The presence of oxygen leads in this connection to permanent damage of the polycarbonate.

15

In previous specifications only the reduction of the oxygen content in the bisphenolate solution (DE-A 1 99 43 643, DE-A 1 99 43 644, WO-A 2000/39060) and the contact of bisphenol melt with oxygen (JP-A 06 025 044,

20 JP-A 06 025 045) has been described, and its positive influence on the colour quality of the polycarbonate has been emphasised. Furthermore the addition of nitrogen in the extrusion of polycarbonate melt has been described (JP-A 08 132 437). In the processes according to the prior
25 art the polycarbonate is nevertheless still damaged.

Polycarbonate that is prepared by the melt transesterification process is as melt subjected in some cases to extreme temperatures ($>270^{\circ}\text{C}$) at absolute
30 pressures down to 0.01 mbar during the course of the reaction. The presence of oxygen similarly leads to a permanent damage of the polycarbonate.

In previous specifications the reduction of the contact of
35 the educts with oxygen during mixing and melting

- 2 -

(JP-A 6 032 887, JP-A 8 157 588), the reduction of the contact of BPA with oxygen during melting (JP-A 8 157 587) as well as the reduction of the contact of the diphenyl carbonate melt with oxygen (JP-A 3 216 832) have been described and the positive effect on the colour quality of the polycarbonate has been emphasised. In the processes according to the prior art the polycarbonate is nevertheless still damaged.

10 In EP-A 708 128 a melt transesterification process for polycarbonate in an inert, low oxygen content gaseous atmosphere is described. The first half of the reaction is preferably carried out without application of a vacuum under cleavage of phenol in a reactor space that is

15 permanently flushed with an inert, possibly pretreated gas with a low oxygen content (at least < 2 ppm). The end phase of the reaction is carried out with an increase in the vacuum. The execution of this process under exclusion of oxygen however proves to be extremely disadvantageous and undesirable in large-scale production. A circulation

20 of the inert gas streams is therefore advantageous for the economy of a continuous process. If these streams are to be recycled they have to be freed from phenol however, which is extremely complicated. A preferred further

25 pretreatment of the inert gas for additional reduction of the oxygen content furthermore makes the method even more cost-intensive.

On the basis of the prior art there was therefore a need to

30 develop a process that permits the largely damage-free preparation or processing of polycarbonate in a comparatively more simple and cost-effective procedure.

It has now surprisingly been found that it is sufficient if

35 the apparatus in which the polycarbonate melt is prepared or processed has a leakage rate of $< 10^{-3}$ litre He x

- 3 -

mbar/sec. Ideally all vessels, apparatus, pumps and pipelines that are used in the preparation and/or processing of polycarbonate, but at the very least the apparatus in which reduced pressure (<1 bar absolute) is applied, such as for example large capacity vessels, pipelines, separators or cyclones; stirred vessels, forced circulation evaporators, falling-film evaporators, pipe/strand evaporators, single-shaft or twin-shaft cage reactors or disc reactors, or other commercially obtainable apparatus as well as associated vacuum equipment and vapour systems, vaporisation extruders, pipe/strand evaporators and injection moulding machines and extruders, will meet this requirement.

15 The invention accordingly provides a process for the preparation or processing of polycarbonate using equipment and apparatus whose leakage rate is $< 10^{-3}$ litre He x mbar/sec, preferably $< 10^{-4}$ litre He x mbar/sec, particularly preferably $< 10^{-5}$ litre He x mbar/sec, and most particularly preferably $< 10^{-6}$ litre He x mbar/sec.

The leakage rates are measured for example by connecting a helium gas measuring instrument from Leybold, type 100, 100 plus or 200 or comparable equipment to the vapour inlets of a plant for the preparation or processing of polycarbonate, optionally with an intermediately connected forepump that optionally heads only a partial stream of the amount of gas to the measuring instrument. The flanges of the whole arrangement, which is under reduced pressure, are flushed with helium gas from a gas cylinder, using a gas lance. The measuring instrument measures the amount of helium that is drawn in through the flanges and indicates a leakage rate. In this connection a leakage rate of $< 10^{-3}$ litre He x mbar/sec is counted as tight, and a leakage rate $> 10^{-3}$ litre He x mbar/sec is counted as a leak. Measurements on a test leak may optionally be carried out

- 4 -

before performing the actual measurement. In addition it is recommended to determine the baseline concentration of helium in the ambient atmosphere by means of the measuring instrument. This concentration is then used as a zero
5 value or reference value. Leaks in the flange connections may also be found by means of ultrasound and using leak spray, though in this case the detection limit is 10^{-2} litre He x mbar/sec and is thus less sensitive than the described helium leakage test.

10

The helium leakage test is first of all carried out when the system is cold. The system is then heated to the desired operating temperatures and all flanges are tightened before repeating the leakage test. Only if this
15 leakage test gives a positive result does the system satisfy the requirements.

The polycarbonate prepared in this way is characterised by an improved colour quality and is also the subject of the
20 present application.

The particular advantage of this process is that the hermeticity of the apparatus can easily be tested by means of a helium leakage test and thus, surprisingly,
25 displacement gases for oxygen, such as for example nitrogen, and the associated equipment are not necessary.

The polycarbonate is prepared for example by the phase interface process. This process for the polycarbonate
30 synthesis is described in many places in the literature, including *inter alia* in

- Schnell, "Chemistry and Physics of Polycarbonates", Polymer Reviews, Volume 9, Interscience Publishers,
35 New York, London, Sydney 1964, pp. 33-70;

- D.C. Prevorsek, B.T. Debona and Y. Kesten, Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960: "Synthesis of Poly(ester Carbonate) Copolymers" in Journal of Polymer Science, 5 Polymer Chemistry Edition, Vol. 18, (1980), pp. 75-90;
- D. Freitag, U. Grigo, P.R. Müller, N. Nouvertne', BAYER AG, "Polycarbonates" in Encyclopedia of Polymer 10 Science and Engineering, Volume 11, 2nd Edition, 1988, pp. 651-692, and finally
- Dres. U. Grigo, K. Kircher and P.R. Müller "Polycarbonate" in Becker/ Braun, Kunststoff-Handbuch, 15 Vol. 3/1, Polycarbonate, Polyacetale, Polyester, Celluloseester, Carl Hanser Verlag Munich, Vienna 1992, pp. 118-145,

as well as for example in EP-A 0 517 044 and many other
20 patent applications.

According to this process the phosgenation of a disodium salt of a bisphenol (or a mixture of different bisphenols) in aqueous-alkaline solution (or suspension) is carried out
25 in the presence of an inert organic solvent or solvent mixture, which forms a second phase. The oligocarbonates that are formed and that are mainly present in the organic phase are condensed with the aid of suitable catalysts to form high molecular weight polycarbonates that are
30 dissolved in the organic phase. The organic phase is finally separated and the polycarbonate is isolated by various working-up steps.

In this process an aqueous phase consisting of NaOH, one or
35 more bisphenols and water is used, wherein the

concentration of this aqueous solution with respect to the sum total of bisphenols, calculated not as sodium salt but as free bisphenol, may vary between 1 and 30 wt.%, preferably between 3 and 25 wt.%, particularly preferably between 3 and 8 wt.% for polycarbonates with an $M_w > 45,000$, and 12 to 22 wt.% for polycarbonates with an $M_w < 45,000$. In this connection it may be necessary in the case of higher concentrations to thermostatically control the solutions. The sodium hydroxide used to dissolve the bisphenols may be employed in solid form or as aqueous sodium hydroxide solution. The concentration of the sodium hydroxide solution is governed by the target concentration of the desired bisphenolate solution, but as a rule is between 5 and 25 wt.%, preferably between 5 and 10 wt.%, or may be chosen to be more concentrated, in which case it is then diluted with water. In the process involving subsequent dilution sodium hydroxide solutions with concentrations between 15 and 75 wt.%, preferably between 25 and 55 wt.%, optionally heated, are used. The alkali content per mole of bisphenol depends very largely on the structure of the bisphenol but varies as a rule between 0.25 mole of alkali per mole of bisphenol and 5.00 mole of alkali per mole of bisphenol, preferably 1.5-2.5 mole of alkali per mole of bisphenol, and in the case where bisphenol A is used as sole bisphenol, is 1.85-2.15 mole of alkali. If more than one bisphenol is used, then these may be dissolved together. It may however also be advantageous to dissolve the bisphenols separately in an optimal alkaline phase and to meter in the solutions separately or alternatively to add them combined to the reaction. In addition it may be advantageous to dissolve the bisphenol or bisphenols not in sodium hydroxide solution but in dilute bisphenolate solution to which additional alkali has been added. The dissolution processes may start from solid bisphenol, generally in flakes or prill form, or also from molten bisphenol. The sodium hydroxide or sodium hydroxide

- 7 -

solution that is used may be prepared by the amalgam process or the so-called membrane process. Both processes have been in use for a long time and are known to the person skilled in the art. Sodium hydroxide prepared by
5 the membrane process is preferably employed.

The thus prepared aqueous phase is phosgenated together with an organic phase consisting of solvents for polycarbonate that are inert to the reactants and that form
10 a second phase.

The optionally employed metering of bisphenol after or during the addition of the phosgene may be continued as long as phosgene or its immediate secondary products,
15 namely chlorinated carbonic acid esters, are present in the reaction solution.

The synthesis of polycarbonates from bisphenols and phosgenes in an alkaline medium is an exothermic reaction
20 and is carried out in a temperature range from -5°C to 100°C, preferably 15°C to 80°C, most particularly preferably 25°C to 65°C, wherein the reaction possibly has to be carried out under excess pressure depending on the solvent or solvent mixture.

25 Suitable diphenols for the preparation of the polycarbonates to be used according to the invention include for example hydroquinone, resorcinol, dihydroxydiphenyl, bis-(hydroxyphenyl)alkanes, bis-
30 (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
35 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, 1,1-bis-(4-hydroxyphenyl)-m/p-diisopropylbenzene, 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-methyl-butane, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-m/p-diisopropylbenzene and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.

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.

20

These and further suitable diphenols are described for example in US-A 2 999 835, 3 148 172, 2 991 273, 3 271 367, 4 982 014 and 2 999 846, in German laid-open specifications 1 570 703, 2 063 050, 2 036 052, 2 211 956 and 3 832 396, in French patent specification 1 561 518, in the monograph by H. Schnell "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York 1964, pp. 28 ff.; pp. 102 ff., and in D.G. Legrand, J.T. Bendler, "Handbook of Polycarbonate Science and Technology", Marcel Dekker, New York 2000, pp. 72 ff.

In the case of homopolycarbonates only one diphenol is used, while in the case of copolycarbonates several diphenols are used, in which connection the bisphenols that are used as well as all other chemicals and auxiliary

35

substances added to the synthesis may obviously be contaminated with impurities originating from their actual synthesis, handling and storage, although it is desirable to use raw materials that are as clean as possible.

5

The organic phase may consist of one solvent or mixtures of several solvents. Suitable solvents include chlorinated hydrocarbons (aliphatic and/or aromatic), preferably dichloromethane, trichlorethylene, 1,1,1-trichloroethane,
10 1,1,2-trichloroethane and chlorobenzene and their mixtures. Aromatic hydrocarbons such as benzene, toluene, m/p/o-xylene or aromatic ethers such as anisole may however also be used, alone, as a mixture, or additionally as a mixture with chlorinated hydrocarbons. Another embodiment of the
15 synthesis uses solvents that do not dissolve but only swell polycarbonate. Accordingly precipitation agents for polycarbonate may also be used in combination with solvents for polycarbonate. In this case solvents such as tetrahydrofuran, 1,3-/1,4-dioxane or 1,3-dioxolane that are
20 also soluble in the aqueous phase may then be used as solvents if the solvent partner forms the second organic phase.

The two phases forming the reaction mixture are mixed in
25 order to accelerate the reaction. This is effected by supplying energy via shear forces, i.e. pumps or stirrers or by static mixers, or by generating turbulent flow by means of nozzles and/or diaphragms. Combinations of these measures are also employed, often also repeated over time
30 or as regards sequence of equipment. Anchor, propeller, MIG stirrers, etc., such as are described for example in Ullmann "Encyclopedia of Industrial Chemistry", 5th Edition, Vol. B2, pp. 251 ff. are preferably used as stirrers. Centrifugal pumps, often also multi-stage pumps are
35 employed as pumps, 2- to 9-stage pumps being preferred.

- 10 -

Perforated diaphragms or alternatively tapering tubular pieces or also Venturi or Lefos nozzles are used as nozzles and/or diaphragms.

5 The phosgene may be added in gaseous or liquid form or dissolved in solvents. The phosgene excess that is employed, referred to the sum total of the bisphenols used, is between 3 and 100 mole %, preferably between 5 and 50 mole %. In this connection the pH value of the aqueous
10 phase during and after addition of phosgene is maintained in the alkaline range, preferably between 8.5 and 12, by single or repeated additional metering in of sodium hydroxide solution or appropriate additional metering in of bisphenolate solution, whereas after the addition of
15 catalyst the pH should be between 10 and 14. The temperature during the phosgenation is 25° to 85°C, preferably 35° to 65°C; the phosgenation may also be carried out under excess pressure depending on the solvent that is used.

20

The phosgene may be metered directly into the aforescribed mixture of the organic and aqueous phase or however may also be wholly or partially metered, before the mixing of the phases, into one of the two phases, which is
25 then mixed with the corresponding other phase. In addition the phosgene may be metered wholly or partially into a recycled partial stream of the synthesis mixture from both phases, this partial stream preferably being recycled before the catalyst addition. In another embodiment the
30 aforescribed aqueous phase is mixed with the phosgene-containing organic phase and is then added after a residence time of 1 second to 5 minutes, preferably 3 seconds to 2 minutes, to the recycled partial stream mentioned above, or alternatively the two phases, namely
35 the aforescribed aqueous phase together with the phosgene-containing organic phase, are mixed directly in

- 11 -

the recycled partial stream mentioned above. In all these embodiments the aforescribed pH ranges should be observed and if necessary maintained by single or repeated additional metering in of sodium hydroxide solution or
5 appropriate additional metering in of bisphenolate solution. Also, the temperature range must be maintained, if necessary by cooling or dilution.

The polycarbonate synthesis may be effected continuously or
10 discontinuously. The reaction may accordingly take place in stirred vessels, tubular reactors, pump reactors or stirred vessel cascades or combinations thereof, in which connection it should be ensured by employing the already mentioned mixing devices that, as far as possible, the
15 aqueous and organic phases demix only when the synthesis mixture has fully reacted, i.e. no longer contains saponifiable chlorine from phosgene or chlorinated carbonic acid esters.

20 The monofunctional chain terminators required to regulate the molecular weight, such as phenol or alkylphenols, in particular phenol, p-tert.-butylphenol, isooctylphenol, cumylphenol, their chlorinated carbonic acid esters or acid chlorides of monocarboxylic acids or mixtures of these
25 chain terminators, are added either together with the bisphenolate or bisphenolates to the reaction, or alternatively are added at any appropriate time during the synthesis as long as phosgene or chlorinated carbonic acid terminal groups are still present in the reaction mixture,
30 or in the case where acid chlorides and chlorinated carbonic acid esters are used as chain terminators, as long as sufficient phenolic terminal groups of the polymer that is being formed are available. Preferably the chain terminator or terminators are however added after the
35 phosgenation at a site or at a time when phosgene is no longer present but the catalyst has not yet been added, or

- 12 -

are added before the catalyst, together with the catalyst, or parallel thereto.

In the same way branching agents or branching agent
5 mixtures that are possibly used are added to the synthesis, normally however before the chain terminators. Trisphenols, quaternary phenols or acid chlorides of tricarboxylic acids or tetracarboxylic acids are normally used, but also mixtures of the polyphenols or acid
10 chlorides.

Some of the compounds containing three or more than three phenolic hydroxyl groups that may be used include for example:

15 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,
20 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.

25 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,

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

The catalysts used in the phase interface synthesis include
35 tertiary amines, in particular triethylamine, tributylamine, trioctylamine, N-ethylpiperidine, N-

- 13 -

- methylypiperidine, N-i/n-propylpiperidine; quaternary ammonium salts such as tetrabutylammonium/tributylbenzylammonium/tetraethylammonium hydroxide/chloride/bromide/hydrogen sulfate/tetrafluoroborate, as
5 well as the phosphonium compounds corresponding to the ammonium compounds. In this context ammonium and phosphonium compounds are also jointly referred to as onium compounds.
- 10 These compounds are described as typical phase interface catalysts in the literature, are commercially available, and are known to the person skilled in the art. The catalysts may be added individually, as a mixture, or also
15 optionally also added before the phosgenation, though addition after the introduction of the phosgene is preferred irrespective of whether one onium compound or mixtures of onium compounds are used as catalysts, in which case an addition before the metering of the phosgene is
20 preferred.

The metering in of the catalyst or catalysts may take place without solvent, in an inert solvent, preferably that used for the polycarbonate synthesis, or also as an aqueous
25 solution, and in the case of tertiary amines as their ammonium salts with acids, preferably mineral acids, in particular hydrochloric acid. When using several catalysts or when metering in partial amounts of the total quantity of catalyst different metering procedures may of course
30 also be used at different sites or at different times.

The total amount of the catalysts that are used is between 0.001 to 10 mole % referred to moles of bisphenols employed, and is preferably 0.01 to 8 mole %, particularly
35 preferably 0.05 to 5 mole %.

- 14 -

After addition of the phosgene it may be advantageous to mix the organic phase and the aqueous phase for a certain time, before optionally branching agent (where this is not metered in jointly with the bisphenolate), chain terminator and catalyst are added. Such a subsequent stirring time may be advantageous after each addition. These subsequent stirring times, insofar as they are employed, are between 10 seconds and 60 minutes, preferably between 30 seconds and 40 minutes and particularly preferably between 1 minute and 15 minutes.

The at least two-phase reaction mixture that has fully reacted and contains at most only traces (preferably <2ppm) of chlorinated carbonic acid esters, is allowed to settle before the phase separation. The aqueous alkaline phase is if necessary recycled in whole or in part to the polycarbonate synthesis as aqueous phase, or is added to the waste water treatment stage, where solvent and catalyst fractions are separated and recycled. In another variant of the working-up process, after separating the organic impurities, in particular solvents and polymer residues, and optionally after adjusting a specific pH value, for example by addition of sodium hydroxide, the salt is separated, which can be fed for example to a chlorine-alkali electrolysis plant, while the aqueous phase is optionally recycled to the synthesis.

The organic phase containing the polymer now only has to be purified to remove all contaminants of an alkaline, ionic or catalytic nature. It also contains after one or more settling stages, optionally assisted by passage through settling tanks, stirred vessels, coalescers or separators or combinations of these measures - in which connection water may optionally be added at each or some of the separating steps, optionally using active or passive mixing equipment - portions of the aqueous alkaline phase in the

- 15 -

form of fine droplets as well as the catalyst, as a rule a tertiary amine.

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

In addition the organic phase is repeatedly washed with deionised or distilled water. The separation of the
15 organic phase, optionally dispersed with portions of the aqueous phase, is carried out after the individual wash stages by means of settling tanks, stirred vessels, coalescers or separators or combinations of these measures, in which connection the wash water may optionally be added
20 between the wash stages, optionally using active or passive mixing equipment.

Acids, preferably dissolved in the solvent used for the polymer solution, may optionally be added between these
25 wash stages or also after the wash process. Gaseous hydrogen chloride and phosphoric acid or phosphorous acid are preferred in this connection, and may optionally also be employed as mixtures.

30 The purified polymer solution thereby obtained should after the last separation process contain not more than 5 wt.%, preferably less than 1 wt.%, and most particularly preferably less than 0.5 wt.% of water.

35 The polymer may be isolated from the solution by evaporating the solvent by means of heat, vacuum or a

- 16 -

heated entrainment gas. Other isolating methods include crystallisation and precipitation.

If the concentration of the polymer solution and possibly
5 also the isolation of the polymer takes place by distilling
off the solvent, optionally by superheating and release of
pressure, this is referred to as a "flash" process; see also
"Thermische Trennverfahren", VCH Verlagsanstalt 1988,
p. 114; if alternatively a heated carrier gas is sprayed
10 together with the solution to be evaporated, then this is
referred to as a "spray evaporation/spray drying", described
for example in Vauck, "Grundoperationen chemischer
Verfahrenstechnik", Deutscher Verlag für Grundstoffindustrie
2000, 11th Edition, p. 690. All these processes are
15 described in the patent literature and in textbooks and are
known to the person skilled in the art.

When removing the solvent by heat (distillation) or the
technically more effective flash process, highly
20 concentrated polymer melts are obtained. In the known
flash process polymer solutions are repeatedly heated under
slight excess pressure to temperatures above the boiling
point under normal pressure, and these solutions,
superheated with respect to normal pressure, are then
25 flashed in a vessel at a lower pressure, for example normal
atmospheric pressure. It may in this connection be
advantageous not to allow the concentration stages to
become too large, or in other words the temperature stages
of the superheating to become too large, but instead to
30 select a two-stage to four-stage process.

The residues of the solvent may be removed from the highly
concentrated polymer melts that are thereby obtained,
either directly from the melt using evaporation extruders
35 (BE-A 866 991, EP-A 0 411 510, US-A 4 980 105,

- 17 -

DE-A 33 32 065), thin-layer evaporators (EP-A 0 267 025), falling-film evaporators, strand evaporators, or by friction compaction (EP-A 0 460 450), optionally also under the addition of an entrainment agent such as nitrogen or carbon dioxide or by employing a vacuum (EP-A 003 996, EP-A 0 256 003, US-A 4 423 207) or alternatively by subsequent crystallisation (DE-A 3 429 960) and heating of the solvent residues in the solid phase (US-A 3 986 269, DE-A 2 053 876).

10

Granules are obtained preferably by direct spinning of the melt and subsequent granulation, or by the use of discharge extruders from which the granules are spun in air or under a liquid, generally water. If extruders are used, then additives may be added to the melt upstream of this extruder, optionally with the use of static mixers or through side extruders in the extruder.

By means of an atomisation procedure the polymer solution, optionally after heating, is sprayed either into a vessel at reduced pressure or is sprayed by means of a nozzle using a heated carrier gas, for example nitrogen, argon or steam, into a vessel at normal atmospheric pressure. In both cases, depending on the concentration of the polymer solution, powder (diluted) or flakes (concentrated) of the polymer are obtained, from which if necessary the last residues of the solvent also have to be removed, as described above. Granules can then be obtained using a compounding extruder followed by spinning. Here too additives, as described above, may be added to the peripheral equipment or to the extruder itself. A compacting step for the polymer powder often has to be employed before the extrusion on account of the low bulk density of the powders and flakes.

35

- 18 -

The polymer can be precipitated largely in crystalline form from the washed and optionally also concentrated solution of the polycarbonate by adding a precipitating agent for polycarbonate. In this connection it is advantageous to
5 add first of all a minor amount of the precipitating agent and optionally also to employ waiting times between the additions of the batches of precipitating agent. It may also be advantageous to use different precipitating agents. Hydrocarbons, in particular heptene, i-octane, cyclohexane
10 and alcohols such as methanol, ethanol and i-propanol may for example be used in this connection as precipitating agents.

In the precipitation the polymer solution is as a rule
15 slowly added to a precipitating agent, alcohols such as methanol, ethanol, i-propanol but also cyclohexane or ketones such as acetone generally being used here as precipitating agents.

20 The materials thereby obtained are processed into granules as described in the spray vaporisation and optionally contain additives.

According to other processes precipitation and
25 crystallisation products or amorphously solidified products are crystallised in finely granular form by passing thereover vapours of one or more precipitating agents for polycarbonate while simultaneously heating below the glass transition temperature, and are condensed further into
30 higher molecular weight products. If these products are oligomers, possibly with different terminal groups (phenolic and chain-terminating groups), this is referred to as solid phase condensation.

- 19 -

In addition the polycarbonate may be prepared according to the invention also by the melt transesterification process. The preparation of aromatic oligocarbonates and polycarbonates by the melt transesterification process is known in the literature and is described for example in the Encyclopedia of Polymer Science, Vol. 10 (1969), Chemistry and Physics of Polycarbonates, Polymer Reviews, H. Schnell, Vol. 9, John Wiley and Sons, Inc. (1964) as well as in DE-C 10 31 512, US-B 3,022,272, US-B 5,340,905 and US-B 5,399,659.

According to this process aromatic dihydroxy compounds are transesterified with carbonic acid diesters in the melt, with the aid of suitable catalysts and optionally further additives.

Suitable dihydroxyaryl compounds for the process according to the invention are those of the Formula (I)

HO-Z-OH (I)

wherein Z is an aromatic group having 6 to 30 C atoms, which may contain one or more aromatic nuclei, may be substituted and may contain aliphatic or cycloaliphatic groups or alkylaryls or heteroatoms as bridging members.

Examples of dihydroxyaryl compounds of the formula (I) include 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-

- 20 -

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).

5 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
10 (bisphenol TMC).

These and further suitable diphenols are described for example in US-A 2 999 835, 3 148 172, 2 991 273, 3 271 367, 4 982 014 and 2 999 846, in German laid-open
15 specifications 1 570 703, 2 063 050, 2 036 052, 2 211 956 and 3 832 396, in French patent specification 1 561 518, in the monograph by H Schnell "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York 1964, pp. 28ff; pp.102ff, and in D.G. Legrand, J.T. Bendler,
20 "Handbook of Polycarbonate Science and Technology", Marcel Dekker New York 2000, pp. 72ff..

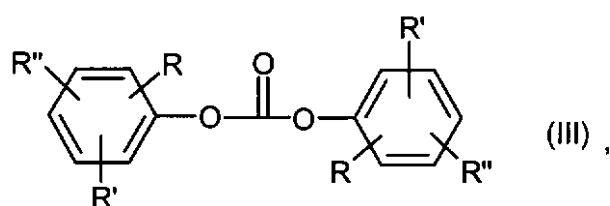
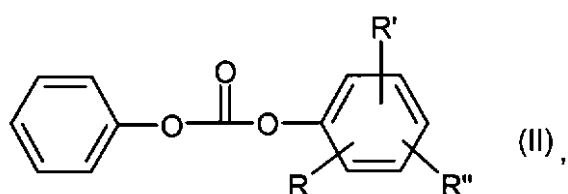
In the case of homopolycarbonates only one diphenol is used, while in the case of copolycarbonates several
25 diphenols are used, in which connection the bisphenols that are used as well as all other chemicals and auxiliary substances added to the synthesis may obviously be contaminated with impurities originating from their actual synthesis, handling and storage, although it is desirable
30 to use raw materials that are as clean as possible.

The dihydroxyaryl compounds may also be used containing residual amounts of the monohydroxyaryl compounds from which they have been prepared. These amounts may be up to

- 21 -

20%, preferably 10%, particularly preferably up to 5% and most particularly preferably up to 2% (see for example EP-A 1 240 232).

- 5 Carbonic acid diesters within the context of the invention are those of the formulae (II) and (III)



10 wherein

R, R' and R'', independently of one another, may denote H, optionally branched C₁-C₃₄-alkyl/cycloalkyl, C₇-C₃₄-alkylaryl or C₆-C₃₄-aryl,

15

for example:

diphenyl carbonate, butylphenyl phenyl carbonate, dibutyl phenyl carbonate, isobutylphenyl phenyl carbonate,
 20 diisobutyl phenyl carbonate, tert.butylphenyl phenyl carbonate, ditert.butyl phenyl carbonate, n-pentylphenyl phenyl carbonate, di(n-pentylphenyl) carbonate, n-hexylphenyl phenyl carbonate, di(n-hexylphenyl) carbonate, cyclohexylphenyl phenyl carbonate, dicyclohexyl phenyl
 25 carbonate, phenylphenol phenyl carbonate, diphenylphenol carbonate, isooctylphenyl phenyl carbonate, diisooctyl phenyl carbonate, n-nonylphenyl phenyl carbonate, di(n-nonylphenyl) carbonate, cumylphenyl phenyl carbonate, dicumyl phenyl carbonate, naphthylphenyl phenyl carbonate,

- 22 -

dinaphthyl phenyl carbonate, ditert.butylphenyl phenyl carbonate, di(di-tert.butylphenyl) carbonate, dicumylphenyl phenyl carbonate, di(dicumylphenyl) carbonate, 4-phenoxyphenyl phenyl carbonate, di(4-phenoxyphenyl) carbonate, 3-pentadecylphenyl phenyl carbonate, di(3-pentadecylphenyl) carbonate, tritylphenyl phenyl carbonate, ditrityl phenyl carbonate, 2-bis-methylsalicyl carbonate, 2-bis-ethylsalicyl carbonate

10 preferably

diphenyl carbonate, tert.butylphenyl phenyl carbonate, ditert.butyl phenyl carbonate, phenylphenol phenyl carbonate, diphenylphenol carbonate, cumylphenyl phenyl carbonate, dicumyl phenyl carbonate,

particularly preferably diphenyl carbonate.

The diarylcarbonates may be used also containing residual amounts of the monohydroxyaryl compounds from which they have been prepared. The amounts may be up to 20%, preferably 10%, particularly preferably up to 5% and most particularly preferably up to 2%.

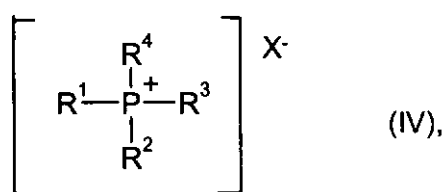
25 In addition, the phenolic compounds employed as carbonates may also be used directly as monohydroxyaryl compound in addition to one of the aforementioned carbonates, in order to influence the end groups of the polycarbonate. In this connection a monohydroxyaryl compound should be chosen whose boiling point lies above that of the monohydroxyaryl compound from which the diaryl carbonate was formed. Preferred mixtures are those with diphenyl carbonate. In the process according to the invention it is possible to add the monohydroxyaryl compound at any point during the reaction, preferably at the start of the reaction, and the addition may be divided into several portions. The content

- 23 -

of free monohydroxyaryl compound may be 0.4 to 17 mole %, preferably 1.3 to 8.6 mole % (referred to the dihydroxyaryl compound). In this connection the addition may take place before the reaction as well as wholly or partially during
5 the reaction.

Referred to the dihydroxyaryl compound, the diaryl carbonates are used in an amount of 1.02 to 1.30 moles, preferably 1.04 to 1.26 moles, particularly preferably 1.06
10 to 1.22 moles per mole of dihydroxyaryl compound. Mixtures of the diaryl carbonates mentioned above may also be used.

As catalysts within the context of the invention there are used in the melt transesterification process basic
15 catalysts as described in the aforementioned literature, such as for example alkali metal and alkaline earth metal hydroxides and oxides, but also ammonium or phosphonium salts, hereinafter termed onium salts. Onium salts are preferably used in this connection, phosphonium salts being
20 particularly preferred. Phosphonium salts within the context of the invention are those of the Formula (IV)



wherein

25

R^{1-4} may be identical or different C_1 - C_{10} -alkyls, C_6 - C_{10} -aryls, C_7 - C_{10} -aralkyls or C_5 - C_6 -cycloalkyls, preferably methyl or C_6 - C_{14} -aryls, particularly preferably methyl or phenyl, and

30

X^- may be an anion such as hydroxide, sulfate, hydrogen sulfate, hydrogen carbonate, carbonate, a halide,

- 24 -

preferably chloride, or an alcoholate of the formula OR, wherein R may be C₆-C₁₄-aryl or C₇-C₁₂-aralkyl, preferably phenyl.

- 5 Preferred catalysts are tetraphenylphosphonium chloride, tetraphenylphosphonium hydroxide, tetraphenylphosphonium phenolate, particularly preferably tetraphenylphosphonium phenolate.
- 10 The catalysts are preferably used in amounts of 10⁻⁸ to 10⁻³ mole, referred to one mole of bisphenol, and particularly preferably in amounts of 10⁻⁷ to 10⁻⁴ mole.

- Further catalysts may be used alone or optionally in
- 15 addition to the onium salt, in order to increase the rate of polymerisation. These include salts of alkali metals and alkaline earth metals, such as hydroxides, alkoxides and aryloxides of lithium, sodium or potassium, preferably sodium hydroxide, sodium alkoxides or sodium aryloxides.
- 20 Sodium hydroxide and sodium phenolate are most particularly preferred. The amounts of the co-catalyst may be in the range from 1 to 500 ppb, preferably 5 to 300 ppb and most particularly preferably 5 to 200 ppb, in each case calculated as sodium.

25

- The addition of the catalysts takes place in solution in order to avoid harmful excess concentrations when they are metered in. The solvents are compounds inherent to the system and process, such as for example dihydroxyaryl
- 30 compounds, diaryl carbonates or monohydroxyaryl compounds. Monohydroxyaryl compounds are particularly preferred since, as is known to the person skilled in the art, the dihydroxyaryl compounds and diaryl carbonates readily alter and decompose even at slightly elevated temperatures,
- 35 especially under the action of catalysts. The compounds that are formed reduce the quality of the polycarbonate.

- 25 -

In the technically important transesterification process for the preparation of polycarbonate, the preferred compound is phenol. Phenol is also particularly recommended since the preferred catalyst, i.e.

- 5 tetraphenylphosphonium phenate, is isolated in the form of mixed crystals with phenol in the preparation.

The temperatures throughout the whole process are between 180 and 330°C, and the pressures are between 15 bar
10 absolute and 0,01 mbar.

In the present invention there are no particular limitations however as regards pressures and temperatures needed to carry out the melt transesterification reaction
15 between the dihydroxyaryl compound and the carbonic acid diester. All conditions are possible as long as the selected temperatures and pressures permit a melt transesterification under appropriately rapid removal of the monohydroxyaryl compound.

20

Also there are no limitations as regards the type of equipment in which the present invention is carried out.

Preferably the continuous process for the preparation of
25 polycarbonates by transesterification of diaryl carbonates with dihydroxyaryl compounds is characterised in that, using catalysts, after a precondensation without separation of the formed monohydroxyaryl compound, an oligocarbonate is prepared in a plurality of successive flash/vaporisation
30 stages with stepwise increase in temperatures and stepwise falling pressures, which is then condensed in a succession of one or more cage reactors under increasing temperatures and falling pressures to form the desired polycarbonate.

- 35 In order to carry out the process the reactants are either melted together or alternatively the solid dihydroxyaryl

- 26 -

compound is dissolved in the diaryl carbonate melt or the solid diaryl carbonate is dissolved in the melt of the dihydroxyaryl compound, or both raw materials are combined as a melt, preferably directly from the preparation. The residence times of the separate melts of the raw materials, in particular the residence time of the melt of the dihydroxyaryl compound, are adjusted to be as short as possible. The melt mixture may however be subject to longer residence times without any harm on account of the reduced melting point of the raw material mixture compared to the individual raw materials, at correspondingly low temperatures. The catalyst, preferably dissolved in phenol, is then mixed in and the melt is heated to the reaction temperature. At the start of the technically important process for the preparation of polycarbonate from bisphenol A and diphenyl carbonate this temperature is 180 to 220°C, preferably 190 to 210°C and most particularly preferably 190°C. The reaction equilibrium is established at residence times of 15 to 90 minutes, preferably 30 to 60 minutes, without removing the hydroxyaryl compound that is formed. The reaction may be carried out at atmospheric pressure, but for technical reasons may also be carried out at excess pressure. The preferred pressure in industrial plants is 2 to 15 bar, preferably 2 to 12 bar.

The melt mixture is flashed into a first vacuum chamber whose pressure is adjusted to 100 to 400 mbar, preferably to 150 to 300 mbar, and is then directly reheated to the inlet temperature in a suitable apparatus at the same pressure. Hydroxyaryl compound that is formed, together with monomers that are still present, are evaporated in the pressure release stage.

After a residence time of 5 to 30 minutes in a sump receiver, optionally with circulation pumping at the same pressure and same temperature, the reaction mixture is

- 27 -

flashed into a second vacuum chamber whose pressure is 50 to 200 mbar, preferably 80 to 150 mbar, and is then directly heated in a suitable apparatus at the same pressure to a temperature of 190 to 250°C, preferably 210 to 240°C and particularly preferably 210 to 230°C. Here too hydroxyaryl compound that is formed, together with monomers that are still present, are evaporated.

After a residence time of 5 to 30 minutes in a sump receiver, optionally with circulation pumping at the same pressure and same temperature, the reaction mixture is flashed into a third vacuum chamber whose pressure is 30 to 150 mbar, preferably 50 to 120 mbar, and is then directly heated in a suitable apparatus at the same pressure to a temperature of 220 to 280°C, preferably 240 to 270°C, and particularly preferably 240 to 260°C. Here too hydroxyaryl compound that is formed, together with monomers that are still present, are evaporated.

After a residence time of 5 to 20 minutes in a sump receiver, optionally with circulation pumping at the same pressure and same temperature, the reaction mixture is flashed into a further vacuum chamber whose pressure is 5 to 100 mbar, preferably 15 to 100 mbar, and particularly preferably 20 to 80 mbar, and is then directly heated in a suitable apparatus at the same pressure to a temperature of 250 to 300°C, preferably 260 to 290°C, and particularly preferably 260 to 280°C. Here too hydroxyaryl compound that is formed, together with monomers that are still present, are evaporated.

The number of these stages, here for example 4, may vary between 2 and 6. The relative viscosity of the oligomer achieved in these stages is between 1.04 and 1.20, preferably between 1.05 and 1.15 and particularly preferably between 1.06 and 1.10. The relative viscosity

- 28 -

is determined as the quotient of the viscosity of the solvent and the viscosity of the polymer dissolved in this solvent. The relative viscosity was determined in dichloromethane at a concentration of 5 g/l at 25°C.

5

The oligomer thus prepared is conveyed after a residence time of 5 to 20 minutes in a sump receiver, optionally with circulation pumping at the same pressure and same temperature as in the last flash/evaporation stage, to a cage reactor and is condensed further at 250 to 310°C, preferably 250 to 290°C and particularly preferably 250 to 280°C, at pressures of 2 to 15 mbar, preferably 4 to 10 mbar, at residence times of 30 to 90 minutes, preferably 30 to 60 minutes. The product reaches a relative viscosity of 1.12 to 1.25, preferably 1.13 to 1.22, particularly preferably 1.13 to 1.20.

The melt leaving this reactor is adjusted in a further cage reactor to the desired final viscosity. The temperatures are 270 to 330°C, preferably 280 to 320°C, particularly preferably 280 to 310°C, the pressure is 0.01 to 3 mbar, preferably 0.2 to 2 mbar, at residence times of 60 to 180 minutes, preferably 75 to 150 minutes. The relative viscosities are adjusted to the necessary value for the intended use and are 1.18 to 1.40, preferably 1.18 to 1.36 and particularly preferably 1.18 to 1.34.

The function of the two cage reactors may also be combined in one cage reactor.

30

The vapours are directly discharged from all process stages and may be processed for example according to German patent application no. 1 01 00 404 (e.g. column 3, sections 14-22, as well as the Examples).

35

- 29 -

The apparatus and reactors suitable for the individual process steps include, corresponding to the course of the process, heat exchangers, apparatus or stirred vessels that ensure the necessary residence time at constant

5 temperature; pressure release apparatus as well as large-volume vessels, separators or cyclones; stirred vessels, forced circulation evaporators, falling-film evaporators or other commercially available apparatus that permits the necessary supply of heat; vessels that ensure the requisite
10 residence times after the heating; single-shaft or twin-shaft cage or disc reactors with the necessary volumes and film-forming surfaces, as well as a construction that takes into account the increasing melt viscosities.

15 The pipelines between parts of the apparatus should obviously be as short as possible and the curvatures of the pipelines should be kept as small as possible. In this connection the external boundary conditions for the installation of chemical plant should be borne in mind.

20

For the preferred implementation of the process a conventional heat exchanger is used to heat the raw material melt. A perforated floor column is used as residence vessel to establish the reaction equilibrium.

25 The pressure release procedures, in other words the flash vaporisations, are carried out in centrifugal separators, preferably cyclones, or in baffle-plate separators. The melt flowing from the centrifugal separators, preferably cyclones, or baffle-plate separators is heated in falling-
30 film evaporators, followed by vessels for adjusting the residence times. The vessels are provided with a pump circulation, whereby the liquids from the falling-film evaporator and the pump circulation flow through built-in grid constructions or perforated plate constructions or
35 packed beds into the sump, where they are collected. The condensation to form a medium viscosity product is carried

- 30 -

out in a disc or cage reactor. The polycondensation is likewise carried out in a disc or cage reactor, which under the very long residence times offers a very large, constantly renewed surface to the vacuum. The disc or cage
5 reactors are geometrically designed corresponding to the increase in the melt viscosity. In a special arrangement one disc or cage reactor may also be sufficient. Suitable for example are reactors as described in DE 44 47 422 C2 and EP A 1 253 163, or twin-shaft reactors as described in
10 WO A 99/28 370.

Particularly suitable materials for the production of the apparatus, reactors, pipelines, pumps and fittings are stainless steels of the type Cr Ni (Mo) 18/10, such as for
15 example 1.4571 or 1. 4541 (Stahlschlüssel 2001, Verlag: Stahlschlüssel Wegst GmbH, Th-Heuss-Straße 36, D-71672 Marbach) and Ni-based alloys of the C type, such as for example 2.4605 or 2.4610 (Stahlschlüssel 2001, Verlag: Stahlschlüssel Wegst GmbH, Th-Heuss-Straße 36, D-71672
20 Marbach). The stainless steels are employed up to process temperatures of about 290°C and the Ni-based alloys are employed at process temperatures above about 290°C.

The thermoplastic polycarbonates obtainable by the melt
25 transesterification process according to the invention are also covered by the present invention. They have an extremely low content of cations and anions of in each case less than 60 ppb, preferably < 40 ppb and particularly preferably < 20 ppb (calculated as Na cations), the cations
30 being present as cations of alkali metal and alkaline earth metals, which may originate for example as impurities from the raw materials and phosphonium and ammonium salts that are used. Further ions such as Fe, Ni, Cr, Zn, Sn, Mo, Al
ions and their homologues may be contained in the raw
35 materials or may originate by abrasion or corrosion from the materials of the equipment that is used. The total

content of these ions is less than 2 ppm, preferably less than 1 ppm and particularly preferably less than 0.5 ppm.

The smallest possible amounts that can be achieved only by
5 using extremely pure raw materials are thus achieved. Such pure raw materials can be obtained for example only by purification processes such as recrystallisation, distillation, precipitation with wash liquors, etc.

10 As anions, those present are anions of inorganic acids and organic acids in equivalent amounts (e.g. chloride, sulfate, carbonate, phosphate, phosphite, oxalate, etc.).

The polycarbonates are also characterised by the fact that
15 they do not contain any detectable amounts of incorporated cleavage products or decomposition products with reactive terminal groups that are formed during the transesterification process. Such cleavage or decomposition products include for example
20 isopropenylmonohydroxyaryl compounds or their dimers.

The mean (weight average) molecular weights that are obtained are between 15,000 and 40,000, preferably 17,000 to 36,000 and particularly preferably 17,000 to 34,000, the
25 mean (weight average) molecular weight being determined from the relative viscosity according to the Mark-Houwling correlation (J. M. G. Cowie, Chemie und Physik der synthetischen Polymeren, Vieweg Lehrbuch, Braunschweig/Wiesbaden, 1997, p. 235).

30

The polycarbonates may be purposefully branched and may therefore contain minor amounts of 0.02 to 3.6 mole % (referred to the dihydroxyaryl compound) of branching agents. Suitable branching agents are the compounds with
35 three or more functional groups that are suitable for the

- 32 -

polycarbonate preparation, preferably those with three or more than three phenolic OH groups.

Some of the compounds containing three or more than three
5 phenolic hydroxyl groups that may be used include for example:

phloroglucinol,
4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)heptene-2,
10 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,
15 2,4-bis-(4-hydroxyphenylisopropyl)phenol,
tetra-(4-hydroxyphenyl)methane.

Some of the other trifunctional compounds are 2,4-
dihydroxybenzoic acid, trimesic acid, cyanuric chloride and
20 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.

25 Residual contents of monomers due to the chemical
equilibrium and as a result of process parameters such as
temperature, pressure and residence time may if necessary
be reduced further by suitable evaporation processes.

30 Granules are obtained by spinning the melt by means of a
gear-type pump from the reactor, cooling the strands in air
or water, followed by granulation.

Additives, auxiliary substances and reinforcing substances may be added to the polycarbonates prepared according to the invention irrespective of the preparation process.

- 5 The addition of additives serves to prolong the useful service life of the objects or articles produced from the polycarbonate or to improve the colour (stabilisers), simplify the processing (e.g. mould release agents, flow improvers, antistatic agents) or to match the polymer
- 10 properties to specific loadings/stresses (impact modifiers such as rubbers; flameproofing agents, colourants, glass fibres).

These additives may be added individually or in arbitrary

15 mixtures or several different mixtures to the polymer melt, and more specifically directly during the isolation of the polymer or after the melting of the granules in a so-called compounding step. In this connection the additives or their mixtures may be added as a solid, i.e. as powder, or

20 as a melt to the polymer melt. Another form of metering is the use of master batches or mixtures of master batches of the additives or additive mixtures.

Suitable additives are described for example in "Additives

25 for Plastics Handbook, John Murphy, Elsevier, Oxford 1999", in "Plastics Additives Handbook, Hans Zweifel, Hanser, Munich 2001".

Suitable antioxidants and thermal stabilisers include for

30 example:

alkylated monophenols,
alkylthiomethylphenols,
hydroquinones and alkylated hydroquinones,
35 tocopherols,
hydroxylated thiodiphenyl ethers,

- alkylidenebisphenols,
O-, N- and S-benzyl compounds,
hydroxybenzylated malonates,
aromatic hydroxybenzyl compounds,
5 triazine compounds,
acylaminophenols,
esters of β -(3,5-di-tert.-butyl-4-hydroxyphenyl)propionic
acid,
esters of β -(5-tert.-butyl-4-hydroxy-3-
10 methylphenyl)propionic acid,
esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic
acid,
esters of 3,5-di-tert.-butyl-4-hydroxyphenylacetic acid,
amides of β -(3,5-di-tert.-butyl-4-hydroxyphenyl)propionic
15 acid,
suitable thiosynergists,
secondary antioxidants, phosphites and phosphonites,
benzofuranones and indolinones.
- 20 Preferred are organic phosphites, phosphonates and
phosphanes, generally those in which the organic radicals
consist wholly or in part of optionally substituted
aromatic radicals.
- 25 Ortho-phosphoric acids and meta-phosphoric acids, wholly or
partially esterified phosphates or phosphites, are suitable
as complexing agents for heavy metals and for neutralising
traces of alkali.
- 30 The following are suitable as light-stability agents (UV
absorbers)
- 2-(2'-hydroxyphenyl)benzotriazoles,
2-hydroxybenzophenones,
35 esters of substituted and unsubstituted benzoic acids,

acrylates,
sterically hindered amines,
oxamides,
2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines,
5 substituted benzotriazoles being preferred.

Polypropylene glycols alone or in combination with for
example sulfones or sulfonamides as stabilisers may be used
against damage caused by gamma radiation.

10

These and other stabilisers may be used individually or in
combinations and added in the aforementioned forms to the
polymer.

15 Processing auxiliaries such as mould release agents,
generally derivatives of long-chain fatty acids, may also
be added. For example pentaerythritol tetrastearate and
glycerol monostearate are preferred. These are generally
used individually or as a mixture, preferably in an amount
20 of 0.02 to 1 wt.%, referred to the mass of the composition.

Suitable flameproofing additives include phosphate esters,
i.e. triphenylphosphate, resorcinol diphosphoric acid
esters, bromine-containing compounds such as brominated
25 phosphoric acid esters, brominated oligocarbonates and
polycarbonates, as well as preferably salts of fluorinated
organic sulfonic acids.

Suitable impact modifiers include butadiene rubber with
30 grafted-on styrene/acrylonitrile or methyl methacrylate,
ethylene/propylene rubbers with grafted-on maleic
anhydride, ethyl acrylate rubbers and butyl acrylate
rubbers with grafted-on methyl methacrylate or
styrene/acrylonitrile, interpenetrating siloxane and
35 acrylate networks with grafted-on methyl methacrylate or
styrene/acrylonitrile.

Colourants such as organic dyes or pigments or inorganic pigments and IR absorbers may furthermore be added individually, as a mixture or also in combination with
5 stabilisers, glass fibres, (hollow) glass spheres or inorganic fillers.

The present application also provides the polycarbonates that are obtained by the process according to the invention
10 and also provides for their use for the production of extrudates and moulded articles, in particular for use in transparent applications, most particularly in the area of optical applications such as for example sheets, multi-wall sheets, glazing, light-diffusing discs, lamp coverings or
15 optical data stores such as audio CDs, CDR(W)s, DVDs, DVD-R(W)s, MiniDiscs in their various read-only or write once, possibly also completely rewriteable forms.

The extrudates and moulded articles made from the polymer
20 according to the invention are also covered by the present application.

Further applications include for example the following, without however restricting the subject matter of the
25 present invention:

1. Safety panels, which as is known are necessary in many areas of buildings, vehicles and aircraft, as well as helmet shields.
30
2. Films.
3. Blow-moulded articles (see also US-A 2 964 794), for example 1-gallon to 5-gallon water tanks.
35

- 37 -

4. Light-permeable sheets such as solid sheets or in particular hollow sheets, for example for covering buildings such as railway stations, greenhouses and lighting installations.
- 5
5. Optical data stores such as audio CDs, CD-R(W)s, DVDs, DVD-R(W)s, MiniDiscs and later generations.
6. Traffic light housings or traffic signs.
- 10
7. Foamed articles with an open or closed, optionally printable surface.
8. Threads and wires (see also DE-A 11 37 167).
- 15
9. Light technology applications, optionally using glass fibres for applications in the light transmission sector.
- 20
10. Translucent modifications containing barium sulfate and/or titanium dioxide and/or zirconium oxide or organic polymeric acrylate rubbers (EP-A 0 634 445, EP-A 0 269 324) for the production of light-permeable and light-scattering moulded parts.
- 25
11. Precision injection-moulded parts such as mountings, e.g. lens mountings; in this connection optionally polycarbonates with glass fibres and optionally an additional content of 1 to 10 wt.% of molybdenum
- 30
- disulfide (referred to the total moulding composition) are used.
12. Optical instrument parts, in particular lenses for camcorders and cameras (DE-A 27 01 173).
- 35

- 38 -

13. Light transmission carriers, in particular fibre optic cables (EP-A 0 089 801) and illumination strips.
14. Electrically insulating materials for electrical
5 conductors and for plug housings and sockets as well as capacitors.
15. Mobile telephone housings.
- 10 16. Network interface devices.
17. Carrier materials for organic photoconductors.
18. Lamps/lights, automobile headlamps, light-diffusing
15 panels or internal lenses.
19. Medical applications such as oxygenators and dialysis machines.
- 20 20. Foodstuffs applications such as bottles, crockery and chocolate moulds.
21. Applications in the automobile sector, such as
glazing, or in the form of blends with ABS, as
25 bumpers.
22. Sports articles such as slalom poles and ski boot fastenings.
- 30 23. Household articles such as kitchen sink units, washbasins and letterbox housings.
24. Housings such as electrical distribution cabinets.
- 35 25. Housings for electrical appliances such as toothbrushes, hairdryers, coffee-making machines and

- 39 -

machine tools such as drills, milling machines, planes and saws.

26. Washing machine portholes.

5

27. Protective goggles, sunglasses, optical correction glasses and their lenses.

28. Lamp coverings.

10

29. Packaging foils.

30. Chip containers, chip carriers and boxes for Si wafers.

15

31. Miscellaneous applications such as stable doors or animal cages.

The following examples are intended to illustrate the present invention without however restricting the scope of the latter.

20

Example

Report on non-destructive testing by means of the helium vacuum test on a vaporisation extruder. The leak
5 detector/helium detector (instrument from Leybold, type 200) was connected in front of the vacuum pump and the extruder, side extruder, separator, inspection windows and extrusion chambers as well as all flange connections in this region were checked. The test instrument has a
10 response time of <5 sec. The baseline level of the apparatus was measured as $< 10^{-5}$ litre He x mbar/sec. The extrusion chamber was found to be gas-tight at 8×10^{-5} litre He x mbar/sec, whereas an inspection window was identified as a leak source with a leakage rate of 10^{-3} litre
15 He x mbar/sec.

The relative solution viscosity was determined in dichloromethane at a concentration of 5 g/l at 25°C.

20 YI (Yellowness Index) was determined according to **ASTM E 313** on 4 mm-thick injection-moulded samples. The injection moulding temperature was 300°C.

The colour index was determined as the difference of the
25 extinction at 420 nm and 700 nm in dichloromethane at a concentration of 2.4 g/50 ml and a layer thickness of 10 cm.

Examples showing the influence of oxygen on polycarbonate:

30

The following commercially available polycarbonates prepared by the Bayer AG phase interface process in a plant consisting of apparatus with a leakage rate of $< 10^{-3}$ litre He x mbar/sec were investigated.

35

- 41 -

1. DP1-1265, a homopolycarbonate based on bisphenol A with a weight average molecular weight M_w of about 28500 and a relative viscosity $\eta_{rel.} = 1.293 - + 0.5$ M_w containing a few additives, which however are irrelevant in the context of this invention.
5
2. Makrolon 2808, a homopolycarbonate based on bisphenol A with a weight average molecular weight of about 17500 and a relative viscosity $\eta_{rel.} = 1.197 + - 0.5$,
10 containing a few additives, which however are irrelevant in the context of this invention.

The samples were weighed out in air into gas-tight closed beaded rim ampoules and sealed in a gas-tight manner.
15 These samples were then heated for 10, 20 and 30 minutes at temperatures of 320°, 350° and 380°C. After cooling the ampoules, the oxygen content in the gas space of the ampoules was determined by means of gas chromatography. The oxygen absorption of the polymer is determined from the
20 difference with respect to the initial sample.

Samples with comparable weighed-out amounts of about 500 mg were compared. In order to estimate the limits of experimental error of the process the analyses were carried
25 out as triple determinations. The measurements have an error range of about $\pm 10\%$. The oxygen contents, measured in vol. %, were converted into ppm or mmole/g of polymer assuming that the ideal gas law applies.

30 The heated polymers were then dissolved and the colour indices of the solutions were determined.

1st Series; a commercially available, relatively low viscosity polycarbonate from Bayer AG was used for the CD

- 42 -

productions, DP1-1265; 400 mg of polymer were weighed out and heated.

Heating at 320°C:

Heating Time	Oxygen Absorption	Colour Index
10	810 ppm	1.8
20	1050 ppm	4.2
30	1345 ppm	5.8

5

Heating at 350°C:

Heating Time	Oxygen Absorption	Colour Index
10	1070 ppm	4.5
20	2260 ppm	14.0
30	3270 ppm	28.0

Heating at 380°C:

Heating Time	Oxygen Absorption	Colour Index
10	2540 ppm	20
20	5290 ppm	56
30	6710 ppm	69

- 10 These experiments show that more oxygen is absorbed with increasing heating time and as a result the colour index rises. The experiments also show that, with increasing temperature of the melt, significantly more oxygen is absorbed at the same residence time.

15

The repetition of the experiment shows that the oxygen absorption of the polycarbonate melt can readily be reproduced:

- 43 -

Heating at 320°C:

Heating Time	Oxygen Absorption
10	760 ppm
20	1000 ppm
30	1390 ppm

Heating at 350°C:

Heating Time	Oxygen Absorption
10	1130 ppm
20	2190 ppm
30	3470 ppm

5 Heating at 380°C:

Heating Time	Oxygen Absorption
10	2370 ppm
20	5120 ppm
30	7150 ppm

2nd Series; a commercially available polycarbonate from Bayer AG, DP1-1265, see above, was used and compared to a high molecular weight polycarbonate, Makrolon 2808, see above; 400 mg of polymer were weighed out and heated.

a) DP1-1265, heating time 20 min:

Heating Temperature	Oxygen Absorption	Colour Index
320°C	770 ppm	3.3
350°C	2670 ppm	16
380°C	5500 ppm	50

- 44 -

b) Makrolon 2808, heating time 20 min:

Heating Temperature	Oxygen Absorption	Colour Index
320°C	640 ppm	6.3
350°C	2270 ppm	26.0
380°C	5160 ppm	---

The values obtained here show that a good reproduction in DP1-1265 is obtained once more. It can also be seen that
5 in the case of the higher viscosity M 2808, although the melt tends to absorb somewhat less oxygen the damage as measured by the colour index is however significantly increased.

10 Further examples, polycarbonates prepared by the Bayer AG melt transesterification process:

1. FS 20 SO natur is a linear melt polycarbonate with a relative solution viscosity of 1.201 and a colour index
15 of 0.11. The phenolic OH value is 540 ppm.

2. FS 26 SO natur is a linear melt polycarbonate with a relative solution viscosity of 1.275 and a colour index of 0,14. The phenolic OH value is 250 ppm.

20

These products obtained from the apparatus according to the invention have an excellent quality. A leakage rate of $>10^{-3}$ litre He x mbar/sec in the apparatus according to the invention would lead to a contamination of the
25 polycarbonate melt with oxygen. In this case a reduced quality of the products should be expected. This is demonstrated by the characterisation of the oxygen absorption and CO₂ cleavage of industrially prepared melt polycarbonate under temperature stress as a function of the
30 heating time:

The samples FS 20 SO and FS 26 SO described above were investigated.

- 5 The samples were heated for 10, 20 and 30 minutes at temperatures of 320°, 350° and 380°C under an air atmosphere in gas-tight, beaded rim ampoules. The oxygen and CO₂ content in the gas space of the ampoules was then determined by means of gas chromatography.

10

Samples containing comparable weighed-out amounts of about 500 mg were compared. In order to estimate the limits of experimental error of the process the analyses were carried out as triple determinations. The measurements have an error range of about +/- 10 %.

15

The oxygen and CO₂ contents, measured in vol. %, were converted into ppm and mmole/g of polymer assuming that the ideal gas law applies.

20

FS20SO

Temperature/ °C	t min	ppm O ₂	ppm CO ₂	Colour Index
320	10	775	550	1.5
	20	1156	1075	4.8
	30	1330	1350	7.5
350	10	1290	1330	5.8
x	20	2895	2870	25
x	30	3900	4478	38
x 380	10	2924	3360	27

- 46 -

	Temperature/ t min	ppm O ₂	ppm CO ₂	Colour Index
x	20	5683	6899	44
x	30	7662	10581	48
FS26S0				
320	10	531	197	1.5
	20	711	541	3.4
	30	971	797	5.2
350	10	933	699	4.1
x	20	1973	1986	16
x	30	3215	3362	32
x 380	10	2409	2404	16
x	20	4508	4884	44
x	30	6711	8064	37

The samples identified by "x" contained insoluble/darkish brown particles, which means that variations have to be expected with these samples.

5

The relationship between the colour index and the CO₂ cleavage (ppm) as a function of the O₂ absorption (ppm) is illustrated in Fig. 1.

- 10 It can be seen from the diagram that up to O₂ absorptions of about 6000 ppm there is to a good approximation a linear relationship between the colour index and CO₂ cleavage as a function of the oxygen absorption. The results of the investigated polycarbonates are summarised in the Figure 1.

The example clearly demonstrates the harmful influence of air and oxygen at elevated temperatures and average residence times on the colour quality of the melt
5 polycarbonate.

Surprisingly, such an influence with all its negative effects can be prevented simply by the process according to the invention, which involves the use of apparatus having a
10 defined hermeticity, without the need for large apparatus expenditure with inert gas metering equipment or the like.

Overall the experiments show that the exposure of the polycarbonate melt to oxygen should be kept as low as
15 possible. Surprisingly it is possible by means of the simple process according to the invention to achieve a low exposure of the polycarbonate melt.

Patent Claims

1. Process for the preparation of polycarbonate using an apparatus whose leakage rate is $<10^{-3}$ litre
5 He x mbar/sec.
2. Polycarbonate obtainable by a process according to claim 1.
- 10 3. Use of the polycarbonate according to claim 2 for the production of moulded articles and extrudates.
4. Moulded articles and extrudates comprising polycarbonate according to claim 2.
- 15 5. Optical data stores comprising polycarbonates according to claim 2.
6. Process for the production of moulded articles and extrudates from polycarbonate using apparatus whose
20 leakage rate is $<10^{-3}$ litre He x mbar/sec.
7. Moulded articles and extrudates obtainable by a process according to claim 6.
- 25 8. Process for determining a leakage rate in an apparatus or system, comprising connecting a helium detector to the vapour lines of the system or apparatus, flushing all potential leaks with helium from a gas lance, and
30 determining the measurement value by means of a detector.