L’invention concerne l’utilisation de polycarbonates contenant du carbonate d’iode de phényle pour la fabrication de pièces moulées spéciales, notamment pour des applications médicales et pour des jouets.
Use of Polycarbonates Containing Iodine Phenyl Carbonate for Producing Special Shaped Parts

Bezeichnung: Verwendung von Jod-Phenyl-Carbonat-haltigen Polycarbonaten zur Herstellung von speziellen Formteilen

Abstract

The invention relates to the use of polycarbonates containing iodine phenyl carbonate for producing special shaped parts, especially for medical applications and toys.

Zusammenfassung

Use of polycarbonates containing iodophenyl carbonate in the production of special mouldings

The present invention relates to the use of polycarbonates containing iodophenyl carbonate in the production of special mouldings.

Within the scope of the present invention, polycarbonates containing iodophenyl carbonate are:

1. polycarbonates having a MW of from 3000 to 40,000 containing iodophenyl carbonate terminal groups,

2. polycarbonates of non-halogenated chain terminators having a MW of from 10,000 to 40,000 and containing diphenol-bis-iodophenyl carbonates,

3. polycarbonates of non-halogenated chain terminators having a MW of from 10,000 to 40,000 and containing bis-iodophenyl carbonate, and

4. mixtures of the polycarbonates according to 1) and the polycarbonates of non-halogenated diphenols and of non-halogenated chain terminators according to 2, or 3, variants 1, 2, 3 and 4 each having iodine concentrations of from 0.1 wt.% to 20 wt.%.

Special mouldings within the scope of the present invention are especially mouldings for medical applications, such as tubes or joint parts, and toys for children, such as building bricks.

For the medical field and for children's toys, materials are sought which are as transparent as possible and have good mechanics, and which can be detected in the body in the course of X-ray examinations. Commercial moulding compositions
based on polycarbonates are not suitable for that purpose, since their contrast in the X-ray image is too low. A material which is used for that purpose is, for example, PVC, whose plasticiser content is undesirable in the medical field and whose mechanical properties do not satisfy requirements. Known iodine-containing polymers also have only unsatisfactory mechanical properties and can be produced only with difficulty.

The object was, therefore, to develop moulding compositions which have good contrast in X-ray examinations while having good mechanical properties and high transparency and a glass temperature that is markedly greater than 100°C.

The major advantage of the mouldings according to the invention is that they have an improved X-ray contrast and are thus readily detectable and, accordingly, can be used successfully on the one hand in specific operations and on the other hand for remedying accidents caused by children swallowing toys.

US-A 3 469 704 describes polycarbonates having iodophenyls as the terminal group (column 2, lines 60 ff).

US-A 3 382 207 discloses iodine-containing diphenyl carbonates and their addition to polycarbonates.

According to DE-A 17 20 812, iodine-containing phenols are known as chain terminators for polycarbonates. See also the corresponding GB-B 11 63 816.

According to US-A 3 535 300, iodine-containing compounds are known as additives to polycarbonates (column 4, line 64; column 5, line 43).

The use according to the invention and, accordingly, also the object cannot be taken from that prior art.
Polycarbonates according to 1) having \( \overline{M}_w \) of from 3000 to 40,000 and containing iodophenyl carbonate terminal groups are preferably those having terminal groups of formula (I)

\[
\begin{align*}
\text{R}_1 & \quad \text{R}_2 \\
\text{O} & \quad \text{O} \\
\text{R}_3 & \quad \text{R}_4
\end{align*}
\]

(I)

wherein

\( \text{R}_1 \) to \( \text{R}_3 \) represent H, optionally branched \( \text{C}_{1-18} \)-alkyl, Cl, Br or I, with the proviso that at least one of the radicals \( \text{R}_1, \text{R}_2 \) and \( \text{R}_3 \) represents I.

Preferred terminal groups are 4-iodophenyl carbonate and 2,4,6-triiodophenyl carbonate terminal groups.

Suitable diphenols for the preparation of the polycarbonates according to 1) are those of formula (II)

\[
\text{HO-Z-OH} \quad \text{(II)}
\]

wherein

\( \text{Z} \) represents a divalent aromatic radical having from 6 to 30 carbon atoms.

Preferred diphenols are 1,1-bis-(4-hydroxyphenyl)-1-phenylethane, 1,1-bis-(4-hydroxyphenyl)cyclohexane, 2,2-bis-(4-hydroxyphenyl)-propane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane.
The polycarbonates according to 1) are either known or can be prepared by processes known from the literature; see, for example, the prior art cited above.

Preferred diphenol-bis-iodophenyl carbonates according to 2) are those of formula (III)

$\text{(III)}$

wherein

$R_1$, $R_2$ and $R_3$ are as defined for formulae (I) and (II).

Preferred bis-iodophenyl carbonates according to 3) are those of formula (IV)

$\text{(IV)}$

wherein

$R_1$, $R_2$ and $R_3$ are as defined for formula (I).

The diphenol-bis-iodophenyl carbonates according to 2) and the iodophenyl carbonates according to 3) are either known from the literature or can be prepared by processes known from the literature.

The conventional polycarbonates of non-halogenated diphenols and of non-halogenated chain terminators used as mixing partners in 2), 3) and 4) are likewise
known or can be prepared by processes known from the literature (see, for example, US-A 3 028 365).

The polycarbonates containing iodophenyl carbonate according to variants 1), 2), 3) or 4) to be used in accordance with the invention are to have iodine concentrations of from 0.1 wt.% to 20 wt.%, preferably from 1 wt.% to 15 wt.%, especially from 3 wt.% to 10 wt.%, in each case based on the total weight of variants 1), 2), 3) or 4).

Examples of the iodophenols (Ia)

\[
\begin{align*}
&\text{HO} \\
&\text{R}_1 \\
&\text{R}_2 \\
&\text{R}_3
\end{align*}
\]

(Ia)

are 2-/3- or 4-iodophenol, 2-/3- or 4-iodo-6-methylphenol, 4- or 6-iodo-3-methylphenol, 2- or 6-iodo-4-methylphenol, 4,5-diiodo-2-methylphenol, 4,6-diiodo-2-methylphenol, 4,5-diiodo-3-methylphenol, 4,6-diiodo-3-methylphenol, 2,4,6-triiodophenol, preferably 4-iodophenol and 2,4,6-triiodophenol.

The iodophenols are compounds which are obtainable in the chemicals trade or are accessible in organic syntheses from aromatic intermediates, optionally via diazonium salts. They can be used individually or in combinations, optionally also in combinations with conventional chain terminators such as phenol, p-tert-butylphenol, hexylphenol, isoctylphenol or nonylphenol.

Both the polycarbonates containing iodophenyl carbonate according to 1) and the conventional polycarbonates used as mixing partners according to 2), 3) and 4) can be linear or branched in a known manner.
Suitable branching agents are triphenols, trimesic acid (trichloride), cyanuric acid trichloride and 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

Both the polycarbonates containing iodophenyl carbonate according to 1) and the conventional polycarbonates used as mixing partners according to 2), 3) and 4) can be provided with additives customary for polycarbonates, such as thermostabilisers, mould release agents, stabilisers against $\gamma$ and $\beta$ radiation, and antistatics.

The polycarbonate variations 1), 2), 3) or 4) to be used in accordance with the invention are processed to mouldings in a known manner.

In the Examples which follow, $\eta_{\text{int}}$ is measured in dichloromethane at 25°C and a concentration of 0.5 wt.%. 
Examples:

Example 1

180 ml of dichloromethane and 25.3 ml of 6.5 % sodium hydroxide solution are placed in a 1000 ml three-necked flask having a stirrer, thermometer and reflux condenser. 22.83 g of 2,2-bis-(4-hydroxyphenyl)propane are dissolved therein, with stirring, and 15.8 g of phosgene are then introduced in the course of 5 minutes. 1.32 g of 4-iodophenol are then added, the mixture is stirred for 5 minutes at room temperature, and 0.137 ml of N-ethylpiperidine is added. Stirring is carried out for one hour at room temperature and then the organic phase is separated off and washed with dilute acid. Washing is then carried out with demineralised water until the washing phases are virtually free of electrolyte. The organic phase is concentrated and dried for 16 hours at 80°C in a vacuum drying cabinet under a water jet vacuum.

Yield: 26.3 g
n<sub>rel</sub> = 1.199

Example 2

As Example 1, but 2.83 g of 2,4,6-triiodobenzene are used as the chain terminator instead of 4-iodophenol.

Yield: 28.7 g
n<sub>rel</sub> = 1.174

Example 3

450 ml of dichloromethane, 19.8 g of pyridine and 44.0 g of iodophenol are placed in a 1000 ml three-necked flask having a stirrer, thermometer and reflux condenser. 35.3 g of bischlorocarboxinic ester of 2,2-bis-(4-hydroxyphenyl)propane, dissolved in 200 ml of dichloromethane, are added dropwise, with stirring, in the course of
40 minutes. Stirring is carried out for one hour at room temperature and then the organic phase is washed with dilute acid. Washing is then carried out with demineralised water until the washing phases are virtually free of electrolyte. The organic phase is concentrated and dried for 16 hours at 50°C in a vacuum drying cabinet under a water jet vacuum.

Yield: 64.0 g

Example 4

900 ml of dichloromethane, 19.8 g of pyridine and 94.4 g of 2,4,6-triiodophenol are placed in a 2000 ml three-necked flask having a stirrer, thermometer and reflux condenser. 35.3 g of bischlorocarbonic ester of 2,2-bis-(4-hydroxyphenyl)propane, dissolved in 200 ml of dichloromethane, are added dropwise, with stirring, in the course of 65 minutes. Stirring is carried out for 15 minutes at room temperature and then the organic phase is washed with dilute acid. Washing is then carried out with demineralised water until the washing phases are virtually free of electrolyte. The organic phase is concentrated and dried for 16 hours at 50°C in a vacuum drying cabinet under a water jet vacuum.

Yield: 89.0 g

The polycarbonates containing iodosphenyl carbonate obtained according to Examples 1 to 4 are shaped in an injection-moulding machine to form building bricks. The X-ray contrast of the mouldings is so great that they can be detected in the stomachs of children.
Patent claims

1. Use of polycarbonates containing iodophenyl carbonate in the production of special mouldings for medical applications and for toys.

2. Use according to claim 1 in the production of mouldings for medical applications.

3. Use according to claim 1 in the production of mouldings for toys.

4. Mouldings for medical applications produced from polycarbonates containing iodophenyl carbonate.

5. Toy produced from polycarbonates containing iodophenyl carbonate.