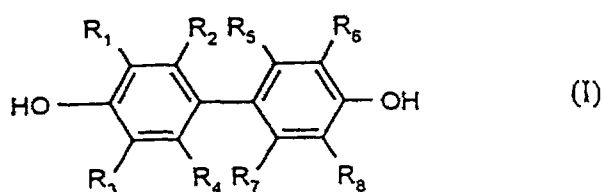


Process for the preparation of special copolycarbonates by melt transesterification

The subject of the present invention is a process for the preparation of thermoplastic copolycarbonates from

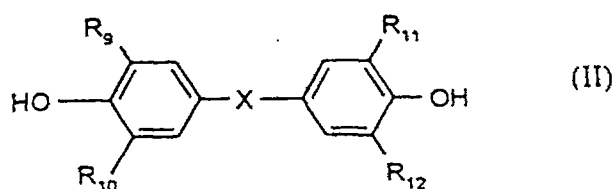
0.1 mol-% to 35 mol-%, preferably from 10 mol-% to 30 mol-% and in particular from 20 mol-% to 30 mol-%, of 4,4-dihydroxydiphenylene corresponding to Formula (I)



15 wherein $R_1 - R_8$ independently of one another are H or C_1-C_3 alkyl, and from complementary quantities,

that is to say from 99.9 mol-% to 65-%, preferably from 90 mol-% to 70 mol-% and in particular from 80 mol-% to 70 mol-%, of other diphenols corresponding to Formula

(II)



25 wherein $R_9 - R_{12}$ independently of one another are H, CH_3 , Cl or Br and X is C_1-C_5 alkylene, C_2-C_5 alkylidene, C_5-C_6 cycloalkylene, C_5-C_{10} cycloalkylidene,

$-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$, -S- or -O-, in accordance with the known polycarbonate preparation

30

process in a melt, said process being characterised in that use is made of N-alkyl-substituted piperidines and/or N-alkyl-substituted morpholines by way of catalysts in quantities from 10^{-2} to 10^{-8} mol, preferably from 10^{-2} to 10^{-5} mol, per mol diphenol, the alkyl substituents being C_2 - C_{12} alkyl groups, preferably C_2 - C_8 alkyl groups and in particular C_2 - C_5 alkyl groups.

Preferred N-alkyl piperidines are N-ethyl piperidine, N-propyl piperidine, N-isopropyl piperidine. Preferred N-alkyl morpholines are N-ethyl morpholine, N-propyl morpholine and N-isopropyl morpholine. N-ethyl piperidine is particularly preferred.

They may be employed on their own or in combination, together or in succession.

Preferred dihydroxydiphenyl is 4,4-dihydroxydiphenyl. Preferred diphenols (II) are 2,2-bis-(4-hydroxyphenyl)propane, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexene and 1,1-bis-(4-hydroxyphenyl)-1-phenylethane.

According to EP-A-544 407 or US-PS-5,401,826 corresponding copolycarbonates are prepared in accordance with the melt-transesterification process. By way of catalysts use may be made of nitrogen bases, ammonium salts, alkali hydroxides, alkali salts, alkaline-earth hydroxides and alkaline-earth salts.

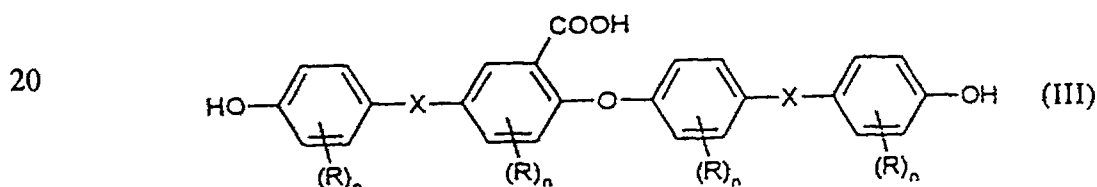
A disadvantageous aspect is that, with the use of alkali catalysts, secondary reactions occur in the form of undesirable branchings which have an influence on the colour and also on the mechanical properties.

Dihydroxydiphenyls are also named as comonomers in DE-OS 3 832 396. They may be employed in quantities from 0 to 98 mol-%, preferably from 0 to 95 mol-%, in particular from 0 to 90 mol-% and in quite particularly preferred manner in quantities between 0 and 80 mol-%.

Preparation may be effected in accordance with the known polycarbonate preparation processes, preferably in accordance with the interphase process.

According to DE-OS 2 119 779 the preparation of polycarbonates with diphenyl structures is preferably effected in solution, to be specific in accordance with the interphase process and the process in homogeneous phase.

- 5 Now it was the object of the present invention to improve the process according to EP-A-544 407 and to prepare solvent-free, sparsely branched, chemical-resistant copolycarbonates with good yields that exhibit good transparency, little intrinsic colour (YT) and high resistance to ageing.
- 10 The polycarbonates that can be obtained by the process according to the invention are distinguished by a bright intrinsic colour and high transmission of light even after relatively long temperature loading. In addition they are largely free from undesirable imperfections in the polycarbonate itself and naturally solvent-free.
- 15 Largely free from undesirable imperfections in the polycarbonate in the sense of the process according to the invention means that the content of branching units corresponding to Formula (III)



with

25

X C_1 - C_8 alkylidene or cycloalkylidene, S or single bond,

R CH_3 , Cl, Br and

30

n 0, 1 or 2,

in the polycarbonate after total saponification and HPLC determination has a value of no more than 300 ppm, preferably no more than 100 ppm.

5 Suitable by way of carbonic acid derivatives in the process according to the invention are carbonic C₆-C₁₄ diaryl esters, preferably the diesters of phenol or alkyl-substituted phenols, that is to say, for example, diphenyl carbonate or dicresyl carbonate. Relative to 1 mol bisphenol the carbonic diesters are employed in quantities from 1.01 to 1.30 mol, preferably 1.02 mol to 1.15 mol.

10 The reaction according to the invention may be carried out in one stage without isolation of an oligocarbonate stage, or in two stages or more than two stages with isolation of at least one oligocarbonate intermediate product.

15 It should be noted that the initial materials for the reaction according to the invention, that is to say the diphenols and the carbonic diaryl esters and catalysts, are free of alkali ions and alkaline-earth ions, it being possible for quantities of less than 0.1 ppm of alkali and alkaline-earth ions to be tolerated. Diphenols or carbonic diaryl esters that are pure in this sense can be obtained by the carbonic diaryl esters or diphenols being recrystallised, washed or distilled. With the process according to the invention
20 the content of alkali and alkaline-earth metal ions both in the diphenol and in the carbonic diester and in the catalyst should amount to less than 0.1 ppm.

In detail, the process according to the invention is preferably carried out as follows:

25 dihydroxy compounds and carbonic diesters are melted down in a molar ratio of 1 mol to between 1.01 and 1.30 mol, preferably 1 mol to between 1.02 and 1.15 mol, and heated to temperatures from 80°C to 250°C, preferably 100°C to 230°C and in particular 120°C to 190°C, under atmospheric pressure in 0.1 hours to 5 hours, preferably 0.25 hours to 3 hours. After addition of the catalyst the monophenol is
30 distilled off and an oligocarbonate is produced by lowering the pressure to 3 mbar and raising the temperature to 260°C.

In the second stage the polycarbonate is produced by polycondensation of the oligocarbonate by further increasing the temperature to between 270°C and 320°C, preferably between 270°C and 295°C, at a pressure between 3 and 0.1 mbar.

5 The oligocarbonates of the first stage have average molecular weights $\overline{M}_w$ of 3,000-24,000, preferably 5,000-20,000, ascertained by measuring the relative solution viscosity in dichloromethane or in mixtures of equal quantities by weight of phenol and o-dichlorobenzene, calibrated by light scattering. The molecular weights of the oligocarbonates of the 1st stage depend on the desired final viscosity of the
10 polycarbonates; accordingly, copolycarbonates of low molecular weight are obtained in the 2nd stage by the condensation of oligocarbonates of low molecular weight and copolycarbonates of higher molecular weight are obtained by the condensation of oligocarbonates of higher molecular weight.

15 The reaction according to the invention of the aromatic dihydroxy compounds and of the carbonic diester may be carried out continuously or discontinuously, for example in stirrer vessels, film-type evaporators, cascades of stirrer vessels, extruders, kneaders, simple disc-type reactors and high-viscosity disc-type reactors.

20 The copolycarbonates obtained are isolated by, for example, the melt being conducted through an extruder, cooled and granulated.

The copolycarbonates that can be obtained by the process according to the invention have average molar masses $\overline{M}_w$ from 18,000 to 60,000, preferably 19,000 to 40,000,
25 ascertained by measuring the rel. solution viscosity in dichloromethane or in mixtures of equal quantities by weight of phenol and o-dichlorobenzene, calibrated by light scattering.

30 With a view to limiting the average molar masses $\overline{M}_w$ of the polymers, phenols that are not readily volatile, such as cumylphenol, 4-phenylphenol, may be employed in quantities from 0.01 to 10 mol-% per mol diphenol.

The copolycarbonates that can be obtained in accordance with the invention may be processed in known manner to form various moulded articles and articles of daily use, for example by extrusion or by injection moulding.

- 5 The polycarbonates that can be obtained in accordance with the invention may by reason of their pattern of properties, in particular on account of their resistance to chemicals, be employed in particular in the automotive field as sheeting, plates, dashboard fittings or housing parts, but also in the optical field as lenses and data storage devices and also as articles of daily use, for example as tableware.

10

Consequently, also a subject of the present invention is the use of the polycarbonates that can be obtained in accordance with the invention for the production of chemical-resistant moulded articles.

- 15 With a view to modifying the properties of the copolycarbonates that can be obtained in accordance with the invention, auxiliary materials and reinforcing materials may also be admixed to said copolycarbonates. Materials to be taken into consideration as such are, inter alia: stabilisers, flow aids, mould-release agents, fire-protection agents, pigments, finely divided minerals, fibrous materials, for example alkyl phosphites and
20 aryl phosphites, alkyl phosphates and aryl phosphates, alkyl phosphanes and aryl phosphanes, low-molecular carbonic esters, halogen compounds, salts, chalk, quartz powder, glass fibres and carbon fibres.

- Moreover, other polymers, for example polyolefins, polyurethanes or polystyrene, may
25 also be admixed to the polycarbonates that can be obtained in accordance with the invention.

- The addition of these substances is preferably carried out with the aid of conventional units to produce the finished polycarbonate but, depending on requirements, may also
30 be carried out at another stage of the process according to the invention.

Example**Preparation of the polycarbonates via the melt-transesterification process**

- 5 114.15 g (0.500 mol) bisphenol A and 113.54 g (0.530 mol) diphenyl carbonate are weighed into a 500 ml three-necked flask with stirrer, internal thermometer and Vigreux column (30 cm, metallised) with bridge. The apparatus is freed of atmospheric oxygen by application of vacuum and flushing with nitrogen (3 times) and the mixture is heated up to 150°C. Now 6.87 µl N-ethyl piperidine (0.01 mol-%, relative to bisphenol A) are added and the phenol that arises is distilled off at 100 mbar. At the same time the temperature is raised to 250°C. The vacuum is now enhanced in stages to 1 mbar and the temperature is increased to 260°C. Subsequently the temperature is increased to 280°C and the reaction mixture is stirred at 0.1 mbar for 1.5 hours. The relative solution viscosity amounts to 1.296 (dichloromethane, 25°C, 5 g/l). The phenolic OH value of the polycarbonate amounts to 70 ppm.
- 10
- 15

The copolycarbonates in Table 1 were produced correspondingly (BPA = 2,2-bis-(4-hydroxyphenyl)propane, TMC = 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane, DOD = 4,4'-dihydroxydiphenyl).

Table 1

Composition of the copolycarbonates

No.	BPA [mol-%]	TMC [mol-%]	DOD [mol-%]	$\eta_{rel.}$ test piece	Tg [°C]	Branching units Formula III [ppm]
1	100	-	-	1.296	153	20
2	90	-	10	1.333	156	6
3	80	-	20	1.356	161	10
4	70	-	30	1.388	163	13
5	65	35	-	1.259	188	5
6	58.5	31.5	10	1.286	186	10
7	52	28	20	1.328	188	14
8	45.5	24.5	30	1.334	188	8

5

In order to investigate the mechanical properties of the material by means of a tensile test in accordance with DIN 53 455 (ISO 527), in each case 20 dumb-bell strips No. 3 (4 mm thickness) were produced by injection moulding. The results of the tensile tests are compiled in Table 2.

Table 2

Mechanical properties of the copolycarbonates

No.	Modulus of elasticity [N/mm ²]	Tear resistance [N/mm ²]	Yield stress [N/mm ²]	Yield elongation [%]	Elongation at tear [%]
1	2385	60	62	6	107
2	2327	58	61	7	83
3	2309	56	61	7	72
4	2270	56	61	8	66
5	2443	53	69	7	69
6	2393	56	68	7	65
7	2376	57	68	7	41
8	2310	58	61	8	56

5

In order to investigate the stress cracking (ESC), 80 x 10 x 4 mm flat bars in a mixture of isooctane/toluene were supported on a template with 0 %, 0.6 % and 1.0 % outer fibre strain for 30 sec at 23°C. After 1 h load-free exposure to air and also 1 h storage at 110°C the specimen is assessed visually and the Charpy impact strength (DIN 53 453, ISO 179) in respect of the unnotched specimen is measured. The results are compiled in Table 3.

10

Table 3

Charpy impact strength in respect of the unnotched specimen of specimens stored in isooctane/toluene.

5

		Isooctane/toluene 70:30		Isooctane/toluene 50:50	
	[kJ/m ²] with 0 % outer fibre strain	[kJ/m ²] with 0.6 % outer fibre strain		[kJ/m ²] with 10 % outer fibre strain	
1	n.b.	n.b.*	3 n.b./22*	7*/**	4*/**
2	n.b.	n.b.	n.b.	n.b.	29*
3	n.b.	n.b.	n.b.	n.b.	58*
4	n.b.	n.b.	n.b.	n.b.	n.b.
5	n.b.	4*/**	4***	****	****
6	n.b.	33*	5*	****	****
7	n.b.	n.b.	27*	7*	5*/**
8	n.b.	n.b.	n.b.	n.b.	10*/**

n. b. not broken

* edge crack

** surface crack

*** transverse cracks

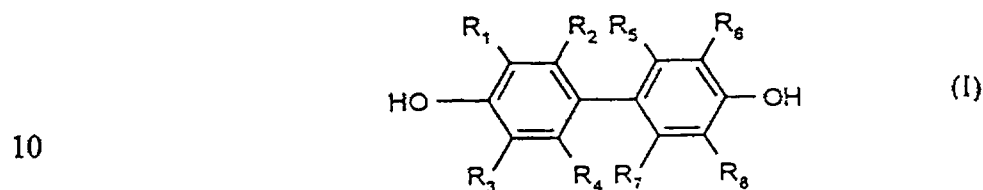
**** broken on template

10

**Claims**

1. Process for the preparation of thermoplastic copolycarbonates from

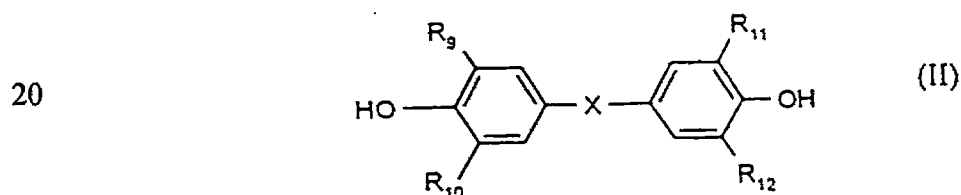
5 0.1 mol-% to 35 mol-% of 4,4-dihydroxydiphenylene corresponding to Formula (I)



wherein $R_1 - R_8$ independently of one another are H or C_1-C_3 alkyl, and from complementary quantities,

15

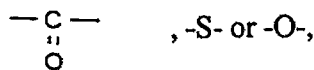
that is to say from 99.9 mol-% to 65-%, of other diphenols corresponding to Formula (II)



wherein $R_9 - R_{12}$ independently of one another are H, CH_3 , Cl or Br and

25

X is C_1-C_5 alkylene, C_2-C_5 alkylidene, C_5-C_6 cycloalkylene, C_5-C_{10} cycloalkylidene,



in accordance with the known polycarbonate preparation process in a melt,

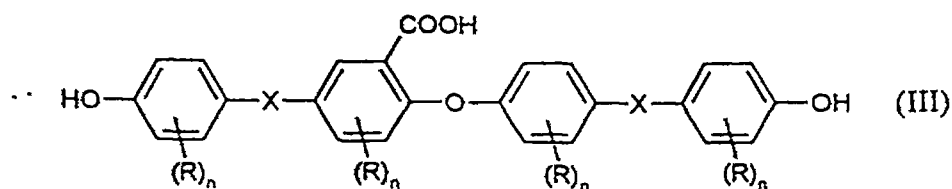
30

wherein use is made of N-alkyl-substituted piperidines or morpholines by way



of catalysts in quantities from 10^{-2} to 10^{-8} mol per mol diphenol, the alkyl substituents being C_2 - C_{12} alkyl groups.

2. Process according to Claim 1, characterised in that use is made of N-ethyl piperidine by way of catalyst.
3. Process according to Claim 1, characterised in that the content of branching units corresponding to Formula (III)



15 with

X C_1 - C_8 alkylidene or cycloalkylidene, S or single bond,

R CH_3 , Cl, Br and

20

n 0, 1 or 2,

in the polycarbonate after total saponification and HPLC determination has a value of no more than 300 ppm.

25

4. Use of the polycarbonates that can be obtained in accordance with Claim 1 for the production of chemical-resistant moulded articles.