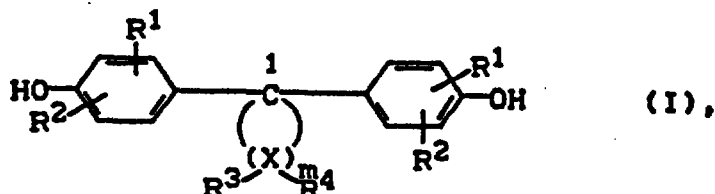


This invention relates to dihydroxydiphenyl cycloalkanes corresponding to formula (I)



10 in which

R^1 and R^2 independently of one another represent hydrogen, halogen, preferably chlorine or bromine, C_{1-8} alkyl, C_{5-6} cycloalkyl, C_{6-10} aryl, preferably phenyl, and C_{7-12} aralkyl, preferably phenyl- C_{1-4} -alkyl, more particularly benzyl,

15 m is 4 or 5,

R^3 and R^4 may be individually selected for each X and independently of one another represent hydrogen or C_{1-6} alkyl

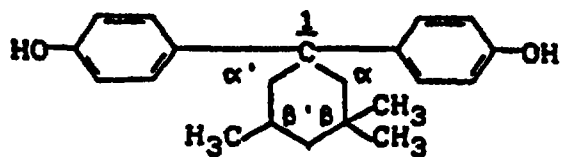
20 and

X represents carbon, with the proviso that, at at least one atom X, both R^3 and R^4 are alkyl.

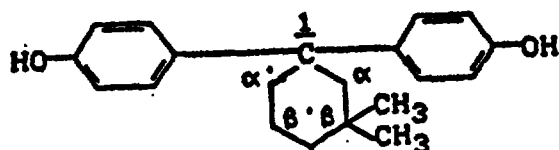
25 Preferably at 1 to 2 atoms X and, more particularly, at only 1 atom X, both R^3 and R^4 are alkyl. The preferred alkyl radical is methyl. The X atoms in the α -position to the diphenyl-substituted C atom (C-1) are preferably not dialkyl-substituted, whereas the X atoms in the β -position to C-1 are preferably dialkyl-substituted. More preferably, one X atom in the β -position is dialkyl-substituted and one X atom in the β' -position monoalkyl-substituted.

30 More particularly, the invention relates to dihydroxydiphenyl cycloalkanes containing 5 and 6 ring C atoms in the cycloaliphatic radical ($m = 4$ or 5 in formula (I)), for example diphenols corresponding to the following formulae

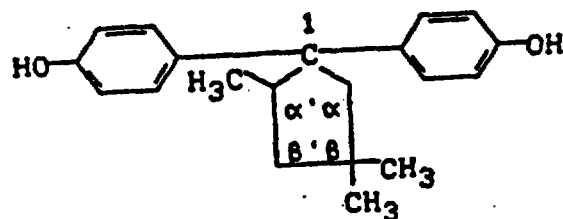
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(II)



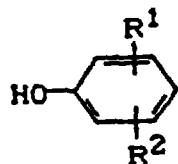
(III) and



(IV)

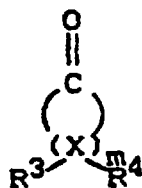
1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (formula II) being particularly preferred.

The dihydroxydiphenyl cycloalkanes corresponding to formula (I) may be obtained in known manner by condensation of phenols corresponding to formula (V)



(V)

and ketones corresponding to formula (VI)



(VI)

where X, R¹, R², R³, R⁴ and m are as defined for formula (I).

The phenols corresponding to formula (V) are either known from the literature or may be obtained by methods known from the literature (for cresols and xylenols, see
5 for example Ullmanns Encyklopädie der technischen Chemie, 4th Revised and Extended Edition, Vol. 15, pages 61-77, Verlag Chemie, Weinheim/New York, 1978; for chlorophenols, Ullmanns Encyklopädie der technischen Chemie, 4th Edition,
10 Verlag Chemie, 1975, Vol. 9, pages 573-582; and for alkylphenols, Ullmanns Encyklopädie der technischen Chemie, 4th Edition, Verlag Chemie 1979, Vol. 18, pages 191-214).

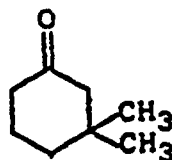
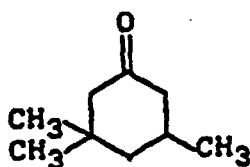
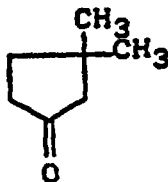
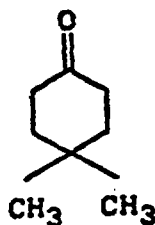
Examples of suitable phenols corresponding to formula (V) are phenol, o-cresol, m-cresol, 2,6-dimethylphenol, 2-chlorophenol, 3-chlorophenol, 2,6-dichlorophenol, 2-cyclo-
15 hexylphenol, 2,6-diphenylphenol and o-benzylphenol.

The ketones corresponding to formula (VI) are known from the literature (cf. for example Beilsteins Handbuch der Organischen Chemie, Vol. 7, 4th Edition, Springer-Verlag, Berlin, 1925 and the corresponding Supplementary
20 Volumes 1 to 4 and J. Am. Chem. Soc. Vol. 79 (1957), pages 1488-1492, US-PS 2,692,289, Allen et al., J. Chem. Soc., (1959), 2186-2192 and J. Org. Chem., Vol. 38, (1973), pages 4431-4435, J. Am. Chem. Soc. 87, (1965), pages 1353-1364. A general process for the production of ketones correspond-
25 ing to formula (VI) is described, for example in "Organikum", 15th Edition, 1977, VEB-Deutscher Verlag der Wissenschaften, Berlin, for example on page 698.

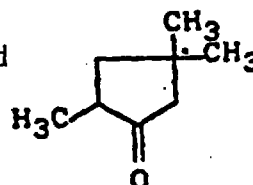
The following are examples of known ketones corresponding to formula (VI): 3,3-dimethylcyclopentanone, 3,3-
30 dimethylcyclohexanone, 4,4-dimethylcyclohexanone, 3-ethyl-3-methylcyclopentanone, 2,3,3-trimethylcyclopentanone, 3,3,4-trimethylcyclopentanone, 3,3-dimethylcycloheptanone, 4,4-dimethylcycloheptanone, 3-ethyl-3-methylcyclohexanone, 4-ethyl-4-methylcyclohexanone, 2,3,3-trimethylcyclohexa-
35 none, 2,4,4-trimethylcyclohexanone, 3,3,4-trimethylcyclo-

hexanone, 3,3,5-trimethylcyclohexanone, 3,4,4-trimethylcyclohexanone, 2,3,3,4-tetramethylcyclopentanone, 4-ethyl-2,3,4-trimethylcyclopentanone, 3-ethyl-4-isopropyl-3-methylcyclopentanone, 4-sec.-butyl-3,3-dimethylcyclopentanone, 2-isopropyl-3,3,4-trimethylcyclopentanone, 3-ethyl-4-isopropyl-3-methyl cyclohexanone, 4-ethyl-3-isopropyl-4-methylcyclohexanone, 3-sec.-butyl-4,4-dimethylcyclohexanone, 2-butyl-3,3,4-trimethylcyclopentanone, 2-butyl-3,3,4-trimethylcyclohexanone, 4-butyl-3,3,5-trimethylcyclohexanone and 3-isohexyl-3-methylcyclohexanone.

The following are examples of preferred ketones:



and



To prepare the bisphenols, the phenol (V) is generally used in a quantity of 2 to 10 mol and preferably in a quantity of 2.5 to 6 mol per mol ketone (VI). Preferred reaction times are from 1 to 100 hours. The reaction is generally carried out at a temperature in the range from -30°C to 300°C and preferably at a temperature in the range from -15°C to 150°C and under a pressure of from 1 to 20 bar and preferably under a pressure of from 1 to 10 bar.

The condensation is generally carried out in the

presence of acidic catalysts such as, for example, hydrogen chloride, hydrogen bromide, hydrogen fluoride, boron trifluoride, aluminium trichloride, zinc dichloride, titanium tetrachloride, tin tetrachloride, phosphorus halides, phosphorus pentoxide, phosphoric acid, concentrated hydrochloric acid or sulfuric acid and also mixtures of acetic acid and acetanhydride. Acidic ion exchangers may also be used.

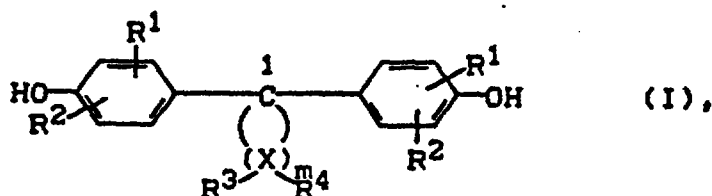
In addition, the reaction may be accelerated by addition of co-catalysts, such as C_{1-18} alkyl mercaptans, hydrogen sulfide, thiophenols, thio acids and dialkyl sulfides, preferably in quantities of 0.01 to 0.4 mol/mol ketone and more preferably in quantities of 0.05 to 0.2 mol/mol ketone.

The condensation may be carried out in the absence of solvents or in the presence of an inert solvent (for example an aliphatic or aromatic hydrocarbon, chlorinated hydrocarbon).

In cases where the catalyst also acts as a dehydrating agent, there is no need to use separate dehydrating agents, although, to obtain good conversions, it is always of advantage to use dehydrating agents when the catalyst used does not bind the water of reaction.

Suitable dehydrating agents are, for example, acetanhydride, zeolites, polyphosphoric acid and phosphorus pentoxide.

Accordingly, the present invention also relates to a process for the production of the dihydroxydiphenyl cycloalkanes corresponding to formula (I)



in which

R^1 and R^2 independently of one another represent hydrogen, halogen, preferably chlorine or bromine, C_{1-8} alkyl, C_{5-8} cycloalkyl, C_{6-10} aryl, preferably phenyl, and C_{7-12} aralkyl, preferably phenyl- C_{1-4} -alkyl, more particularly benzyl,

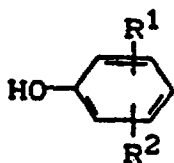
m is 4 or 5,

R^3 and R^4 may be individually selected for each X and independently of one another represent hydrogen or C_{1-8} alkyl

and

X represents carbon, with the proviso that, at at least one atom X, both R^3 and R^4 are alkyl,

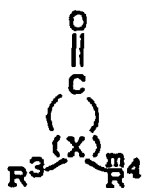
characterized in that phenols corresponding to formula (V)



(V)

in which

R^1 and R^2 are as defined for formula (I), are reacted with ketones corresponding to formula (VI)



(VI)

in which

X, m , R^3 and R^4 are as defined for formula (I),

in a molar ratio of (V):(VI) of from 2:1 to 10:1 and preferably in a molar ratio of from 2.5:1 to 6:1 at temper-

atures in the range from -30°C to 300°C and preferably at temperatures in the range from -15 to 150°C and under pressures of from 1 to 20 bar and preferably 1 to 10 bar in the presence of acidic catalysts and optionally in the presence of co-catalysts and/or solvents and/or dehydrating agents.

In formula (I), R^3 and R^4 are both alkyl at preferably 1 to 2 atoms X, but more especially at only 1 atom X. The preferred alkyl radical is methyl, although ethyl or linear or branched C_{3-6} alkyl radicals may also be used. The X atoms in the α -position to the diphenyl-substituted C atom (C-1) are preferably not dialkyl-substituted, whereas the X atoms in the β -position to C-1 are preferably dialkyl-substituted. More preferably, one X atom in the β -position is dialkyl-substituted and one X atom in β' -position is monoalkyl-substituted.

In some cases, the reaction is not entirely uniform, i.e. several different products can be formed, so that the desired compound first has to be isolated from a mixture. For particulars of the condensation, reference may be made to Schnell, Chemistry and Physics of Polycarbonates, Interscience Publishers, New York 1964. In some cases, it is possible to control the reaction through the choice of suitable catalysts and reaction conditions in such a way that the desired compound precipitates or crystallizes out, which makes it easier to isolate.

Example A.1

Preparation of the diphenol corresponding to formula (II)

7.5 mol (705 g) phenol and 0.15 mol (30.3 g) dodecylthiol are introduced into a 1-liter round-bottomed flask equipped with a stirrer, dropping funnel, thermometer, reflux condenser and gas inlet pipe and are saturated with dry HCl gas at 28 to 30°C . A solution of 1.5 mol (210 g) dihydroisophorone (3,3,5-trimethylcyclohexan-1-one) and 1.5 mol (151 g) phenol is added dropwise to the resulting solu-

tion over a period of 3 hours, HCl gas continuing to be passed through the reaction solution. After the addition, HCl gas is introduced for another 5 hours. The mixture is then left to react for 8 hours at room temperature. The excess phenol is then removed by steam distillation. The residue is hot-extracted twice with petroleum ether (60-90) and once with methylene chloride and filtered off. Yield: 370 g, Mp.: 205-207°C.

10 **Example A.2**

Preparation of diphenol corresponding to formula (II)

1692 g (18 mol) phenol, 60.6 g (0.3 mol) dodecylthiol and 420 g (3 mol) dihydroisophorone (3,3,5-trimethyl cyclohexan-1-one) are introduced at 28-30°C into a stirred reactor equipped with a stirrer, thermometer, reflux condenser and gas inlet pipe. Dry HCl gas is then introduced into the solution for 5 h at 28-30°C. The reaction mixture is then left to react for about 10 h at 28-30°C. After a 95% conversion of the ketone (GC control), 2.5 l water are added to the reaction mixture and a pH value of 6 is adjusted by addition of 45% NaOH solution. The reaction mixture is then stirred for 1 hour at 80°C and cooled to 25°C. The aqueous phase is decanted off and the residue is washed with water at 80°C. The crude product obtained is filtered off and hot-extracted twice with n-hexane and methylene chloride and filtered. The residue is recrystallized from xylene. Yield: 753 g, Mp.: 209-211°C.

30 **Example A.3**

Preparation of diphenol corresponding to formula (II)

564 g (6 mol) phenol, 10.8 g (0.12 mol) butane thiol and 140 g (1 mol) dihydroisophorone (3,3,5-trimethyl cyclohexan-1-one) are introduced at 30°C into a stirred reactor equipped with a stirrer, thermometer, reflux

condenser and gas inlet pipe. 44 g 37% HCl are then added at that temperature. The reaction mixture is then stirred for about 70 h at 28-30°C. After a 95% conversion of the ketone (GC control), 2 l water are added to the reaction mixture and a pH value of 6 is adjusted by addition of 45% NaOH solution. The reaction mixture is then stirred for 1 hour at 80°C and cooled to 25°C. The aqueous phase is decanted off and the residue is washed with water at 80°C. The crude product obtained is filtered off and hot-extracted twice with n-hexane and toluene and filtered at 30°C. Yield: 253 g, Mp.: 205-208°C.

Example A.4

Preparation of the diphenol corresponding to formula (Ib) ($R^1, R^2 = CH_3$)

2196 g (18 mol) 2,6-dimethylphenol, 38.2 g (0.36 mol) β -mercaptopropionic acid and 420 g (3 mol) dihydroisophorone (3,3,5-trimethyl cyclohexan-1-one) are introduced at 35°C into a stirred reactor equipped with a stirrer, thermometer, reflux condenser and gas inlet pipe. Dry HCl gas is then introduced into the solution for 5 h at 35°C. The reaction mixture is then left to react for about 10 h at 30-35°C. After a 95% conversion of the ketone (GC control), 2.5 l water are added to the reaction mixture and a pH value of 6 is adjusted by addition of 45% NaOH solution. The reaction mixture is then stirred for 1 hour at 80°C and cooled to room temperature. The aqueous phase is decanted off and the residue is washed with water at 60°C. The crude product obtained is filtered off and hot-extracted three times with n-hexane and filtered. Yield: 856 g, Mp.: 236-238°C.

Example A.5

Preparation of the diphenol corresponding to formula (III)
The procedure is as in Example A2, except that 3 mol

3,3-dimethyl cyclohexanone are used instead of 3 mol dihydroisophorone. The product had a melting point of 199-201°C.

5 The diphenols of formula (I) according to the invention are particularly suitable for the production of high molecular weight, thermoplastic polycarbonates which are distinguished by high heat resistance in combination with other favorable properties.

10 Accordingly, the present invention also relates to the use of the diphenols of formula (I) for the production of high molecular weight thermoplastic, aromatic polycarbonates.

15 It is possible to use both a single diphenol corresponding to formula (I), in which case homopolycarbonates are formed, and also several diphenols corresponding to formula (I), in which case copolycarbonates are formed.

20 In addition, the diphenols corresponding to formula (I) may also be used in admixture with other diphenols, for example with those corresponding to the formula HO-Z-OH (VII), for the production of high molecular weight, thermoplastic aromatic polycarbonates.

25 Suitable other diphenols corresponding to the formula HO-Z-OH (VII) are those in which Z is an aromatic radical containing 6 to 30 C atoms which may contain one or more aromatic nuclei, may be substituted and may contain aliphatic radicals or other cycloaliphatic radicals than those corresponding to formula (I) or heteroatoms as bridge members.

30 Examples of diphenols corresponding to formula (VII) are hydroquinone, resorcinol, dihydroxydiphenyls, 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 and nucleus-alkylated and nucleus-

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halogenated compounds thereof.

These and other suitable other diphenols are described, for example, in US-PSS 3,028,365, 2,999,835, 3,148, 172, 3,275,601, 2,991,273, 3,271,367, 3,062,781, 2,970,131
5 and 2,999,846; in DE-OSS 1 570 703, 2 063 050, 2 063 052, 2 211 0956, in FR-PS 1 561 518 and in the book by H. Schnell entitled "Chemistry and Physics of Polycarbonates", Interscience Publishers, New York, 1964.

Preferred other diphenols are, for example, 4,4'-
10 dihydroxydiphenyl, 2,2-bis-(4-hydroxyphenyl)-propane, 2,4-bis-(4-hydroxyphenyl)-2-methylbutane, 1,1-bis-(4-hydroxyphenyl)-cyclohexane, α,α' -bis-(4-hydroxyphenyl)-p-diisopropylbenzene, 2,2-bis-(3-methyl-4-hydroxyphenyl)-propane, 2,2-bis-(3-chloro-4-hydroxyphenyl)-propane, bis-(3,5-
15 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, 1,1-bis-(3,5-dimethyl-4-hydroxyphenyl)-cyclohexane, α,α' -bis-(3,5-dimethyl-4-hydroxyphenyl)-p-
20 diisopropylbenzene, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane and 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane.

Particularly preferred diphenols corresponding to formula (VII) are, for example, 2,2-bis-(4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl)-propane,
25 2,2-bis-(3,5-dichloro-4-hydroxyphenyl)-propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-cyclohexane.

2,2-Bis-(4-hydroxyphenyl)-propane is particularly preferred.

30 The other diphenols may be used both individually and in admixture with one another.

The molar ratio of diphenols corresponding to formula (I) to be used in accordance with the invention to the other diphenols optionally used, for example those corresponding to formula (VII), should be between 100 mol-% (I)
35

to 0 mol-% other diphenol and 2 mol-% (I) to 98 mol-% other diphenol, preferably between 100 mol-% (I) to 0 mol-% other diphenol and 5 mol-% (I) to 95 mol-% other diphenol and, more preferably, between 100 mol-% (I) to 0 mol-% other diphenol and 10 mol-% (I) to 90 mol-% other diphenol and, most preferably, between 100 mol-% (I) to 0 mol-% other diphenol and 20 mol-% (I) to 80 mol-% other diphenol.

The high molecular weight polycarbonates of the diphenols corresponding to formula (I) according to the invention, optionally in combination with other diphenols, may be prepared by any of the known methods used to produce polycarbonates. The various diphenols may be attached to one another both statistically and also in blocks.

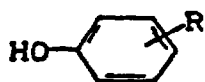
Accordingly, the present invention also relates to a process for the production of high molecular weight, thermoplastic aromatic polycarbonates from diphenols, optionally chain terminators and optionally branching agents by the known methods for the production of polycarbonates, preferably by the interfacial process, characterized in that diphenols of formula (I) are used as the diphenols in quantities of from 100 mol-% to 2 mol-%, preferably in quantities of from 100 mol-% to 5 mol-%, more preferably in quantities of from 100 mol-% to 10 mol-% and most preferably in quantities of from 100 mol-% to 20 mol-%, based on the total mols diphenols used.

The branching agents used, if any, are in known manner small quantities, preferably of from 0.05 to 2.0 mol-% (based on diphenols used), of trifunctional or more than trifunctional compounds, particularly those containing three or more than three phenolic hydroxyl groups. Some of the compounds containing three or more than three phenolic hydroxyl groups which may be used as branching agents include phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl)-hept-2-ene, 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, 2,6-bis-(2-hydroxy-5'-methylbenzyl)-4-methylphenol, 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl)-propane, hexa-(4-(4-hydroxyphenylisopropyl)-phenyl)-orthoterephthalic acid ester, tetra-(4-hydroxyphenyl)-methane, tetra-(4-(4-hydroxyphenylisopropyl)-phenoxy)-methane and 1,4-bis-((4',4"-dihydroxytriphenyl)-methyl)-benzene.

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.

Monofunctional compounds may be used in the usual concentrations as chain terminators for regulating the molecular weight of the polycarbonates (a) in known manner. Suitable compounds are, for example, phenol, tert.-butylphenols or other alkyl-C₁₋₇-substituted phenols. Small quantities of phenols corresponding to formula (VIII)



(VIII)

in which R is a branched C₃ and/or C₉ alkyl radical, are particularly suitable for regulating molecular weight. In the alkyl radical R, the percentage of CH₃ protons is between 47 and 89% and the percentage of CH and CH₂ protons between 53 and 11%. R is preferably in the o- and/or p-position to the OH group, 20% being the particularly preferred upper limit to the ortho component. The chain terminators are generally used in quantities of from 0.5 to 10 mol-% and preferably in quantities of from 1.5 to 8 mol-%, based on the diphenols used.

The polycarbonates according to the invention may be produced in known manner, preferably by the interfacial

polycondensation process (cf. H. Schnell "Chemistry and Physics of Polycarbonates", Polymer Reviews, Vol. IX, pages 33 et seq, Interscience Publ., 1964). In this process, the diphenols corresponding to formula (I) are dissolved in aqueous alkaline phase. To prepare copolycarbonates with other diphenols, mixtures of diphenols corresponding to formula (I) and the other diphenols, for example those corresponding to formula (VII), are used. Chain terminators, for example corresponding to formula (VIII), may be added to regulate molecular weight. The reaction is then carried out with phosgene by the interfacial condensation method in the presence of an inert, preferably polycarbonate-dissolving, organic phase. The reaction temperature is in the range from 0 to 40°C.

The branching agents optionally used (preferably 0.05 to 2 mol-%) may be initially introduced either with the diphenols in the aqueous alkaline phase or may be added in solution in the organic solvent before the phosgenation.

In addition to the diphenols of formula (I) and, optionally, other diphenols (VII), mono- and/or bis-chlorocarbonic acid esters thereof may also be used, being added in solution in organic solvents. The quantity of chain terminators and branching agents used is then determined by the molar quantities of diphenolate structural units corresponding to formula (I) and, optionally, the other diphenols, for example (VIII). Where chlorocarbonic acid esters are used, the quantity of phosgene may be reduced accordingly in known manner.

Suitable organic solvents for dissolving the chain terminators and, optionally, the branching agents and the chlorocarbonic acid esters are, for example, methylene chloride, chlorobenzene, acetone, acetonitrile and mixtures of these solvents, particularly mixtures of methylene chloride and chlorobenzene. The chain terminators and branching agents used may optionally be dissolved in the

same solvent.

The organic phase for the interfacial polycondensation may be formed, for example, by methylene chloride, chlorobenzene and by mixtures of methylene chloride and chlorobenzene.

Aqueous NaOH solution for example is used as the aqueous alkaline phase.

The production of the polycarbonates according to the invention by interfacial polycondensation may be catalyzed in the usual way by such catalysts as tertiary amines, particularly tertiary aliphatic amines, such as tributylamine or triethylamine. The catalysts may be used in quantities of from 0.05 to 10 mol-%, based on mols diphenols used. The catalysts may be added before the beginning of phosgenation or during or even after phosgenation.

The polycarbonates according to the invention are isolated in known manner.

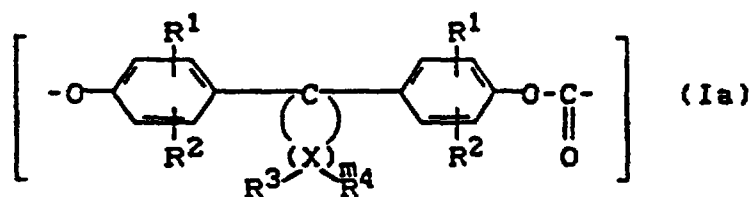
The high molecular weight, thermoplastic aromatic polycarbonates according to the invention may also be produced by the known homogeneous-phase process, the so-called "pyridine process" and also by the known melt transesterification process using diphenyl carbonate for example instead of phosgene. In this case, too, the polycarbonates according to the invention are isolated in known manner.

The polycarbonates obtainable by the process according to the invention preferably have molecular weights $\bar{M}_w$ (weight average, as determined by gel chromatography after preliminary calibration) of at least 10,000 g/mol and, more preferably, in the range from 10,000 to 300,000 g/mol. Where the polycarbonates according to the invention are used as injection moulding compounds, molecular weights of 20,000 to 80,000 g/mol are particularly preferred. Where the polycarbonates according to the invention are used as cast films, molecular weights $\bar{M}_w$ of 100,000 to 250,000

g/mol are particularly preferred. Polycarbonates according to the invention having molecular weights M_w of 25,000 to 150,000 g/mol are preferred for the production of extruded films. The polycarbonates according to the invention may be linear or branched and are homopolycarbonates or copolycarbonates based on the diphenols corresponding to formula (I).

Accordingly, the present invention also relates to high molecular weight, thermoplastic, aromatic polycarbonates having $\bar{M}_w$ values (weight average molecular weights) of at least 10,000, preferably in the range from 10,000 to 300,000 and, for injection moulding applications, more preferably in the range from 20,000 to 80,000 obtainable by the process according to the invention from diphenols of formula (I) which may be linear or branched.

Accordingly, the present invention also relates to high molecular weight, thermoplastic, aromatic polycarbonates having $\bar{M}_w$ values (weight average molecular weights) of at least 10,000, preferably in the range from 10,000 to 300,000 g/mol and, for injection moulding applications, more preferably in the range from 20,000 to 80,000 which contain bifunctional carbonate structural units corresponding to formula (Ia)



in which

X, R^1 , R^2 , R^3 , R^4 and m are as defined for formula (I), in quantities of from 100 mol-% to 2 mol-%, preferably in quantities of from 100 mol-% to 5 mol-%, more preferably in

quantities of from 100 mol-% to 10 mol-% and, most preferably, in quantities of from 100 mol-% to 20 mol-%, based in each case on the total quantity of 100 mol-% of difunctional carbonate structural units in the polycarbonate.

5 Accordingly, the polycarbonates according to the invention contain quantities - complementary in each case to 100 mol-% - of other difunctional carbonate structural units, for example those corresponding to formula (VIIa)

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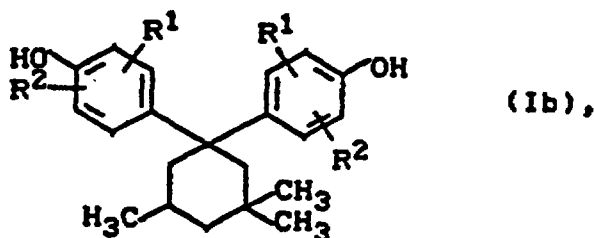


15 i.e. in quantities of from 0 mol-% (inclusive) to 98 mol-% inclusive, preferably from 0 mol-% to 95 mol-%, more preferably from 0 mol-% to 90 mol-% and most preferably from 0 mol-% to 80 mol-%, based in each case on the total quantity of 100 mol-% of difunctional carbonate structural units in
20 the polycarbonate.

Polycarbonates based on cycloaliphatic bisphenols are basically known and are described, for example, in EP-A 164 476, EP-A 166 834, DE-OS 33 45 945, DE-OS 20 63 052, FR-PS 1 427 998, WO 80 00 348, BE-PS 785 189. They frequently
25 have relatively high glass transition temperatures, but other important physical properties, such as UV stability and heat ageing resistance, are unsatisfactory.

It has now surprisingly been found that, as already mentioned, it is possible by incorporation of the diphenols
30 of formula (I) according to the invention to obtain new polycarbonates combining high heat resistance with other favorable properties. This applies in particular to the polycarbonates based on diphenols corresponding to formula (Ib)

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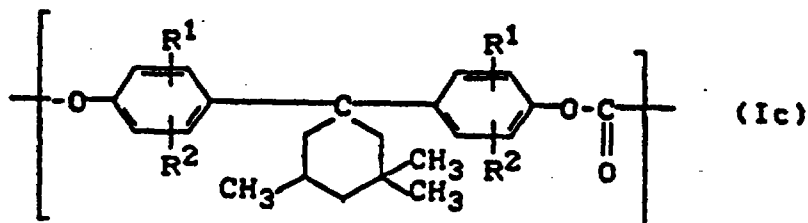


in which

10 R^1 and R^2 independently of one another have the meaning defined for formula (I) and, more preferably, represent hydrogen.

Accordingly, the present invention preferably relates to polycarbonates in which, in the structural units corresponding to formula (Ia), $m = 4$ or 5, and, more especially, to those containing structural units corresponding to formula (Ic)

15



25 in which

R^1 and R^2 are as defined for formula (Ia), but are preferably hydrogen.

Unexpectedly, these polycarbonates based on the diphenols corresponding to formula (Ib), in which R^1 and R^2 are preferably hydrogen, also show high UV stability and good flow behaviour in the melt in addition to their high heat resistance.

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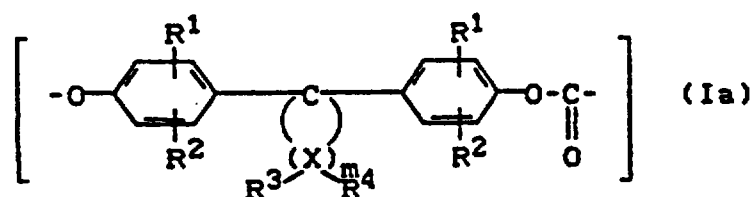
In addition, the properties of the polycarbonates may be varied with advantage through their combination with

35

g/mol are particularly preferred. Polycarbonates according to the invention having molecular weights M_w of 25,000 to 150,000 g/mol are preferred for the production of extruded films. The polycarbonates according to the invention may be linear or branched and are homopolycarbonates or copolycarbonates based on the diphenols corresponding to formula (I).

Accordingly, the present invention also relates to high molecular weight, thermoplastic, aromatic polycarbonates having $\bar{M}_w$ values (weight average molecular weights) of at least 10,000, preferably in the range from 10,000 to 300,000 and, for injection moulding applications, more preferably in the range from 20,000 to 80,000 obtainable by the process according to the invention from diphenols of formula (I) which may be linear or branched.

Accordingly, the present invention also relates to high molecular weight, thermoplastic, aromatic polycarbonates having $\bar{M}_w$ values (weight average molecular weights) of at least 10,000, preferably in the range from 10,000 to 300,000 g/mol and, for injection moulding applications, more preferably in the range from 20,000 to 80,000 which contain bifunctional carbonate structural units corresponding to formula (Ia)



in which

X, R^1 , R^2 , R^3 , R^4 and m are as defined for formula (I),

in quantities of from 100 mol-% to 2 mol-%, preferably in quantities of from 100 mol-% to 5 mol-%, more preferably in

other diphenols, particularly with the diphenols corresponding to formula (VII).

5 The polycarbonates obtainable by the process according to the invention are isolated in known manner by separating off the organic phase obtained in the interfacial process, washing it until it is neutral and electrolyte-free and then isolating it in the form of granules, for example in an evaporation extruder.

10 The additives normally used for thermoplastic polycarbonates, such as stabilizers, mould release agents, pigments, flameproofing agents, antistatic agents, fillers and reinforcing materials may be added in the usual quantities to the polycarbonates according to the invention before or after their processing.

15 More particularly, it is possible to add, for example, carbon black, graphite, kieselguhr, kaolin, clays, CaF_2 , CaCO_3 , aluminium oxides, glass fibers and inorganic pigments both as fillers and as nucleating agents and, for example, glycerol stearates, pentaerythritol tetrastearate and
20 trimethylol propane tristearate as mould release agents.

The polycarbonates according to the invention may be processed to mouldings, for example by extruding the polycarbonates isolated in known manner to granules and processing the resulting granulate in known manner by injection moulding to form various articles, optionally after
25 incorporation of the additives mentioned above.

The polycarbonates according to the invention may be used as mouldings for any applications where hitherto known polycarbonates are used, i.e. both in the electrical field
30 and in the building field for covering and glazing purposes, particularly when high heat resistance coupled with good processibility are required, i.e. when complicated components of high heat resistance are required.

35 Further applications of the polycarbonates according to the

invention:

A.

5 As optical data storage media, for example in the form of compact discs:

10 The production of such discs is known (see, for example, J. Hennig, paper presented at the "Neue Polymere (New Polymers)" Conference in Bad Neuheim, 14./15.04.1986 "Polymere als Substrate für optische Plattenspeicher (Polymers as Substrates for Optical Discs)" or Philips Tech. Rev. 33, 178-180, 1973, No. 7 and 33, 186-189, 1973, No. 7).

B.

15 For the production of safety glass.

20 Safety glass generally has a thickness of 2 mm to 10 mm and may be coated by vapour deposition with SiO_x , where x has a value of 1 to 2, or used in conjunction with glass. Safety glass is widely used in buildings, motor vehicles and aircraft and in shields and helmets.

C.

As raw materials for paints.

25 D.

For the production of blow mouldings (see, for example, US-PS 2,964,794).

E.

30 For the production of light-permeable sheets, more particularly double-skin sheets, for example for covering buildings, such as stations, greenhouses and lighting installations.

35 F.

For the production of foams (see, for example, DE-AS 1 031 507).

G.

- 5 For the production of filaments and wires [see, for example, DE-AS 1 137 167 and DE-OS 1 785 137].

H.

- 10 As translucent plastics containing glass fibres for optical-fibre applications (see, for example, DE-OS 1 544 020).

I.

- 15 For the production of precision injection mouldings, such as lens holders for example. Polycarbonates containing glass fibres and, optionally, approx. 1% by weight to 10% by weight MoS_2 , based on the total weight, are used for this purpose.

K.

- 20 For the production of optical components, more particularly lenses for photographic and film cameras (see, for example, DE-OS 2 701 173).

L.

- 25 As light transmission media, more particularly as optical cables (see, for example, EP-OS 0 089 801).

M.

- 30 As electrical insulating materials for electrical conductors.

O.

As a carrier material for organic photoconductors.

P.

- 5 For the production of lamps, for example headlamps or diffusors.

More particularly, films can be produced from the high molecular weight aromatic polycarbonates according to the invention. The films preferably have thicknesses of 1 to 1,500 μm and, more preferably, 10 to 900 μm .

The films obtained may be monoaxially or biaxially stretched in known manner, preferably in a ratio of 1:1.5 to 1:3.

15 The films may be produced by known methods for making films, for example by extrusion of a polymer melt through a flat sheet die, by blowing in a film blowing machine, thermoforming or casting. To this end, a concentrated solution of the polymer in a suitable solvent is cast onto a flat substrate, the solvent is evaporated and the film formed is lifted off the substrate.

20 The films may be stretched in known manner on known machines at temperatures between room temperature and a temperature at which the viscosity of the polymer melt is not too low, generally at a temperature of up to about 370°C.

25 The production of films by casting of the polycarbonate solutions is carried out, for example, by casting of concentrated solutions of the polycarbonate in a suitable solvent onto flat surfaces and subsequently evaporating the solvent at a temperature of the flat surfaces between room temperature and 150°C. The concentrated solutions of the polycarbonates may also be applied to liquids which have a higher density than the concentrated solutions and which are not compatible with the solvent used and, after spread-

30

35

ing, recovering the films by evaporation of the solvent used for the polycarbonate and, optionally, the higher density liquid as well.

5 The films according to the invention have particularly high heat resistance and are permeable to many gases while still showing high selectivity. Accordingly, they may be used with advantage as gas permeation membranes.

The films may be used on their own for this purpose.

10 They may of course also be used to produce composite films with other plastic films, for which purpose any known films may in principle be used, depending on the intended application and final properties of the composite film. For example, a composite may be produced from two or more films by placing the individual films, including the
15 polycarbonate film according to the invention, one on top of the other and pressing them together under pressure at suitable temperatures determined by the softening points of the individual films. The known film co-extrusion process may also be used.

20 The composite films are produced by initially producing the films of the individual components in known manner or as described above under optimal temperature control. The uncooled films are then heated to a common temperature, preferably between room temperature and 370°C, without
25 significant stretching. The films are then combined with one another on rollers and briefly pressed. A pressure of 2 to 500 bar may be applied. The process may also be carried out with more than one other film than that produced from the polycarbonates. In this case, for example,
30 the other films are first combined with one another in known manner and then pressed with the film of the polycarbonates under the pressure described above.

In addition, the films or composite films may be produced or used in known manner as homogeneous membranes,
35 composition membranes or asymmetrical membranes. The

membranes, films or composite films may be flat, may form hollow articles of various geometries (cylindrical, spherical, tubular) or may even be hollow fibres. Such mouldings may be produced by methods known to the expert.

5 Various polymers mentioned in the following may be used as the polymers from which films can be produced for the production of composite films with the polycarbonate films according to the invention, depending on the particular application envisaged. Depending on the particular
10 application, therefore, it is also possible to make gas-impermeable composite films which have better heat resistance by comparison with the prior art or heat-resistant, gas-permeable composite films according to the particular partners used for the composite film.

15 Materials which give films suitable for combination with the films according to the invention are mentioned in the following. These materials are called components (b).

Thermoplastics suitable as component (b) are

b1) amorphous thermoplastics, preferably those having a
20 glass temperature above 40°C and, more particularly, in the range from 60 to 220°C and

b2) partly crystalline thermoplastics, preferably those having a melting temperature above 60°C and, more particularly, in the range from 80 to 400°C.

25 Elastomers for component b) are

b3) those having a glass temperature below 0°C, preferably below -10°C and, more particularly, in the range from -15 to -140°C.

30 Examples of amorphous thermoplastics b1) are amorphous polymers from the class of polycarbonates, polyamides, polyolefins, polysulfones, polyketones, thermoplastic vinyl polymers, such as polymethyl acrylates, or homopolymers of aromatic vinyl compounds, copolymers of aromatic vinyl compounds or graft polymers of vinyl monomers on rubbers,
35 polyethers, polyimides, thermoplastic polyurethanes,

aromatic polyester(carbonate)s and liquid-crystalline polymers.

5 Examples of crystalline thermoplastics b2) are aliphatic polyesters, polyarylene sulfides and the partially crystalline representatives of the thermoplastics listed above under b1).

10 Examples of elastomers b3) are the various rubbers, such as ethylene-propylene rubber, polyisoprene, polychloroprene, polysiloxanes, atactic polypropylene, diene, olefin and acrylate rubbers and natural rubbers, styrene-butadiene block copolymers, copolymers of ethylene with vinyl acetate or with (meth)acrylates, elastic polyurethanes where they are not listed as thermoplastics under b1) or b2) and elastic polycarbonate-polyether block
15 copolymers.

Amorphous thermoplastics b1) are, in particular, polycarbonates (other than the polycarbonates according to the invention). Polycarbonates may be both homopolycarbonates and also copolycarbonates and may be both linear and
20 branched. The particularly preferred bisphenol for the polycarbonates is bisphenol A.

The molecular weights $\bar{M}_w$ (weight average molecular weight, as determined by gel permeation chromatography in tetrahydrofuran) of the thermoplastic polycarbonates are in
25 the range from 10,000 to 300,000 and preferably in the range from 12,000 to 150,000.

The thermoplastic polycarbonates may be used both individually and in admixture as component b).

30 Preferred other thermoplastics are also aliphatic, thermoplastic polyesters, more preferably polyalkylene terephthalates, i.e. for example those based on ethylene glycol, propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol and 1,4-bis-hydroxymethylcyclohexane.

The molecular weights ($\bar{M}_w$) of these polyalkylene terephthalates are in the range from 10,000 to 80,000. The
35

polyalkylene terephthalates may be obtained by known methods, for example from terephthalic acid dialkyl ester and the corresponding diol by transesterification (cf. for example US-PSS 2,647,885, 2,643,989, 2,534,028, 2,578,660, 2,742,494, 2,901,466).

Preferred other thermoplastics also include thermoplastic polyamides.

Suitable thermoplastic polyamides are any partially crystalline polyamides, particularly polyamide-6, polyamide-6,6, and partially crystalline copolyamides based on these two components. Other suitable thermoplastic polyamides are partially crystalline polyamides of which the acid component consists completely or in part of, in particular, adipic acid or caprolactam of terephthalic acid and/or isophthalic acid and/or suberic acid and/or sebacic acid and/or azelaic acid and/or dodecane dicarboxylic acid and/or adipic acid and/or a cyclohexane dicarboxylic acid, and of which the diamine component consists completely or in part of, in particular, m- and/or p-xylylenediamine and/or hexamethylenediamine and/or 2,2,4- and/or 2,4,4-trimethyl hexamethylenediamine and/or isophoronediamine and/or 1,4-diaminobutane and of which the compositions are known in principle from the prior art (cf. for example Encyclopedia of Polymers, Vol. 11, pages 315 et seq.).

Other suitable thermoplastic polyamides are partially crystalline polyamides produced completely or in part from lactams containing 6 to 12 carbon atoms, optionally using one or more of the starting components mentioned above.

Particularly preferred partially crystalline polyamides are polyamide-6 and polyamide-6,6 or copolyamides containing a small amount (up to about 10% by weight) of other components.

Suitable polyamides are also amorphous polyamides obtained, for example, by polycondensation of diamines, such as for example hexamethylenediamines, decamethylene-

diamine, 2,2,4- and 2,4,4-trimethyl hexamethylenediamine, m- or p-xylylenediamine, bis-(4-aminocyclohexyl)-methane, mixtures of 4,4'- and 2,2'-diaminodicyclohexyl methanes, 2,2-bis-(4-aminocyclohexyl)-propane, 3,3'-dimethyl-4,4'-
5 diaminodicyclohexyl methane, 3-aminoethyl-3,5,5-trimethyl cyclohexyl amine, 2,5-bis-(aminomethyl)-norbornane, 2,6-bis-(aminomethyl)-norbornane, 1,4-diaminomethyl cyclohexane, and of mixtures of these diamines, with dicarboxylic acids, such as for example oxalic acid, adipic acid, azelaic acid, decane dicarboxylic acid, heptadecane dicarboxylic acid, 2,2,4-trimethyl adipic acid, 2,4,4-trimethyl adipic acid, isophthalic acid and terephthalic acid, and with mixtures of these dicarboxylic acids. Accordingly, amorphous copolyamides obtained by polycondensation of
10 several of the diamines and/or dicarboxylic acids mentioned above are also included. Amorphous copolyamides prepared using ω -aminocarboxylic acids, such as ω -aminocaproic acid, ω -aminoundecanoic acid or ω -aminolauric acid, or lactams thereof, are also included.

20 Particularly suitable amorphous, thermoplastic polyamides are those obtainable from isophthalic acid, hexamethylenediamine and other diamines, such as 4,4'-diaminodicyclohexyl methane, isophoronediamine, 2,2,4- and 2,4,4-trimethyl hexamethylenediamine, 2,5- and/or 2,6-bis-(aminomethyl)-norbornane; those obtainable from isophthalic acid, 4,4'-diaminodicyclohexyl methane and ω -caprolactam; those obtainable from isophthalic acid, 3,3-dimethyl-4,4'-diaminodicyclohexyl methane and ω -lauric lactam; and those obtainable from terephthalic acid and the isomer mixture of
25 2,2,4- and 2,4,4-trimethyl hexamethylenediamine.
30

Instead of using pure 4,4'-diaminodicyclohexyl methane, it is also possible to use mixtures of the position-isomeric diaminodicyclohexyl methanes which consist of

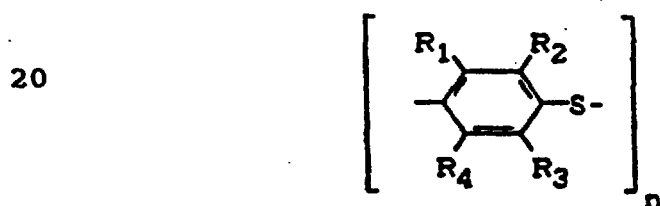
35 70 to 99 mol-% of the 4,4'-diamino isomer,

1 to 30 mol-% of the 2,4'-diamino isomer,
0 to 2 mol-% of the 2,2'-diamino isomer

and, optionally, correspondingly more highly condensed di-
amines obtained by hydrogenation of diaminodiphenyl methane
of technical quality.

Suitable thermoplastic polyamides may also consist of
mixtures of partially crystalline and amorphous polyamides,
the amorphous polyamide component preferably being smaller
than the partially crystalline polyamide component. The
amorphous polyamides and their production are also known
from the prior art (cf. for example Ullmann, Enzyklopädie
der technischen Chemie, Vol. 19, page 50).

Preferred other thermoplastics b) also include thermo-
plastic, linear or branched polyarylene sulfides. They
have structural units corresponding to the following gener-
al formula



in which R_1 to R_4 may be the same or different and represent
 C_{1-6} alkyl, phenyl or hydrogen. The polyarylene sulfides may
also contain diphenyl units.

Polyarylene sulfides and their production are known
(see for example US-PS 3,354,129 and EP-A 0 171 021).

Preferred other thermoplastics b) are thermoplastic
polyarylene sulfones.

Suitable polyarylene sulfones have average weight
average molecular weights $\bar{M}_w$ (as measured by light scat-
tering method in $CHCl_3$) in the range from 1,000 to 200,000
and preferably in the range from 20,000 to 60,000. Ex-

amples are the polyarylene sulfones obtainable in known manner from 4,4'-dichlorodiphenyl sulfone and a bisphenol, particularly 2,2-bis-(4-hydroxyphenyl)-propane, which have average weight average molecular weights $\bar{M}_w$ of from 2,000 to 200,000.

These polyarylene sulfones are known (cf. for example US-PS 3,264,536, DE-AS 1 794 171, GB-PS 1,264,900, US-PS 3,641,207, EP-A-0 038 028, DE-OS 3 601 419 and DE-OS 3 601 420). The polyarylene sulfones may also be branched in known manner (cf. for example DE-OS 2 305 413).

Preferred other thermoplastics b) also include thermoplastic polyphenylene oxides, preferably poly-(2,6-dialkyl-1,4-phenylene oxides), having weight average molecular weights $\bar{M}_w$ (as measured by the light scattering method in chloroform) of from 2,000 to 100,000 and preferably from 20,000 to 60,000.

They may be obtained in known manner by oxidizing condensation of 2,6-dialkylphenols with oxygen in the presence of copper salts and tertiary amines as catalyst (see for example DE-OS 21 26 434 and US-PS 3,306,875).

Suitable poly-(2,6-dialkyl-1,4-phenylene oxides) are, in particular, poly-[2,6-di-(C_{1-4} -alkyl)-1,4-phenylene oxides], for example poly-(2,6-dimethyl-1,4-phenylene oxide).

Preferred other thermoplastics b) also include aromatic polyether ketones (cf. for example GB-PS 1,078,234, US-PS 4,010,147 and EP-OS 0 135 938) other than those based on diphenols corresponding to formula I.

They contain the recurring structural element

$$-O-E-O-E'-$$

in which $-E'-$ is the residue of a bisaryl ketone having two bonds and $-O-E-O-$ is a diphenolate residue having two bonds.

They may be obtained, for example, in accordance with

GB-PS 1,078,234 from dialkali metal diphenolates having the formula alkali-O-E-O-alkali and bis-(haloaryl)-ketones having the formula hal-E'-hal (hal = halogen). One suitable dialkali metal diphenolate is, for example, that of
5 2,2-bis-(4-hydroxyphenyl)-propane, while a suitable bis-(haloaryl)-ketone is 4,4'-dichlorobenzophenone.

Preferred other thermoplastics b) also include thermoplastic vinyl polymers.

8 Vinyl polymers in the context of the invention are
10 homopolymers of vinyl compounds, copolymers of vinyl compounds and graft polymers of vinyl compounds on rubbers.

Homopolymers and copolymers suitable for the purposes of the invention are those of styrene, α -methyl styrene, acrylonitrile, methacrylonitrile, C_{1-12} (cyclo)alkyl esters
15 of (meth)acrylic acid, C_{1-4} carboxylic acid vinyl esters, the copolymers also being obtainable from mixtures of these vinyl compounds by known methods.

The homopolymers or copolymers should have intrinsic viscosities of from 0.3 to 1.5 dl/g (as measured at 23°C in
20 toluene in known manner).

Suitable vinyl polymers are, for example, thermoplastic poly- C_{1-4} -alkyl methacrylates, for example those of methyl, ethyl, propyl or butyl methacrylate, preferably methyl or ethyl methacrylate. Both homopolymers and co-
25 polymers of these methacrylates are included. In addition, other ethylenically unsaturated, copolymerizable monomers, such as for example (meth)acrylonitrile, (α -methyl) styrene, bromostyrene, vinyl acetate, C_{1-8} alkyl acrylate, (meth)acrylic acid, ethylene, propylene and N-vinyl pyrrol-
30 idone, may be copolymerized in small quantities.

The thermoplastic poly- C_{1-4} -alkyl methacrylates suitable for the purposes of the invention are known from the literature or may be obtained by methods known from the literature.

35 Suitable vinyl polymers also include copolymers of

styrene or α -methyl styrene and acrylonitrile optionally containing up to 40% by weight of esters of acrylic or methacrylic acid, particularly methyl methacrylate or n-butyl acrylate. Styrene derivatives must always be present as monomers. The styrene derivatives are present in proportions of 100 to 10% by weight, preferably 90 to 20% by weight and more preferably 80 to 30% by weight and may be obtained by standard methods, such as radical polymerization in bulk, solution, suspension or emulsion, but preferably by radical emulsion polymerization in water.

Suitable graft polymers are formed by polymerization of the above-mentioned vinyl monomers or mixtures of vinyl monomers in the presence of rubbers having glass temperatures below 0°C and preferably below -20°C. The graft polymers generally contain 1 to 85% by weight and preferably 10 to 80% by weight rubber. The graft polymers may be prepared by standard methods in solution, bulk or emulsion, preferably in emulsion; mixtures of vinyl monomers may be simultaneously or successively graft-polymerized.

Suitable rubbers are, preferably, diene rubbers and acrylate rubbers.

Diene rubbers are, for example, polybutadiene, polyisoprene and copolymers of butadiene with up to 35% by weight comonomers, such as styrene, acrylonitrile, methyl methacrylate and C₁₋₆ alkyl acrylates.

Acrylate rubbers are, for example, crosslinked, particulate emulsion polymers of C₁₋₆ alkyl acrylates, particularly C₂₋₆ alkyl acrylates, optionally in admixture with up to 15% by weight of other unsaturated monomers, such as styrene, methyl methacrylate, butadiene, vinyl methyl ether, acrylonitrile, and of at least one polyfunctional crosslinking agent, such as for example divinylbenzene, glycol-bis-acrylates, bis-acrylamides, phosphoric acid triallyl ester, citric acid triallyl ester, allyl esters of acrylic acid and methacrylic acid, triallyl isocyanurate,

the acrylate rubbers containing up to 4% by weight of the crosslinking comonomers.

5 Mixtures of diene rubbers with acrylate rubbers and also rubbers having a core-shell structure are also suitable for the production of the graft polymers.

For graft polymerization, the rubbers must be present in the form of discrete particles, for example in the form of a latex. These particles generally have mean diameters of from 10 nm to 2000 nm.

10 The graft polymers may be produced by known methods, for example by radical emulsion graft polymerization of the vinyl monomers in the presence of rubber latices at temperatures of from 50 to 90°C using water-soluble initiators, such as peroxodisulfate, or redox initiators.

15 Emulsion graft polymers produced by radical graft polymerization onto particulate, highly crosslinked rubbers (diene or alkyl acrylate rubbers) having gel contents of more than 80% by weight and mean particle diameters (d_{50}) of from 80 to 800 nm are preferred.

20 Technical ABS polymers are particularly suitable.

Mixtures of vinyl homopolymers and/or vinyl copolymers with graft polymers are also suitable.

25 Preferred other thermoplastics b) also include thermoplastic polyurethanes. These are reaction products of diisocyanates, completely or predominantly aliphatic oligo- and/or polyesters and/or ethers and one or more chain-extending agents. These thermoplastic polyurethanes are substantially linear and have thermoplastic processing characteristics.

30 The thermoplastic polyurethanes are known or may be obtained by known methods (cf. for example US-PS 3,214,411; J.H. Saunders and K.C. Frisch, "Polyurethanes, Chemistry and Technology", Vol. II, pages 299 to 451, Interscience Publishers, New York, 1964; and Mobay Chemical Corporation
35 "A Processing Handbook for Texin Urethane Elastoplastic

Materials", Pittsburgh, PA).

Starting materials for the production of the oligo-
esters and polyesters are, for example, adipic acid, suc-
cinic acid, sebacic acid, suberic acid, oxalic acid, methyl
5 adipic acid, glutaric acid, pimelic acid, azelaic acid,
phthalic acid, terephthalic acid and isophthalic acid.

Adipic acid is preferred.

Suitable glycols for the production of the oligoesters
and polyesters are, for example, ethylene glycol, 1,2- and
10 1,3-propylene glycol, butane-1,2-, -1,3-, -1,4-, -2,3- and
-2,4-diol, hexanediol, bis-hydroxymethyl cyclohexane, di-
ethylene glycol and 2,2-dimethyl propylene glycol. In ad-
dition, small quantities, i.e. up to 1 mol-%, of trihydric
or higher alcohols, for example trimethylol propane, gly-
cerol, hexanetriol etc., may be used together with the
15 glycols.

The resulting hydroxyl oligoesters or polyesters have
a molecular weight of at least 600, a hydroxyl value of
from about 25 to 190 and preferably from about 40 to 150,
20 an acid value of from about 0.5 to 2 and a water content of
from about 0.01 to 0.2%.

Oligoesters and polyesters also include oligomeric or
polymeric lactones, such as for example oligocaprolactone
or polycaprolactone, and aliphatic polycarbonates, such as
25 for example polybutane-1,4-diol carbonate or polyhexane-
1,6-diol carbonate.

A particularly suitable oligoester which may be used
as starting material for the thermoplastic polyurethanes is
prepared from adipic acid and a glycol containing at least
30 one primary hydroxyl group. The condensation is terminated
when an acid value of 10 and preferably of about 0.5 to 2
is reached. The water formed during the reaction is thus
separated off simultaneously or afterwards, so that the
final water content is between about 0.01 and 0.05% and
35 preferably between 0.01 and 0.02.

Oligoethers and polyethers for the production of the thermoplastic polyurethanes are, for example, those based on tetramethylene glycol, propylene glycol and ethylene glycol.

5 Polyacetals may also be regarded as polyethers and may be used as such.

The oligoethers or polyethers should have average molecular weights $\bar{M}_n$ (number average determined via the OH value of the products) of from 600 to 2,000 and preferably
10 from 1,000 to 2,000.

4,4'-Diphenyl methane diisocyanate is preferably used as the organic diisocyanate for the production of the polyurethanes. It should contain less than 5% 2,4'-diphenyl methane diisocyanate and less than 2% of the dimer of di-
15 phenyl methane diisocyanate. In addition, the acidity, expressed as HCl, should be in the range from about 0.005 to 0.2%. The acidity expressed as % HCl is determined by extraction of the chloride from the isocyanate in hot, aqueous methanol solution or by liberation of the chloride
20 during hydrolysis with water and titration of the extract with standard silver nitrate solution in order to obtain the concentration of chloride ions present therein.

It is also possible to use other diisocyanates for the production of the thermoplastic polyurethanes, including
25 for example the diisocyanates of ethylene, ethylidene, propylene, butylene, cyclo-1,3-pentylene, cyclo-1,4-hexylene, cyclo-1,2-hexylene, 2,4-tolylene, 2,6-tolylene, p-phenylene, n-phenylene, xylene, 1,4-naphthylene, 1,5-naphthylene, 4,4'-diphenylene; 2,2-diphenylpropane-4,4'-diisocyanate, azobenzene-4,4'-diisocyanate, diphenylsulfone-4,4'-diiso-
30 cyanate, dichlorohexane methylene diisocyanate, penta-methylene diisocyanate, hexamethylene diisocyanate, 1-chlorobenzene-2,4-diisocyanate, furfuryl diisocyanate, dicyclohexyl methane diisocyanate, isophorone diisocyanate,
35 diphenyl ethane diisocyanate and bis-(isocyanatophenyl)-

ethers of ethylene glycol, butanediol, etc.

Suitable chain-extending agents are organic difunctional compounds containing active hydrogen reactive to isocyanates, for example diols, hydroxycarboxylic acids, dicarboxylic acids, diamines and alkanolamines and water. Examples of such chain-extending agents are, for example, ethylene, propylene and butylene glycol, butane-1,4-diol, butanediol, butynediol, xylylene glycol, amylene glycol, 1,4-phenylene-bis- β -hydroxyethyl ether, 1,3-phenylene-bis- β -hydroxyethyl ether, bis-(hydroxymethylcyclohexane), hexanediol, adipic acid, ω -hydroxycaproic acid, thiodiglycol, ethylenediamine, propylene, butylene, hexamethylene, cyclohexylene, phenylene, tolylene and xylylenediamine, diaminodicyclohexyl methane, isophoronediamine, 3,3'-dichlorobenzidine, 3,3'-dinitrobenzidine, ethanolamine, aminopropyl alcohol, 2,2-dimethyl propanolamine, 3-aminocyclohexyl alcohol and p-aminobenzyl alcohol. The molar ratio of oligoester or polyester to bifunctional chain extender is in the range from 1:1 to 1:50 and preferably in the range from 1:2 to 1:30.

In addition to difunctional chain-extending agents, it is also possible to use trifunctional or more than trifunctional chain-extending agents in small quantities of up to about 5 mol-%, based on mols of difunctional chain-extending agents used.

Examples of trifunctional or more than trifunctional chain-extending agents are glycerol, trimethylol propane, hexanetriol, pentaerythritol and triethanolamine.

Monofunctional components, for example butanol, may also be used for the production of the thermoplastic polyurethanes.

The diisocyanates, oligoesters, polyesters, polyethers, chain-extending agents and monofunctional components mentioned as structural units for the thermoplastic polyurethanes are either known from the literature or may

be obtained by methods known from the literature.

The known production of the polyurethanes may be carried out, for example, as follows:

For example, the oligoesters or polyesters, the organic diisocyanates and the chain-extending agents may be individually heated, preferably to a temperature of from about 50 to 220°C, and then mixed. The oligoesters or polyesters are preferably first individually heated, then mixed with the chain-extending agents and the resulting mixture mixed with the preheated isocyanate.

The starting components for the production of the polyurethanes may be mixed by any mechanical stirrer which provides for intensive mixing in a short time. If the viscosity of the mixture should prematurely rise too quickly during stirring, either the temperature may be lowered or a small quantity (0.001 to 0.05% by weight, based on ester) citric acid or the like may be added to reduce the reaction velocity. To increase the reaction velocity, suitable catalysts, such as for example the tertiary amines mentioned in US-PS 2,729,618, may be used.

Preferred other thermoplastics are also so-called "LC" polymers. LC polymers are polymers capable of forming liquid crystalline melts. Polymers of this type, which are also termed "thermotropic", are sufficiently well-known (see for example EP-PS 0 131 846, EP-OS 0 132 637 and EP-OS 0 134 959). More literature is cited in these literature references which also describe determination of the liquid crystalline state of polymer melts.

Examples of LC polymers are aromatic polyesters based on optionally substituted p-hydroxybenzoic acid, optionally substituted iso- and/or terephthalic acids, 2,7-dihydroxynaphthalene and other diphenols (EP-OS 0 131 846), aromatic polyesters based on optionally substituted p-hydroxybenzoic acid, diphenols, carbonic acid and, optionally, aromatic dicarboxylic acids (EP-OS 0 132 637) and aromatic poly-

esters based on optionally substituted p-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid, isophthalic acid, hydroquinone and 3,4'- and/or 4,4'-dihydroxydiphenyl, 3,4'- and/or 4,4'-dihydroxydiphenyl ether and/or 3,4'- and/or 4,4'-dihydroxydiphenyl sulfide (EP-OS 0 134 959).

The LC polymers have a persistence length at room temperature of from 18 to 1300 Å, preferably from 25 to 300 Å and more preferably from 25 to 150 Å. The persistence length of a polymer at room temperature characterizes the average entanglement of a molecular chain in a dilute solution under theta conditions (cf. for example P.J. Flory, Principles of Polymer Chemistry, Cornell Univ. Press, Ithaca, New York) and half Kuhn's step length. The persistence length may be determined by various methods in dilute solutions, for example by light scattering and X-ray small angle measurements. After suitable preparation, the persistence length may also be determined by neutron small angle scattering in the solid. Other theoretical and experimental methods are described, for example, in J.H. Wendorff in "Liquid Crystalline Order in Polymers", e.g. A. Blumstein, Academic Press 1978, pages 16 et seq, and in the references cited in S.M. Aharoni, Macromolecules 19, (1986), pages 429 et seq.

Preferred other thermoplastics are also aromatic polyester carbonates.

According to the invention, aromatic polyesters and polyester carbonates suitable as the thermoplastic b) are synthesized from at least one aromatic bisphenol, for example corresponding to formula (VII), at least one aromatic dicarboxylic acid and, optionally, carbonic acid. Suitable aromatic dicarboxylic acids are, for example, orthophthalic acid, terephthalic acid, isophthalic acid, tert. butyl isophthalic acid, 3,3'-diphenyl dicarboxylic acid, 4,4'-diphenyl dicarboxylic acid, 4,4'-benzophenone dicarboxylic acid, 3,4'-benzophenone dicarboxylic acid,

4,4'-diphenyl ether dicarboxylic acid, 4,4'-diphenyl sulfone dicarboxylic acid, 2,2-bis-(4-carboxyphenyl)-propane, trimethyl-3-phenylindane-4,5'-dicarboxylic acid.

5 Of the aromatic dicarboxylic acids, terephthalic acid and/or isophthalic acid are particularly preferred.

Aromatic polyesters and polyester carbonates may be produced by methods known from the literature for the production of polyesters and polyester carbonates, for example by processes carried out in homogeneous solution,
10 by melt transesterification processes and by the two-phase interfacial process. Melt transesterification processes and, in particular, the two-phase interfacial process are preferably used.

Melt transesterification processes (the acetate
15 process and the phenyl ester process) are described, for example, in US-PSS 3,494,885, 4,386,186, 4,661,580, 4,680,371, and 4,680,372; in EP-A-26 120, 26 121, 26 684, 28 030, 39 845, 91 602, 97 970, 79 075, 146 887, 156 103, 234 913, 234 919 and 240 301 and in DE-ASS 1 495 626 and 2
20 232 977. The two-phase interfacial process is described, for example, in EP-A-68 014, 88 322, 134 898, 151 750, 182 189, 219 708 and 272 426, in DE-OSS 2 940 024, 3 007 934 and 3 440 020 and in Polymer Reveiws, Volume 10, Condensation Polymers by Interfacial and Solution Methods, Paul W.
25 Morgan, Interscience Publishers New York, 1965, Chapter VIII, page 325, Polyesters.

In the acetate process, generally bisphenol diacetate and, in the phenyl ester process, generally bisphenol, an aromatic dicarboxylic acid or diphenyl ester of the aromatic
30 dicarboxylic acid and, optionally, diphenyl carbonate are generally reacted with elimination of phenol and, optionally, CO₂ to form the polyester or polyester carbonate. In the two-phase interfacial process, alkali metal bisphenolate, an aromatic dicarboxylic acid dichloride and,
35 optionally, phosgene are used as starting materials for the

production of polyesters or polyester carbonates. In this condensation reaction, the polyester or the polyester carbonate is prepared with formation of alkali metal chloride. In general, the salt formed is dissolved in the aqueous phase while the polyester formed or the polyester carbonate formed is present in solution in the organic phase and is isolated therefrom.

Preferred elastomers b3) for component b) for the production of the mixtures according to the invention are the polyurethanes mentioned above, providing they are elastic, styrene-butadiene block copolymers which may be partially hydrogenated (for example Kraton G[®], a Shell product), the rubbers mentioned above for the graft polymers, the graft polymers themselves, providing they are elastic, and elastic polycarbonate-polyether block copolymers.

These elastomers are known.

The films or composite films may be flat, hollow, spherical, tubular and hollow-fiber-like. Films such as these are obtainable in known manner by thermoforming, blowing, etc.

The films according to the invention, particularly the composite films, are used for example for boil-proof and oven-proof, leak-proof packs and for microwave-proof packs, depending on which component b) is used for the composite film according to the invention.

The composite films according to the invention may be produced by co-extrusion of the thermoplastics with the polycarbonates according to the invention in a single operation.

The films of the polycarbonates according to the invention and the composite films according to the invention based on these films of the polycarbonates according to the invention may be used as homogeneous membranes, composition membranes or asymmetrical membranes.

In the following Examples, the relative viscosity was

measured on 0.5% by weight solutions of the polycarbonate in CH_2Cl_2 .

The glass temperature was measured by differential scanning calorimetry (DSC).

5

Example B.1

31.0 g (0.1 mol) of the diphenol according to Example (A.1), 33.6 g (0.6 mol) KOH and 560 g water are dissolved while stirring in an inert gas atmosphere. A solution of 10 0.188 g phenol in 560 ml methylene chloride is then added. 19.8 g (0.2 mol) phosgene were introduced into the thoroughly stirred solution at pH 13 to 14 and at 21 to 25°C. 0.1 ml ethyl pyridine is then added, followed by stirring for 45 minutes. The bisphenolate-free aqueous phase is separated off, the organic phase is washed with water until 15 neutral after acidification with phosphoric acid and is freed from the solvent. The polycarbonate had a relative solution viscosity of 1.259.

The glass temperature of the polymer was found to be 20 233°C (DSC).

Example B.2

68.4 g (0.3 mol) bisphenol A (2,2-bis-(4-hydroxyphenyl)-propane, 217.0 g (0.7 mol) diphenol according to 25 Example (A.1), 336.6 g (6 mol) KOH and 2700 g water are dissolved with stirring in an inert gas atmosphere. A solution of 1.88 g phenol in 2500 ml methylene chloride is then added. 198 g (2 mol) phosgene were introduced into the thoroughly stirred solution at pH 13 to 14 and at 21 to 30 25°C. 1 ml ethyl piperidine is then added, followed by stirring for 45 minutes. The bisphenolate-free aqueous phase is separated off, the organic phase is washed with water until neutral after acidification with phosphoric acid and is freed from the solvent. The polycarbonate had 35 a relative viscosity of 1.336.

The glass temperature of the polymer was found to be 212°C (DSC).

Example B.3

5 A mixture of 114 g (0.5 mol) bisphenol A and 155 g (0.5 mol) of the diphenol according to Example (A.1) was reacted as in Example B.2 to form the polycarbonate.

The polycarbonate had a relative solution viscosity of 1.386.

10 The glass temperature of the polymer was found to be 195°C (DSC).

Example B.4

15 A mixture of 159.6 g (0.7 mol) bisphenol A and 93 g (0.3 mol) of the diphenol according to Example (A.3) was reacted as in Example B.2 to form the polycarbonate.

The polycarbonate had a relative solution viscosity of 1.437.

20 The glass temperature of the polymer was found to be 180°C (DSC).

Example B.5

25 31.0 g (0.1 mol) of the the diphenol according to Example (A.3), 24.0 g (0.6 mol) NaOH and 270 g water are dissolved with stirring in an inert gas atmosphere. A solution of 0.309 g 4-(1,1,3,3-tetramethylbutyl)-phenol in 250 ml methylene chloride is then added. 19.8 g (0.2 mol) phosgene were introduced into the thoroughly stirred solution at pH 13 to 14 and at 21 to 25 °C. 0.1 ml ethyl
30 piperidine is then added, followed by stirring for 45 minutes. The bisphenolate-free aqueous phase is separated off, the organic phase is washed with water until neutral after acidification with phosphoric acid and is freed from the solvent. The polycarbonate had a relative solution
35 viscosity of 1.314.

The glass temperature of the polymer was found to be 234°C (DSC).

To assess the UV stability of the new polycarbonates, the formation of primary radicals under UV irradiation with a mercury vapor lamp (edge filter 305 nm) was determined in comparison with a polycarbonate based on 2,2-bis-(4-hydroxyphenyl)-propane. It was found that the polycarbonate of Example B.1 shows a lower primary radical formation rate and, therefore, higher UV stability.

Example B.6

148.2 g (0.65 mol) 2,2-bis-(4-hydroxyphenyl)-propane, 108.5 g (0.35 mol) of the diphenol according to Example (A.1), 336.6 g (6 mol) KOH and 2700 g water are dissolved with stirring in an inert gas atmosphere. A solution of 8.86 g 4-(1,1,3,3-tetramethylbutyl)-phenol in 2500 ml methylene chloride is then added. 198 g (2 mol) phosgene were introduced into the thoroughly stirred solution at pH 13 to 14 and at 21 to 25 °C. 1 ml ethyl piperidine is then added, followed by stirring for 45 minutes. The bisphenolate-free aqueous phase is separated off, the organic phase is washed with water until neutral after acidification with phosphoric acid and is freed from the solvent. The polycarbonate had a relative solution viscosity of 1.20.

Example B.7

3.875 kg (12.5 mol) bisphenol according to Example (A.2) are dissolved with stirring in 6.675 kg 45% NaOH and 30 l water in an inert gas atmosphere. 9.43 l methylene chloride, 11.3 l chlorobenzene and 23.5 g phenol are then added. 2.475 kg phosgene are introduced into the thoroughly stirred solution at pH 13-14 and at 20-25°C. After the phosgene has been introduced, 12.5 ml N-ethyl piperidine are added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the

organic phase is acidified with phosphoric acid and is then washed free from electrolyte with water and freed from the solvent. Rel. viscosity: 1.300, glass temperature: 238°C.

5 **Example B.8**

15.5 g (0.05 mol) bisphenol according to Example (A.3), 13.4 g (0.05 mol) bis-(4-hydroxyphenyl)-cyclohexane (bisphenol Z) and 24.0 g (0.6 mol) NaOH are dissolved with stirring in 362 ml water in an inert gas atmosphere. 0.516 g 4-(1,1,3,3-tetramethylbutyl)-phenol dissolved in 271 ml methylene chloride is then added. 19.8 g phosgene are introduced into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 0.1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is with phosphoric acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.297, glass temperature: 208°C.

20

Example B.9

15.5 g (0.05 mol) bisphenol according to Example (A.1), 17.6 g (0.05 mol) 4,4'-dihydroxytetraphenyl methane and 24.0 g (0.6 mol) NaOH are dissolved with stirring in 411 ml water in an inert gas atmosphere. 0.516 g 4-(1,1,3,3-tetramethylbutyl)-phenol dissolved in 308 ml methylene chloride is then added. 19.8 g phosgene are introduced into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 0.1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is with phosphoric acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.218, glass temperature: 212°C.

35 **Example B.10**

18.3 g (0.05 mol) bisphenol according to Example (A.4) and 23.6 g (0.42 mol) KOH are dissolved with stirring in 100 ml water in an inert gas atmosphere. 100 ml methylene chloride are then added. 17.3 g phosgene are introduced
5 into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 0.3 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with
10 phosphoric acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.310, glass temperature: 241°C.

Example B.11

15 29.6 g (0.1 mol) bisphenol according to Example (A.5) and 24.0 g (0.6 mol) NaOH are dissolved with stirring in 370 ml water in an inert gas atmosphere. 0.413 g 4-(1,1,3,3-tetramethylbutyl)-phenol dissolved in 277 ml methylene chloride are then added. 19.8 g phosgene are introduced
20 into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 0.1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with
25 phosphoric acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.370, glass temperature: 193°C.

Example B.12

30 62.0 g (0.2 mol) bisphenol according to Example (A.1), 182.4 g (0.8 mol) bisphenol A and 240 g (6 mol) NaOH are dissolved with stirring in 2400 ml water in an inert gas atmosphere. 6.603 g 4-(1,1,3,3-tetramethylbutyl)-phenol dissolved in 2400 ml methylene chloride are then added.
35 198 g phosgene are introduced into the thoroughly stirred

solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with phosphoric acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.298, glass temperature: 172°C.

Example B.13

10 170.5 g (0.55 mol) bisphenol according to Example (A.3), 102.6 g (0.45 mol) bisphenol A and 240 g (6 mol) NaOH are dissolved with stirring in 2400 ml water in an inert gas atmosphere. 5.158 g 4-(1,1,3,3-tetramethyl-butyl)-phenol dissolved in 2400 ml methylene chloride are
15 then added. 198 g phosgene are introduced into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with phosphoric
20 acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.302, glass temperature: 203°C.

Example B.14

25 108.5 g (0.35 mol) bisphenol according to Example (A.1), 148.2 g (0.65 mol) bisphenol A and 240 g (6 mol) NaOH are dissolved with stirring in 2400 ml water in an inert gas atmosphere. 6.189 g 4-(1,1,3,3-tetramethyl-butyl)-phenol dissolved in 2400 ml methylene chloride are
30 then added. 198 g phosgene are introduced into the thoroughly stirred solution at pH 13-14 and at 20-25°C. 5 minutes after the phosgene has been introduced, 1 ml N-ethyl piperidine is added and the mixture is left to react for 45 mins. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with phosphoric
35

acid and is then washed until neutral and freed from the solvent. Rel. viscosity: 1.305, glass temperature: 185°C.

Example C

5 Compact discs 12 cm in diameter were made from the copolycarbonate of Example (B.6) and from a bisphenol A homopolycarbonate, η_{rel} 1.20, in a Netstal injection moulding machine (melt temperature 330 to 350°C). The axial birefringence was tested by measuring the differences in pitch
10 with a standard comparator in conjunction with a polarization microscope. Transparency was visually evaluated and the glass temperature was determined by DSC.

15	Material	Pitch difference [nm/mm]	T_g [°C]	Transparency
	Example B6	+ 13	185	Yes
	Bisphenol A polycarbonate	+ 12	145	Yes

20

Example D (Film production)

D.1

20 g of the polycarbonate of Example B.1 were dissolved with stirring in 200 ml methylene chloride at 30°C,
25 the solution was concentrated and a 204 μ m thick film was produced by pouring out the solution onto a flat glass plate at 25°C. The film was dried in vacuo for 4 hours at 90°C and then measured for gas permeability.

30 Determination of the permeability to gases (permeation) of polymer membranes

The passage of a gas through an impervious polymer membrane is described by a dissolving/diffusion process. The characteristic constant for this process is the permeation coefficient P which indicates the gas volume V that
35 passes through a film of known surface area F and thickness

d in a certain time t for a given pressure difference Δp . For the steady state, the following may be deduced from the differential equations of the permeation process:

$$P = \frac{V \cdot d}{F \cdot t \cdot \Delta p} \quad (1)$$

In addition, permeation is dependent on the temperature and water content of the gas.

The measuring arrangement consists of a thermostatically controlled 2-chamber system. One chamber is designed to accommodate the test gas and the other to accommodate the permeate. The two chambers are separated by the polymer membrane to be measured.

The two chambers are evacuated to 10^{-3} mbar and the first chamber is filled with gas. The permeated gas (inert gases) then produces an increase in pressure in the permeate chamber for constant volume, the increase in pressure being quantitatively recorded by a pressure recorder (an MKS Baratron) as a function of time until the passage of gas reaches the steady state. V can be calculated from the increase in pressure (for normal pressure and normal temperature), t is known. Δp is adjusted in each case to 10^5 Pa taking the outside pressure into account. The surface area of the membrane F is known. The membrane thickness d is determined by micrometer guage as the mean value of ten independent thickness measurements distributed over the membrane surface.

From these values, the permeation coefficient P may be determined in accordance with (1) with the following dimension:

$$\left[\frac{\text{cm}^3 \text{ (NTP)} \cdot \text{mm}}{\text{m}^2 \cdot 24 \text{ h} \cdot 10^5 \text{ Pa}} \right]$$

based on a membrane thickness of 1 mm.

Further measurement parameters are:

Temperature : $25 \pm 1^\circ\text{C}$
Relative gas humidity : 0 %

5

Result: permeation coefficient

for O_2 : 280.8
for N_2 : 84.5
for CO_2 : 2174.0
10 for CH_4 : 149.4

The film was still dimensionally stable at 180°C .

D.2 (Comparison Example)

15 A $154\text{ }\mu\text{m}$ thick film was made from bisphenol A polycarbonate, relative viscosity 1.28, and tested as in Example D.1.

Result: permeation coefficient

20 for O_2 : 72.0
for N_2 : 366.0
for CO_2 : 35.0
for CH_4 : 27.0

25 The film was no longer dimensionally stable at 180°C .

Example D.3

As described in Example D.1, a $92\text{ }\mu\text{m}$ thick film is made from 20 g of the polycarbonate of Example B.12 and
30 measured for gas permeability.

Example D.4

As described in Example D.1, a $95\text{ }\mu\text{m}$ thick film is made from 20 g of the polycarbonate of Example B.13 and
35 measured for gas permeability.

Example D.5

As described in Example D.1, an 89.7 μm thick film is made from 20 g of the polycarbonate of Example B.14 and measured for gas permeability.

Example D.6

The polycarbonate of Example B.7 is melted in an extruder (temperature: 360-370°C), extruded through flat sheeting dies to form a 163 μm thick film and then measured for gas permeability.

Example D.7

31 g (0.1 mol) bisphenol A.1, 24 g (0.6 mol) NaOH are dissolved with stirring in 270 ml water in an inert gas atmosphere. 250 ml methylene chloride are then added. 19.8 g phosgene are introduced into the thoroughly stirred solution at pH 13-14/20-25°C. 5 minutes after the phosgene has been introduced, 0.1 ml N-ethyl piperidine is added. The mixture is then left to react for 45 minutes. The bisphenolate-free aqueous phase is separated off, the organic phase is acidified with phosphoric acid and then washed until neutral. A transparent film was cast from the concentrated solution in methylene chloride.

GPC analysis: The molecular weight was determined on the basis of a calibration with bisphenol A polycarbonate. M_w 246,000, M_n = 38,760

Results - permeation values

Sample	Permeation Gases			
	N ₁	O ₂	CO ₂	CH ₄
D.3	23.9	109.2	634.9	30.2
D.4	49.7	227.9	1629.5	64.3
D.5	33.6	138.8	828.1	46.8
D.6	78.2	400.5	2555.0	n.d.

n.d. = not determined

D.8 (Composite film)

After evaporation of the solvent, the films made in accordance with D.1 and D.2 were placed on top of one another and pressed for 4 minutes under a pressure of approx. 234 bar at 235°C to form an approx. 307 μ m thick film.

The gas permeability of the composite film was measured as described in D.1.

Result: permeation coefficient

for O₂: 208.3

for CO₂: 1209.4

for CH₄: 77.1

This composite film was still dimensionally stable at 180°C.

Example D.9

Composite film of the polycarbonate of Example B.14 and polymethyl methacrylate

After preheating for 30 seconds, a 130 μ m thick polymethyl methacrylate film (PMMA) and a 131 μ m thick film of the polycarbonate B.14 were pressed under a pressure of

200 bar at 160°C. The gas permeabilities of the composite film were measured as described in Example D.1.

Example D.10

5 Composite film of the polycarbonate of Example B.14 and polystyrene

10 After preheating for 30 seconds, a 78 μm thick polystyrene film (Polystyrol N 168 of BASF AG) and a 101 μm thick film of the polycarbonate B.14 were pressed under a pressure of 200 bar at 160°C to form a 168 μm thick composite film. The gas permeabilities of the composite film were measured as described in Example D.1.

Results - permeation values

15

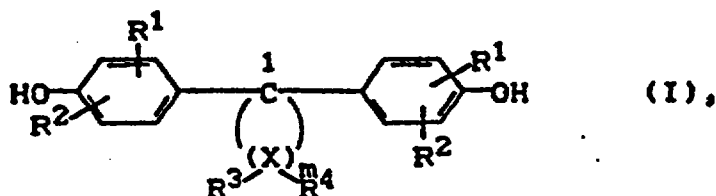
Sample	Permeation Gases			
	N ₂	O ₂	CO ₂	CH ₄
D.9	0.7*	4.5	20.3	0.42*
20 D.10	18.0	102.9	488.5	25.6

25

*: Since this composite film produced a very small increase in pressure after the gases had been introduced into the first measuring cell, the permeation value was determined from the permeate after a permeation time of 3 days.

**CLAIMS**

1. Dihydroxydiphenyl cycloalkanes corresponding to the formula



10 in which

R^1 and R^2 independently of one another represent hydrogen, halogen, C_{1-8} alkyl, C_{5-8} cycloalkyl, C_{6-10} aryl and C_{7-12} aralkyl,

15 $m = 4$ or 5 ,

R^3 and R^4 may be individually selected for each X and independently of one another represent hydrogen or C_{1-6} alkyl

and

20 X represents carbon,

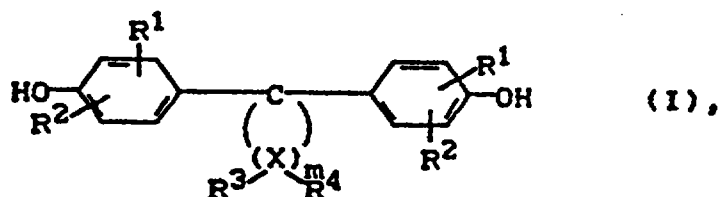
with the proviso that, at at least one atom X, both R^3 and R^4 are alkyl.

25 2. Dihydroxydiphenyl cycloalkanes corresponding to formula (I) as claimed in claim 1, characterized in that, in formula (I), neither of the two X atoms in the α -position to C-1 is dialkyl-substituted.

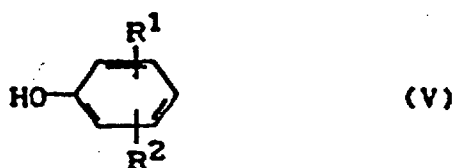
30 3. Dihydroxydiphenyl cycloalkanes corresponding to formula (I) as claimed in claim 2, characterized in that, in formula (I), a dialkyl-substituted X-atom is in the β -position to C-1.

4. 1,1-Bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane.

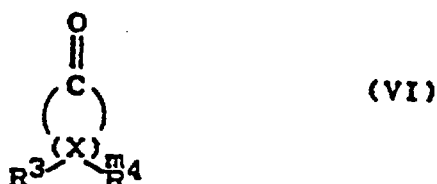
5. A process for the production of the dihydroxydiphenyl cycloalkanes corresponding to formula (I)



10 in which X, R¹, R², R³, R⁴ and m are as defined in claim 1,
characterized in that phenols corresponding to formula (V)



15 in which
R¹ and R² are as defined for formula (I),
are reacted with ketones corresponding to formula (VI)



25 in which
X, m, R³ and R⁴ are as defined for formula (I),
in a molar ratio of (V):(VI) of from 2:1 to 10:1 and
preferably in a molar ratio of from 2.5:1 to 6:1 at temper-
30 atures in the range from -30°C to 300°C and preferably at
temperatures in the range from -15 to 150°C and under
pressures of 1 to 10 bar and preferably 1 to 20 bar and in
the presence of acidic catalysts and optionally in the
presence of co-catalysts and/or solvents and/or dehydrating
35 agents.

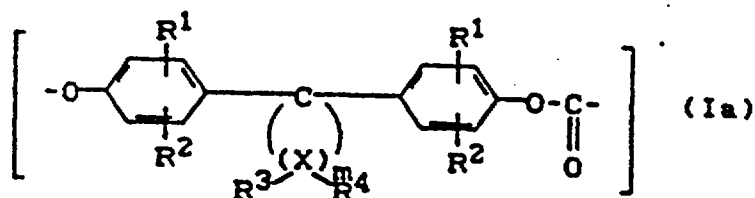


6. The use of the diphenols corresponding to formula (I) claimed in claim 1 for the production of high molecular weight, thermoplastic aromatic polycarbonates.

7. A process for the production of high molecular weight aromatic polycarbonates from diphenols, optionally chain terminators and optionally branching agents by the known methods for the production of polycarbonates, preferably by the two-phase interfacial process, characterized in that the diphenols of formula (I) in claim 1 are used as the diphenols in quantities of 100 mol-% to 2 mol-%, based on the total mols of diphenols used.

8. High molecular weight, thermoplastic aromatic polycarbonates having weight average molecular weights $\bar{M}_w$ of at least 10,000 obtainable by the process claimed in claim 8.

9. High molecular weight, thermoplastic, aromatic polycarbonates having $\bar{M}_w$ values (weight average molecular weights) of at least 10,000 which contain bifunctional carbonate structural units corresponding to formula (Ia)



in which

30 X, R¹, R², R³, R⁴ and m are as defined for formula (I) in claim 1,

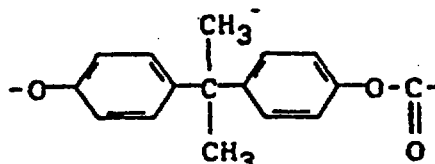
in quantities of 100 mol-% to 2 mol-%, based on the total quantity of 100 mol-% of difunctional carbonate structural units in the polycarbonate.

35 10. Polycarbonates as claimed in claim 9, characterized



in that they contain the carbonate structural units corresponding to formula (Ia) in quantities of 100 mol-% to 5 mol-%.

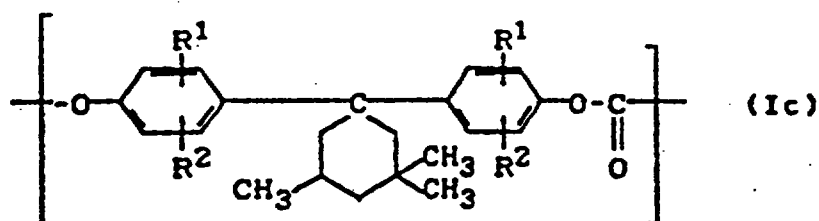
11. Polycarbonates as claimed in claim 9, characterized in that they contain quantities complementary to 100 mol-% of difunctional carbonate structural units corresponding to the formula



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12. Polycarbonates as claimed in claim 9 containing structural units of formula (Ia) correspond to formula (Ic)

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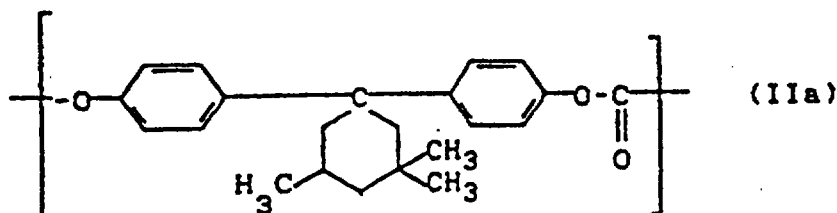
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in which

R¹ and R² are as defined for formula (Ia) in claim 9.

13. Polycarbonates as claimed in claim 9 containing structural units corresponding to formula (IIa)

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14. Films of the polycarbonates claimed in claim 9.
15. 1 to 1500 μm thick films of the polycarbonates claimed in claim 9.
- 5 16. 1 to 1500 μm thick films of the polycarbonates claimed in claim 9 monoaxially or biaxially stretched in a ratio of 1:1.5 to 1:3.0.
17. Composite films of a film as claimed in claim 14 and a film of another plastic.
- 10 18. The use of the films claimed in claim 14 as gas permeation membranes.