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Use of copolycarbonates

5 The present invention provides the use of stress-crack resistant and impact resistant copolycarbonates with particularly good low temperature properties and good ageing stability for applications in which particularly good low temperature properties and/or a high ageing stability are required, for example for automobile construction or external applications, as well as new copolycarbonates *per se*.

10 For automobile construction and other external applications attempts have long been made to find polycarbonates that are as resistant as possible to chemicals and preferably transparent, and that on the one hand are resistant to low temperatures and on the other hand have a high ageing stability.

15 Polycarbonates are typically brittle at low temperatures, i.e. they tend to fracture and to lose their notch-impact strength.

20 Polycarbonates exhibit in addition after storage at temperatures below the glass transition temperature, an ageing effect that depends on the storage time and temperature, as a result of which the high energy level in the notch-impact strength is significantly reduced (Bottenbruch et al., "Engineering Thermoplastics Polycarbonates, Polyacetals, Polyesters, Cellulose Esters", Carl Hanser Verlag, Munich, Vienna, New York, 1996, p. 183 ff.), i.e. as a result polycarbonates also become brittle.

25 Copolycarbonates based on 4,4'-dihydroxydiphenyl and 2,2-bis(4-hydroxyphenyl)-propane are already known from JP 5 117 382, and are described in EP-A1 0 544 407, US 5 470 938, US 5 532 324 and US 5 401 826 as being particularly resistant to chemicals, heat stable and particularly flame-resistant, while having in comparison to commercially available polycarbonate formed from pure bisphenol the same
30 mechanical properties and transparency. However, there is no indication at all in the prior art that these copolycarbonates have particularly good low temperature



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properties, quite apart from whether these polycarbonates have a special ageing stability.

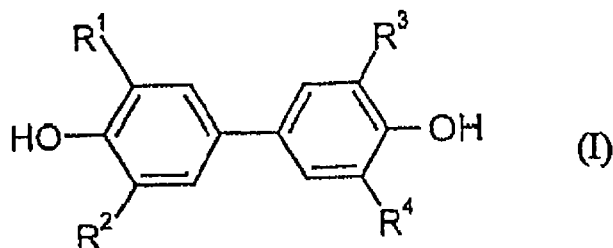
5 The object was accordingly to find a transparent polycarbonate that on the one hand has improved low temperature strength compared to polycarbonate of pure 2,2-bis(4-hydroxyphenyl)propane, and on the other hand has an improved ageing stability combined with improved stress-crack behaviour.

10 It has now surprisingly been found that the copolycarbonate according to the invention when stored below the glass transition temperature of the copolycarbonate does not exhibit any ageing effect that depends on the storage time and temperature, with the result that the high energy level in the notch-impact strength is retained and the polycarbonates do not become brittle.

15 This unexpected ageing behaviour of the copolycarbonate according to the invention is particularly important for practical applications. Many applications involve constantly alternating thermal stresses. The copolycarbonate according to the invention thus constitutes a material that has a very good notch-impact strength at low temperatures, but which does not lose this property on storage at temperatures
20 below the glass transition temperature on account of ageing effects.

The present invention accordingly relates to the use of copolycarbonates that are composed of 0.1 mole % to 46 mole %, preferably 11 mole % to 34 mole % and in particular 26 mole % to 34 mole % of compounds of the formula (I),

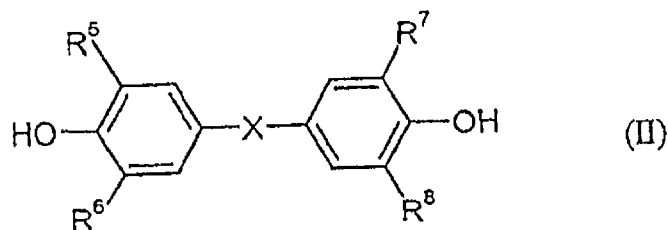
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wherein R^1 to R^4 independently of one another denote H, C_1 - C_4 -alkyl, phenyl, substituted phenyl or halogen, preferably H, C_1 - C_4 -alkyl or halogen, and particularly preferably all denote the same radical, in particular H or tert.-butyl, and complementary amounts, i.e. 99.9 mole % to 54 mole %, preferably 89 mole % to 66 mole % and in particular 74 mole % to 66 mole %, of compounds of the formula (II)



wherein R^5 to R^8 independently of one another denote H, CH_3 , Cl or Br, and X denotes C_1 - C_5 -alkylene, C_2 - C_5 -alkylidene, C_5 - C_6 -cycloalkylene, C_5 - C_{10} -cycloalkylidene, as monomers, as materials in areas in which particularly good low temperature properties and thermal stability are required.

Most particularly preferred and themselves covered by the present invention are copolycarbonates composed of 34-26 mole %, especially 33-27 mole %, in particular 32-28 mole %, more especially 31-29 mole % and particularly preferably 30 mole % of monomers of the formula (I), in each case supplemented by a complementary content of monomers of the formula (II).

The percentage data given for the bisphenol monomers refer to the total content, defined as 100%, of bisphenols in the polycarbonates. A pure bisphenol A polycarbonate would then consist of 100% of bisphenol A. The carbonate proportion from carbonic acid esters or halides is disregarded in this connection.

Preferred, particularly preferred or most particularly preferred are polycarbonates that have the preferred, particularly preferred or most particularly preferred compositions specified hereinafter.

The definitions, quantitative ratios and explanations given above in general terms or as preferred ranges may however also be combined as desired with one another, i.e. between the respective ranges and preferred ranges. They apply as appropriate to the end products as well as the precursors and intermediate products.

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It has now surprisingly been found that such copolycarbonates on the one hand have particularly good low temperature properties, and on the other hand also have particularly good ageing properties. They may therefore be used as moulded articles everywhere where the polycarbonates known up to now are inadequate as regards their property profiles, for example in the electrical sector as well as in the construction sector, for coverings or glazing, in particular in the vehicle sector as films, sheets, fittings, mountings or housing parts, but also in the optical sector as lenses and data storage devices, as well as articles of daily use, and more specifically where improved thermal stability or resistance to chemicals combined at the same time with good low temperature properties and/or ageing stability are required. In addition they may also replace other materials in which conventional polycarbonates have not hitherto been used on account of their insufficient low temperature properties.

20 Good low temperature properties are understood according to the invention to mean for example, but not exclusively, a good low temperature toughness, since conventional polycarbonates at low temperatures undergo brittle fracture in the notched-bar impact test.

25 Low temperatures are understood according to the invention to be temperatures below -10°C , preferably below -20°C , more preferably below -30°C , most particularly preferably below -40°C and especially below -50°C .

30 Good thermal stability and ageing stability are understood according to the invention to mean for example, but not exclusively, a good notch-impact strength after

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tempering, since conventional polycarbonates after tempering become brittle and thus tend to exhibit fracture and cracking.

5 Tempering is understood according to the invention to mean storage at temperatures below the glass transition temperature of 155°C, the temperature range preferably being from 40°C to 140°C, particularly preferably from 60°C to 140°C and most particularly preferably from 80°C to 140°C.

10 Preferred compounds of the formula (I) are 4,4'-dihydroxydiphenyl (DOD) and 4,4'-dihydroxy-3,3',5,5'-tetra(tert.-butyl)diphenyl, 4,4'-dihydroxydiphenyl-3,3',5,5'-tetra(n-butyl)diphenyl and 4,4'-dihydroxydiphenyl-3,3',5,5'-tetra(methyl)diphenyl; 4,4'-dihydroxydiphenyl is particularly preferred.

15 Preferred compounds of the formula (II) are 2,2-bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane and 1,3-bis[2-(4-hydroxyphenyl)-2-propyl]benzene, 1,1-bis(4-hydroxyphenyl)-1-phenylethane, 1,1-bis(4-hydroxyphenyl)-cyclohexane, in particular 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and 1,1-bis(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (bisphenol TMC), and most particularly preferably 2,2-bis(4-hydroxyphenyl)-propane
20 (bisphenol A).

One compound of the formula (I) may be used, with the formation of binary copolycarbonates, as well as several compounds of the formula (I).

25 Similarly one compound of the formula (II) may be used, with the formation of binary copolycarbonates, as well as several compounds of the formula (II).

The educts of the formulae (I) and (II) may obviously contain impurities due to the synthesis. A high degree of purity is however desirable and sought after, and
30 accordingly these educts are employed in as high a state of purity as possible.

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The production of polycarbonates and copolycarbonates is generally known in the literature, and is also carried out correspondingly in the cases according to the invention:

- 5 According to DE-OS 2 119 779 the production of polycarbonates is carried out with the participation of monomers of the formula (I) preferably in solution, and more specifically according to the phase interface process and the homogeneous phase process.
- 10 For the production of polycarbonates according to the phase interface process reference may be made for example to "Schnell", Chemistry and Physics of Polycarbonates, Polymer Reviews, Vol. 9, Interscience Publishers, New York, London, Sydney 1964 and to Polymer Reviews, Vol. 10, "Condensation Polymers by Interfacial and Solution Methods", Paul W. Morgan, Interscience Publishers, New
- 15 York 1965, Chapter VIII, p. 325 and EP 971 790.

- In addition it is also possible to produce polycarbonates by the known polycarbonate production process in the melt (so-called melt transesterification process), which is described for example in DE-OS 19 64 6401 or in DE-OS 1 42 38 123. In addition,
- 20 transesterification processes (acetate process and phenyl ester process) are described for example in US-PS 3 494 885, 4 386 186, 4 661 580, 4 680 371 and 4 680 372, in EP-A 26120, 26121, 26684, 28030, 39845, 91602, 97970, 79075, 146887, 156103, 234913 and 240301 as well as in DE-A 1 495 626 and 2 232 997.

- 25 The copolycarbonates may have molecular weights M_w (weight-averaged molecular weight) between 10,000 and 60,000, preferably M_w of 20,000 to 55,000, determined by measuring the relative solution viscosity in dichloromethane or in mixtures of equal amounts by weight of phenol/o-dichlorobenzene, calibrated by light scattering.

- 30 The polycarbonates according to the invention can be processed in the conventional way at temperatures of 240°C to 380°C, preferably 260°C to 360°C. Suitable

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moulded articles and sheets can be produced in a known manner by injection moulding or by extrusion. Moulded articles and extrudates of the copolycarbonates according to the invention are also covered by the present application.

- 5 The polycarbonates according to the invention are readily soluble in solvents such as chlorinated hydrocarbons, for example methylene chloride, and may thus be processed for example in a known way into cast films or sheets.

10 The combination of properties such as thermal stability, good low temperature properties, ageing stability and resistance to chemicals enables the copolymers according to the invention to be used in a broad range of applications. Possible applications of the polycarbonates according to the invention include:

- 15 1. Safety panels, which as is known are required in many areas of buildings, vehicles and aircraft, as well as helmet shields.
2. Production of foils, especially ski foils.
- 20 3. Production of blow-moulded articles (see for example US patent A 2 964 794).
- 25 4. Production of light-permeable sheets, in particular hollow-cavity sheets, for example for covering buildings such as railways, greenhouses and lighting installations.
5. Production of traffic light housings or road signs.
6. Production of foams (see for example DE-AS 1 031 507).
- 30 7. Production of fibres and threads (see for example DE-AS 1 137 167 and DE-OS 1 785 137).

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8. As translucent plastics materials with a glass fibre content for light technology purposes (see for example DE-OS 1 554 020).
- 5 9. Production of precision injection-moulded small parts, such as for example lens mountings. For this purpose polycarbonates are used that contain glass fibres, which optionally may additionally contain about 1 - 10 wt.% of MoS₂, referred to the total weight.
- 10 10. Production of optical instrument parts, in particular lenses for photographic cameras and film cameras (see for example DE-OS 2 701 173).
11. As light-transmission carriers, in particular as light-conducting cables (see for example EP-A1 0 089 801).
- 15 12. As electrical insulation materials for electrical leads and for plug housings as well as plug-and-socket connectors.
13. As carrier material for organic photoconductors.
- 20 14. Production of lamps/lights, e.g. headlamps or scattered light panels.
15. For medical applications, e.g. oxygenators, dialysis equipment.
- 25 16. For foodstuff applications, e.g. bottles, utensils and chocolate moulds.
17. For applications in the automobile sector where contact with fuels and lubricants may occur.
- 30 18. For sports articles, such as for example slalom poles.

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19. For household articles, for example kitchen sink units and letter box housings.

20. For housings, for example electrical distribution cabinets.

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21. For other applications, such as for example stall-feeding doors or animal cages.

10 In particular films may be produced from the high molecular weight aromatic polycarbonates of the invention. The films have preferred thicknesses of between 1 and 1500 μm , and particularly preferred thicknesses between 10 and 900 μm .

The films obtained may be monoaxially or biaxially stretched in a manner known *per se*, preferably in a ratio of 1:1.5 to 1:5.

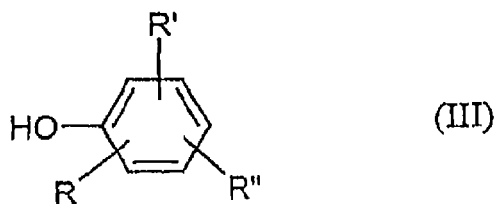
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The films may be produced by the known methods for film production, for example by extrusion of a polymer melt through a slot die, by blowing in a film blowing machine, by thermoforming or by casting. In this connection it is possible to use the films as such alone. Composite films with other plastics films can of course also be produced with them according to conventional methods, in which connection all known films may in principle be used as partners depending on the desired application and final property profile of the composite film. A composite of two or more films can be produced.

25 In addition the copolycarbonates according to the invention may also be used in other layer systems, such as for example in co-extruded sheets.

30 The polycarbonates according to the invention may contain various terminal groups. These are introduced by chain terminators. Chain terminators within the meaning of the invention are compounds of the formula (III)

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wherein R, R' and R'' may independently of one another denote H, optionally branched C₁-C₃₄-alkyl/cycloalkyl, C₇-C₃₄-alkaryl or C₆-C₃₄-aryl, for example butyl phenol, trityl phenol, cumyl phenol, phenol or octyl phenol, preferably butyl phenol or phenol.

10

The polycarbonates may contain minor amounts of 0.02 to 3.6 mole % (referred to the dihydroxy compound) of branching agents. Suitable branching agents are the compounds containing three or more functional groups that are suitable for polycarbonate production, preferably those with three or more than three phenolic OH groups, for example branching agents such as are named in EP-A 708 130, p. 4, preferably 1,1,1-tri-(4-hydroxyphenyl)ethane and isatin bisresol.

15

Auxiliary substances and reinforcing agents may be mixed with the polycarbonates according to the invention in order to alter their properties. Suitable auxiliary substances and reinforcing agents include, *inter alia*: thermal and UV stabilisers, anti-blocking agents/flow auxiliaries, mould release agents, flameproofing agents, pigments, finely divided minerals, fibre substances, e.g. alkyl and aryl phosphites, phosphates, phosphanes, low molecular weight carboxylic acid esters, halogenated compounds, salts, chalk, quartz flour, glass and carbon fibres, pigments and their combinations. Such compounds are described for example in WO 99/55772, pp. 15-25, and in "Plastics Additives", R. Gächter and H. Müller, Hanser Publishers 1983.

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Moreover, other polymers, for example polyolefins, polyurethanes, polyesters, acrylonitrile/butadiene/styrene and polystyrene may also be mixed with the polycarbonates according to the invention.

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These substances are preferably added to the finished polycarbonate in conventional equipment, though depending on requirements the addition may also take place at a different stage in the production process,.

- 5 The following examples are intended to illustrate the present invention without however restricting it.

Examples

Various polycarbonates were synthesised according to the known melt production processes, such as are described for example in DE 4 238 123, and via the phase interface process, such as described for example in "Schnell", Chemistry and Physics of Polycarbonates, Polymer Reviews, Vol. 9, Interscience Publishers, New York, London, Sydney 1964, and were compared with commercially available Makrolon of comparable viscosity.

10 The relative solution viscosity was measured in dichloromethane at a concentration of 5 g/l at 25°C, calibrated by light scattering.

The flexural impact test according to ISO 180/4A was used to determine the impact strength.

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Example 1

A polycarbonate containing 30 mole % of dihydroxydiphenyl (DOD) and 70 mole % of bisphenol A was produced in the phase interface process. Tert.-butylphenol was used as chain terminator. The granules had a relative solution viscosity of 1.298.

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Example 2

A polycarbonate containing 30 mole % of DOD and 70 mole % of bisphenol A was produced in the phase interface process. Tert.-butylphenol was used as chain terminator. The granules had a relative solution viscosity of 1.341.

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Example 3

5 A polycarbonate containing 30 mole % of DOD and 70 mole % of bisphenol A was produced in the melt transesterification process. The product had a relative solution viscosity of 1.28.

Comparison example 1

10 A polycarbonate containing 35 mole % of DOD and 65 mole % of bisphenol A was produced in the melt transesterification process. The product had a relative solution viscosity of 1.295.

Comparison example 2

15 A polycarbonate containing 25 mole % of DOD and 75 mole % of bisphenol A was prepared in the melt transesterification process. The product had a relative solution viscosity of 1.295.

20 **Comparison example 3**

A polycarbonate containing 20 mole % of DOD and 80 mole % of bisphenol A was produced in the melt transesterification process. The product had a relative solution viscosity of 1.295.

25

A comparison with commercially available Makrolon is given in Tables 1-2.

Polycarbonate	Relative solution viscosity
Makrolon 2808/58	1.293
Makrolon 3108	1.318
Example 1	1.298
Example 2	1.341
Example 3	1.277
Comparison example 1	1.295
Comparison example 2	1.298
Comparison example 3	1.286

Table 1: Comparison of the solution viscosities

Polycarbonate	Notch-impact strength according to ISO 180/4A			
	23°C [kJ/m ²]	-40°C [kJ/m ²]	-50°C [kJ/m ²]	-60°C [kJ/m ²]
Makrolon 2808/58	90z	8s	9s	7s
Makrolon 3108	95z	11s	8s	8s
Example 1	82z	56z	58z	60z
Example 2	67z	67z	65z	66z
Example 3	54z	60z	38z	42z
Comparison ex. 1	Not measured	35z	26s	20s
Comparison ex. 2	Not measured	19s	Not measured	13s
Comparison ex. 3	Not measured	14s	Not measured	11s

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Table 2: Comparison of the notch-impact strength and softening temperature

s = brittle fracture

z = tough fracture

Table 2 shows the superior low temperature toughness of the copolycarbonates according to the invention of Examples 1-3 at -60°C.

Storage conditions	Example 1	Makrolon 2808
46 hours at 135°C	52x	8s
7 days at 135°C	54z	
20 days at 135°C	52z	
2 hours at 150°C	53z	
24 hours at 150°C	53z	

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Table 3: Comparison of the notch-impact strengths according to ISO 180/4A in [kJ/m²]

s = brittle fracture

z = tough fracture

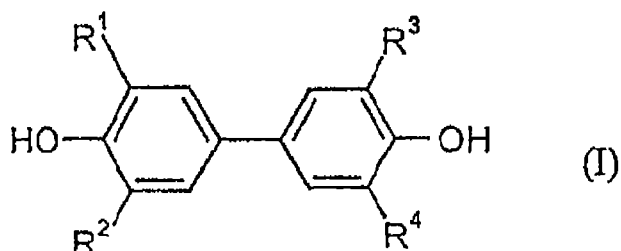
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As can be seen from Table 3, the copolycarbonate according to the invention exhibits a significantly changed property profile also after ageing. Polycarbonate formed from pure bisphenol A already exhibits brittle fracture behaviour after a storage time of 46 hours at 135°C, whereas the tough behaviour of the copolycarbonate can still be observed even after 7 days. Moreover the copolymer, even when stored at 150°C followed by a notched-bar impact test, still exhibits a good tough fracture behaviour.

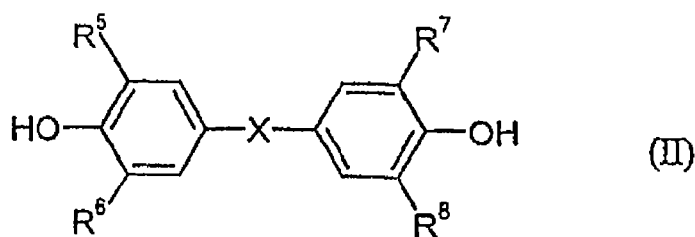
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Patent Claims

1. Use of thermoplastic copolycarbonates composed of 0.1 mole % to 46 mole %, preferably 11 mole % to 34 mole % and in particular 26 mole % to 34 mole % of compounds of the formula (I),



wherein R¹ to R⁴ independently of one another denote H, C₁-C₄-alkyl, phenyl, substituted phenyl or halogen, preferably H, C₁-C₄-alkyl or halogen, and particularly preferably all denote the same radical, in particular H or tert.-butyl, and complementary amounts, i.e. 99.9 mole % to 54 mole %, preferably 89 mole % to 66 mole % and in particular 74 mole % to 66 mole %, of compounds of the formula (II)



wherein R⁵ to R⁸ independently of one another denote H, CH₃, Cl or Br, and X denotes C₁-C₅-alkylene, C₂-C₅-alkylidene, C₅-C₆-cycloalkylene, C₅-C₁₀-cycloalkylidene, as monomers, as materials in areas in which particularly good low temperature properties and/or ageing stability are required.

2. Use of the copolycarbonates according to claim 1 for external applications.
3. Use of the copolycarbonates according to claim 1 for films.

4. Use of the copolycarbonates according to claim 1 for optical applications.
5. Use of the copolycarbonates according to claim 1 for medical and foodstuffs applications.
6. Use of the copolycarbonates according to claim 1 in the automobile sector.
7. Use of the copolycarbonates according to claim 1 in the electrical sector.
8. Copolycarbonates according to claim 1, characterised in that they are composed of 34 to 26 mole % of monomers of the formula (I), as well as a complementary content of monomers of the formula (II).