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An agency of Industry Canada

CA 2553330 A1 2005/07/28

(21) 2 553 330

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2005/01/07
(87) Date publication PCT/PCT Publication Date: 2005/07/28
(85) Entrée phase nationale/National Entry: 2006/07/13
(86) N° demande PCT/PCT Application No.: EP 2005/000065
(87) N° publication PCT/PCT Publication No.: 2005/068525
(30) Priorité/Priority: 2004/01/16 (DE10 2004 002 523.1)

(51) Cl.Int./Int.Cl. *C08G 8/10* (2006.01), *B65D 23/02* (2006.01), *C08G 64/00* (2006.01), *C09D 161/06* (2006.01)

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(54) Titre : POLYFORMALS ET COPOLYFORMALS COMME COUCHE DE PROTECTION CONTRE L'HYDROLYSE APPLIQUEE SUR DU POLYCARBONATE

(54) Title: POLYFORMALS AND COPOLYFORMALS AS A PROTECTIVE LAYER AGAINST HYDROLYSIS ON POLYCARBONATE

(57) Abrégé/Abstract:
The invention relates to a multilayered products which are protected against hydrolysis, comprising at least one layer containing a thermoplast and at least one layer containing at least one polyformal or copolyformal, in addition to compositions containing polyformal or copolyformals and possible additives, in addition to the use of polyformals or copolyformals in the production of a layer which protects against hydrolysis.

Polyformals and copolyformals as a hydrolysis protection layer on polycarbonate

Abstract

The present invention concerns hydrolysis-protected multilayer products comprising at least one layer containing a thermoplastic and at least one layer containing at least one polyformal or copolyformal, and compositions containing polyformals or copolyformals and possible additives, and the use of polyformals and/or copolyformals to produce a hydrolysis protection layer.

Polyformals and copolyformals as a hydrolysis protection layer on polycarbonate

The present invention concerns hydrolysis-protected multilayer products, in particular sheets, films, containers such as e.g. water bottles, baby bottles or medical articles, comprising at least one layer containing a thermoplastic and at least one layer containing at least one polyformal or copolyformal, and compositions containing polyformals or copolyformals and possible additives, and the use of polyformals and/or copolyformals to produce a hydrolysis protection layer.

The present invention also concerns a process for producing such multilayer products, such as sheets, medical articles or various containers, such as bottle products, baby bottles, water bottles and other products containing the cited sheets.

Solid or multi-wall sheets, for example, are generally coated on one or two sides with UV coextrusion layer(s) on the outer sides to protect them from damage (e.g. yellowing) by UV light. Other multilayer products are also protected in the same way from damage by UV light, however. By contrast, the application of a thermoplastic as a layer providing protection against hydrolysis damage is not described in the prior art.

The prior art in relation to multilayer, protected products is summarised below:

EP-A 0 110 221 discloses sheets comprising two layers of polycarbonate, one layer containing at least 3 wt.% of a UV absorber. These sheets can be produced by coextrusion according to EP-A 0 110 221.

EP-A 0 320 632 discloses moulded articles comprising two layers of thermoplastic polymer, preferably polycarbonate, one layer containing special substituted benzotriazoles as UV absorbers. EP-A 0 320 632 also discloses the production of these moulded articles by coextrusion.

EP-A 0 247 480 discloses multilayer sheets in which in addition to one sheet made from thermoplastic polymer, one sheet made from branched polycarbonate is present, the sheet made from polycarbonate containing special substituted benzotriazoles as UV absorbers. The production of these sheets by coextrusion is likewise disclosed.

EP-A 0 500 496 discloses polymer compositions stabilised with special triazines against UV light and their use as an outer layer in multilayer systems. Polycarbonate, polyesters, polyamides, polyacetals, polyphenylene oxide and polyphenylene sulfide are cited as polymers.

According to the prior art, water bottles, such as e.g. 5-gallon bottles, do not have a multilayer construction (DE 19943642, DE 19943643, EP-A 0411433). The same applies to reusable milk bottles or baby bottles.

Polycarbonate containers are produced for example by extrusion blow moulding or injection blow moulding.

In extrusion blow moulding the granules are generally melted with a single-screw extruder and moulded through a die to form a free-standing parison, which is then enclosed by a blow mould which pinches the parison together at the lower end. Inside the mould the parison is inflated to give the parison the desired shape. After a cooling period the mould is opened and the blow moulded article can be removed (described in more detail e.g. in Brinkschröder, F. J. "Polycarbonate" in Becker, Braun, Kunststoff-Handbuch, Volume 3/1, Polycarbonate, Polyacetale, Polyester, Celluloseester, Carl Hanser Verlag, Munich, Vienna 1992, pages 257 to 264).

For extrusion blow moulding it is advantageous to use a highly pseudoplastic polycarbonate in order to obtain a high melt stability. Branched polycarbonates are particularly pseudoplastic.

Injection blow moulding is a combination of injection moulding and blow moulding.

The process takes place in three steps:

1) Injection moulding of the parison in the plastic temperature range of the polycarbonate

2) Inflation of the parison in the thermoplastic range of the polycarbonate (the core of the injection mould is also the blowing mandrel)

3) Stripping the blow moulded article and optionally cooling the blowing mandrel with air

(described in more detail e.g. in Anders, S., Kaminski, A., Kappenstein, R., "Polycarbonate" in Becker/Braun, Kunststoff-Handbuch, Volume 3/1, Polycarbonate, Polyacetale, Polyester, Celluloseester, Carl Hanser Verlag, Munich, Vienna 1992, pages 223 to 225).

However, none of the products known from the prior art achieves satisfactory results in every respect, particularly as far as long-term stability in relation to hydrolysis is concerned. Water damages polycarbonate above 60°C. Extended contact with boiling water leads to molecular weight reduction, which is further accelerated in the presence of heat stabilisers such as organic phosphites. In addition, polycarbonates can be preferably alkaline-hydrolysed. Microwave radiation further accelerates this degradation.

In patents of the prior art no mention is ever made of hydrolysis protection layers to overcome this disadvantage.

Starting from the prior art the object was therefore to provide a multilayer sheet or coated containers such as e.g. water bottles or medical articles, which should be able to be sterilised in superheated steam, which display improved properties in comparison to the prior art, such as improved long-term stability in relation to hydrolysis in water, even at elevated temperatures, and in the acid and also the basic environment.

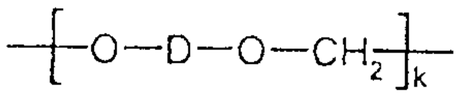
This object underlies the present invention.

This object is surprisingly achieved by coatings containing certain polyformals or copolyformals as the polymer basis.

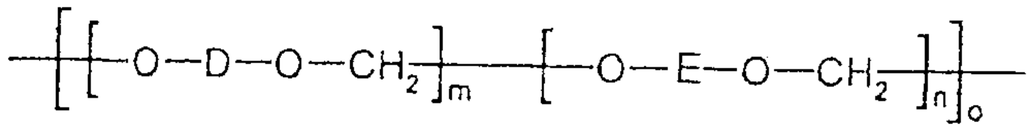
The coatings of products based on polyformals or copolyformals display a surprising superiority over the prior art in terms of the markedly greater hydrolysis resistance in comparison to polycarbonate.

This is particularly surprising because polyformals can be thought of as full acetals, which according to current doctrine held by the person skilled in the art should display great sensitivity to hydrolysis, in the acid environment at least. By contrast, however, the coatings made from polyformals are resistant to hydrolysis even in relation to acid solutions, and even at elevated temperatures.

The present application thus provides coatings containing polyformals or copolyformals having the general formulae (1a) or (1b),



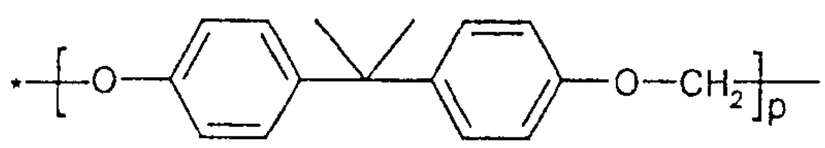
1a



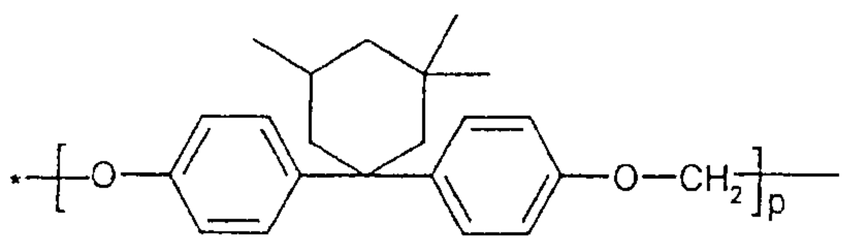
1b

wherein the radicals O-D-O and O-E-O stand for any diphenolate radicals in which -D- and -E- are aromatic radicals having 6 to 40 C atoms, preferably 6 to 21 C atoms, which can contain one or more aromatic or condensed aromatic nuclei, optionally containing heteroatoms, and are optionally substituted with C_1-C_{12} alkyl radicals or halogen and can contain aliphatic radicals, cycloaliphatic radicals, aromatic nuclei or heteroatoms as binding links and in which k stands for a whole number between 1 and 1500, preferably between 2 and 1000, particularly preferably between 2 and 700 and most particularly preferably between 5 and 500 and especially preferably between 5 and 300, o stands for numbers between 1 and 1500, preferably between 1 and 1000, particularly preferably between 1 and 700 and most particularly preferably between 1 and 500 and especially preferably between 1 and 300, and m stands for a fraction z/o and n for a fraction (o-z)/o, where z stands for numbers between 0 and o.

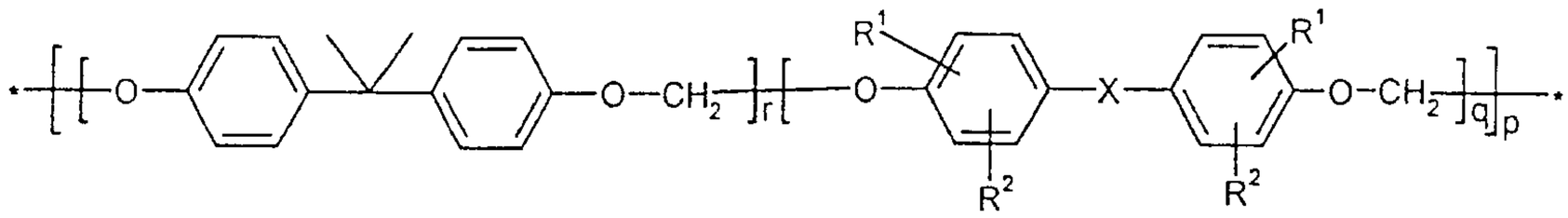
Preferred structural units of the polyformals and copolyformals according to the invention derive from general structures having the formulae (2a), (2b), (2c) and (2d),



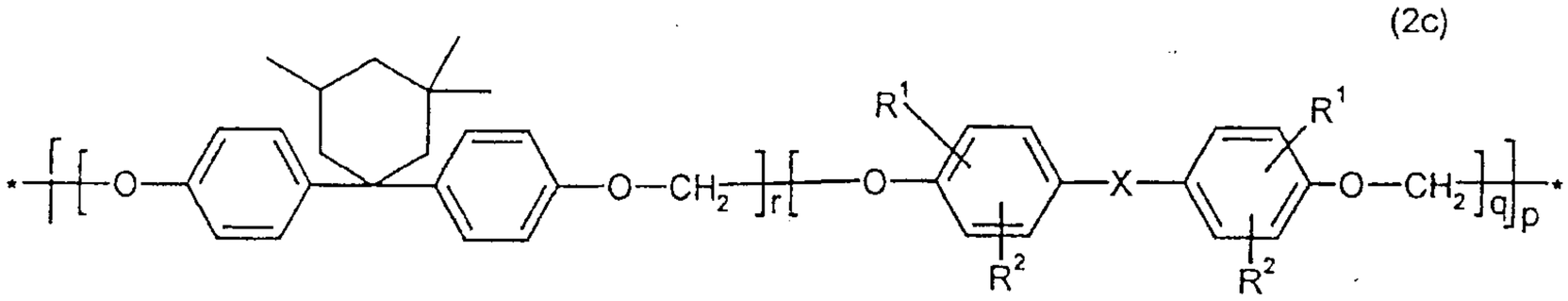
(2a)



(2b)



(2c)



(2d)

wherein the brackets describe the underlying diphenolate radicals, in which R^1 and R^2 mutually independently stand for H, linear or branched C_1-C_{18} alkyl or alkoxy radicals, halogen such as Cl or Br or for an optionally substituted aryl or aralkyl radical, preferably for H or linear or branched C_1-C_{12} alkyl, particularly preferably for H or C_1-C_8 alkyl radicals and most particularly preferably for H or methyl,

X stands for a single bond, a C_1 to C_6 alkylene, C_2 to C_5 alkylidene, C_5 to C_6 cycloalkylidene radical, which can be substituted with C_1 to C_6 alkyl, preferably methyl or ethyl radicals, or a C_6 to C_{12} arylene radical, which can optionally be condensed with other heteroatom-containing aromatic rings, where p stands for a whole number between 1 and 1500, preferably between 2 and 1000, particularly preferably between 2 and 700 and most particularly preferably between 5 and 500 and especially between 5 and 300, p stands for numbers between 1 and 1500, preferably between 1 and 1000, particularly preferably between 1 and 700 and most particularly preferably between 1 and 500 and especially preferably between 1 and 300, and q stands for a fraction z/p and r for a fraction (p-z)/p, where z stands for

numbers between 0 and p, and a part of the radicals -O-D-O- and -O-E-O- mutually independently also stands for a radical derived from one or more trifunctional compounds, as a result of which a third binding site, a branching of the polymer chain, occurs at this point.

The polyformals or copolyformals can thus be linear or branched.

The bisphenolate radicals in formulae (1) and (2) particularly preferably derive from the suitable bisphenols cited below.

Hydroquinone, resorcinol, dihydroxybiphenyls, 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) diisopropyl benzenes, and ring-alkylated and ring-halogenated compounds thereof, and also α,ω-bis(hydroxyphenyl) polysiloxanes are cited by way of example for the bisphenols underlying the general formula (1).

Preferred bisphenols are for example 4,4'-dihydroxybiphenyl (DOD), 4,4'-dihydroxybiphenyl ether (DOD ether), 2,2-bis-(4-hydroxyphenyl) propane (bisphenol A), 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (bisphenol TMC), 1,1-bis-(4-hydroxyphenyl) cyclohexane, 2,4-bis-(4-hydroxyphenyl)-2-methyl butane, 1,1-bis-(4-hydroxyphenyl)-1-phenyl ethane, 1,4-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene, 1,3-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene (bisphenol M), 2,2-bis-(3-methyl-4-hydroxyphenyl) propane, 2,2-bis-(3-chloro-4-hydroxyphenyl) propane, bis-(3,5-dimethyl-4-hydroxyphenyl) methane, 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl) propane, bis-(3,5-dimethyl-4-hydroxyphenyl) sulfone, 2,4-bis-(3,5-dimethyl-4-hydroxyphenyl)-2-methyl butane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl) propane and 2,2-bis-(3,5-dibromo-4-hydroxyphenyl) propane.

Particularly preferred bisphenols are for example 2,2-bis-(4-hydroxyphenyl) propane (bisphenol A), 4,4'-dihydroxybiphenyl (DOD), 4,4'-dihydroxybiphenyl ether (DOD ether), 1,3-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene (bisphenol M), 2,2-bis-(3,5-dimethyl-4-hydroxyphenyl) propane, 1,1-bis-(4-hydroxyphenyl)-1-phenyl ethane, 2,2-bis-(3,5-dichloro-4-hydroxyphenyl) propane, 2,2-bis-(3,5-dibromo-4-hydroxyphenyl) propane, 1,1-bis-(4-hydroxyphenyl) cyclohexane and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (bisphenol TMC).

Most particularly preferred are 2,2-bis-(4-hydroxyphenyl) propane (bisphenol A), 4,4'-dihydroxybiphenyl (DOD), 4,4'-dihydroxybiphenyl ether (DOD ether), 1,3-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene (bisphenol M) and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (bisphenol TMC).

Most particularly preferred in particular are 2,2-bis-(4-hydroxyphenyl) propane (bisphenol A) and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (bisphenol TMC).

The bisphenols can be used both alone and in a mixture with one another; both homopolyformals and copolyformals are included. The bisphenols are known from the literature or can be produced by methods known from the literature (see e.g. H. J. Buysch et al., Ullmann's Encyclopedia of Industrial Chemistry, VCH, New York 1991, 5th Edition, Vol. 19, p. 348).

The polyformals according to the invention can be deliberately branched in a controlled manner by the use of small amounts of trifunctional compounds known as branching agents. Some suitable branching agents are: phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl) heptene-2; 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl) heptane; 1,3,5-tri-(4-hydroxyphenyl) benzene; 1,1,1-tri-(4-hydroxyphenyl) ethane; tri-(4-hydroxyphenyl) phenyl methane; 2,2-bis-[4,4-bis-(4-hydroxyphenyl) cyclohexyl] propane; 2,4-bis-(4-hydroxyphenyl isopropyl) phenol; 2,6-bis-(2-hydroxy-5'-methyl benzyl)-4-methyl phenol; 2-(4-hydroxyphenyl)-2-(2,4-

dihydroxyphenyl) propane; hexa-(4-(4-hydroxyphenyl isopropyl) phenyl) orthoterephthalic acid ester; tetra-(4-hydroxyphenyl) methane; tetra-(4-(4-hydroxyphenyl isopropyl) phenoxy) methane; α,α,α"-tris-(4-hydroxyphenyl)-1,3,5-triisopropyl benzene; 2,4-dihydroxybenzoic acid; trimesic acid; cyanuric chloride; 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole; 1,4-bis-(4',4"-dihydroxytriphenyl) methyl) benzene and in particular: 1,1,1-tri-(4-hydroxyphenyl) ethane and bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

The use of such branching agents leads to corresponding deviations in formulae (1) and (2) from their idealised structure. This means that according to the amount of branching agent used, structural units having three binding units, which can also be formed as ester functions, etc., depending on the branching agent used, are produced which are derived from the branching agents used.

The 0.05 to 2 mol% of branching agents or mixtures of branching agents that can optionally be incorporated, relative to diphenols used, can be added together with the diphenols but can also be added at a later stage of the synthesis.

Phenols such as phenol, alkyl phenols such as cresol and 4-tert-butyl phenol, chlorophenol, bromophenol, cumyl phenol or mixtures thereof are preferably used as chain terminators for the polyformals used as materials in the coextruded coating, in quantities of 1-20 mol%, preferably 2-10 mol%, per mol of bisphenol. Phenol, 4-tert-butyl phenol or cumyl phenol are preferred.

Polyformals and copolyformals having the formulae (1a) and (1b) or (2 a-d) are produced for example by a solution process, characterised in that bisphenols and chain terminators are reacted with methylene chloride or alpha,alpha-dichlorotoluene in a homogeneous solution of methylene chloride or α,α-dichlorotoluene and a suitable high-boiling solvent such as e.g. N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), dimethyl sulfoxide (DMSO), N-methyl caprolactam (NMC), chlorobenzene, dichlorobenzene, trichlorobenzene or tetrahydrofuran (THF) in the

presence of a base, preferably sodium hydroxide or potassium hydroxide, at temperatures between 30 and 160°C. Preferred high-boiling solvents are NMP, DMF, DMSO and NMC, particularly preferably NMP, NMC, DMSO and most particularly preferably NMP and NMC. The reaction can also be conducted in several stages. Separation of the cyclic impurities which is optionally necessary takes place after neutral washing of the organic phase by means of a precipitation process in or by means of fractional compounding of the crude product with a solvent that dissolves the cyclic compounds, e.g. acetone. The cyclic impurities are virtually entirely dissolved in the solvent and can be almost completely separated off by compounding in portions and changing the solvent. After compounding, a content of cyclic compounds of well below 1 % can be achieved using for example approx. 10 litres of acetone, which is added in e.g. 5 portions to an amount of polyformal of approx. 6 kg.

The cyclic polyformals and copolyformals can also be separated off by a precipitation process in suitable solvents, which act as precipitants for the desired polymer and as solvents for the undesirable cyclic compounds. These are preferably alcohols or ketones.

The reaction temperature for the polycondensation is 30°C to 160°C, preferably 40°C to 100°C, particularly preferably 50°C to 80°C and most particularly preferably 60°C to 80°C.

The present invention thus provides the use of the polyformals and copolyformals described to produce multilayer products, for example coextrudates such as multilayer sheets, these multilayer sheets themselves and also a process for producing these multilayer sheets by coextrusion, and for coating suitable compositions containing these polyformals or copolyformals.

The present invention also provides a product containing the cited multilayer sheet or other coated products based on polyformals. This product, which for example

contains the cited multilayer sheet or is itself coated, is preferably selected from the group consisting of baby bottles, water bottles or medical articles that can be sterilised in superheated steam.

The multilayer product according to the invention has numerous advantages. In particular it has the advantage that a clear improvement in long-term stability, in particular in hydrolysis stability in relation to aqueous media, is achieved through the hydrolysis protection layer based on polyformals. Moreover the sheet is easy and inexpensive to produce, all starting materials are available and inexpensive. In addition, the other positive properties of polycarbonate, for example its good optical and mechanical properties, are unimpaired or only insubstantially impaired in the multilayer product according to the invention.

The multilayer products according to the invention have further advantages in comparison to the prior art. The multilayer products according to the invention, such as bottles, can be produced by coextrusion blow moulding, for example. This leads to advantages over a product produced by coating. For example, no solvents evaporate in coextrusion as is the case with coating systems.

Furthermore, coatings have a limited storage capacity. Coextrusion does not have this disadvantage.

Furthermore, coatings require complex technology. For example, they require explosion-proof units if organic solvents are used, recycling of solvents and hence expensive investment in equipment. Coextrusion does not have this disadvantage.

A preferred embodiment of the present invention is the cited multilayer sheet or various types of bottle, the base layer consisting of polycarbonate and/or copolycarbonate and/or polyester and/or copolyester and/or polyester carbonates and/or polymethyl methacrylate and/or polyacrylates and/or blends of polycarbonate and polyesters and/or polymethyl methacrylates and the coex layer consisting of

polyformals or copolyformals or blends thereof with (co)polycarbonate and/or (co)polyesters.

Multilayer products in which the hydrolysis protection layer is 1 to 5000 µm thick, preferably 5 to 2500 µm, most particularly preferably 10 to 500 µm, are preferred according to the invention.

The sheets can be solid sheets, multi-wall sheets, twin-wall sheets, triple-wall sheets, quadruple-wall sheets, etc. The multi-wall sheets can also have various profiles, such as e.g. X-profiles or XX-profiles. The multi-wall sheets can in addition be corrugated multi-wall sheets.

A preferred embodiment of the present invention is a two-layer sheet consisting of one layer of polycarbonate and a hydrolysis protection layer of polyformal or copolyformal or a polycarbonate-polyformal blend.

A further preferred embodiment of the present invention is a three-layer sheet consisting of one layer of polycarbonate as the base sheet and two overlying hydrolysis protection layers which are the same or different and consist of polyformal or copolyformal or a polycarbonate-polyformal blend.

Likewise preferred as an embodiment of the present invention are various types of containers, such as bottles, e.g. water bottles (5-gallon bottles), baby bottles or reusable milk bottles.

Containers within the meaning of the present invention can be used for the packaging, storage or transport of liquids, solids or gases. Containers for the packaging, storage or transport of liquids are preferred (liquid containers), containers for the packaging, storage or transport of water (water bottles) being particularly preferred.

Containers within the meaning of the invention are blown containers having a volume of preferably 0.1 l to 50 l, preferably 0.5 l to 50 l, volumes of 1 l, 5 l, 12 l and 20 l being most particularly preferred.

Water bottles having a volume of 3 to 5 gallons are most particularly preferred.

The containers have an empty weight of preferably 0.1 g to 3000 g, by preference 50 g to 2000 g and particularly preferably 650 g to 900 g.

The wall thicknesses of the containers are preferably 0.5 mm to 5 mm, by preference 0.8 mm to 4 mm.

Containers within the meaning of the present invention have a length of preferably 5 mm to 2000 mm, particularly preferably 100 mm to 1000 mm.

The containers have a maximum perimeter of preferably 10 mm to 250 mm, by preference 50 mm to 150 mm and most particularly preferably 70 to 90 mm.

Containers within the meaning of the invention preferably have a bottle neck of a length of preferably 1 mm to 500 mm, by preference 10 mm to 250 mm, particularly preferably 50 mm to 100 mm and most particularly preferably 70 to 80 mm.

The wall thickness of the bottle neck of the containers varies between preferably 0.5 mm and 10 mm, particularly preferably between 1 mm and 10 mm and most particularly preferably between 5 mm and 7 mm.

The diameter of the bottle neck varies between preferably 5 mm and 200 mm. 10 mm to 100 mm are particularly preferred, and 45 mm to 75 mm are most particularly preferred.

The bottle base of the containers according to the invention has a diameter of preferably 10 mm to 250 mm, preferably 50 mm to 150 mm and most particularly preferably 70 to 90 mm.

Containers within the meaning of the present invention can have any geometrical shape, they can be e.g. round, oval or polygonal or angular with e.g. 3 to 12 sides. Round, oval and hexagonal shapes are preferred.

The design of the containers can be based on any surface texture. The surface textures are preferably smooth or ribbed. The containers according to the invention can also display several different surface textures. Ribs or beads can run around the perimeter of the containers. They can be any distance apart or can be several different distances apart. The surface textures of the containers according to the invention can display roughened or integrated textures, symbols, ornaments, coats of arms, company logos, trademarks, monograms, manufacturer's instructions, material descriptions and/or volume information.

The containers according to the invention can display any number of handles, which can be located on the side, top or bottom. The handles can be external or can be integrated into the contour of the container. The handles can be folding or fixed. The handles can be of any shape, e.g. oval, round or polygonal. The length of the handles is preferably from 0.1 mm to 180 mm, preferably from 20 mm to 120 mm.

In addition to the polycarbonate according to the invention the containers according to the invention can also contain other substances to a small extent, e.g. seals made from rubber or handles made from other materials.

The containers according to the invention are preferably produced by extrusion blow moulding or injection blow moulding.

In a preferred embodiment of the process for producing the containers according to the invention, the polycarbonates according to the invention are processed on extruders having a smooth or grooved, preferably a smooth, feed section.

The drive power of the extruder is chosen according to the screw diameter. By way of example, with a screw diameter of 60 mm the drive power of the extruder is approx. 30 to 40 kW, with a screw diameter of 90 mm it is approx. 60 to 70 kW.

The universal three-section screws conventionally used in the processing of engineering thermoplastics are suitable.

For the production of containers having a volume of 1 l a screw diameter of 50 to 60 mm is preferred. For the production of containers having a volume of 20 l a screw diameter of 70 to 100 mm is preferred. The length of the screws is preferably 20 to 25 times the diameter of the screw.

In the case of blow moulding, the blow mould is preferably heated to 50 to 90°C to obtain a sparkling and high-quality container surface.

To ensure uniform and effective heating of the blow mould, the base area and the jacket area can be heated separately.

The blow mould is preferably closed with a compressive force of 1000 to 1500 N per cm of pinch-off weld length.

Before processing, the polycarbonate according to the invention is preferably dried so that the optical quality of the containers is not diminished by streaks or bubbles and the polycarbonate is not degraded hydrolytically during processing. The residual moisture content after drying is preferably less than 0.01 wt.%. A drying temperature of 120°C is preferred. Lower temperatures do not guarantee adequate drying, whilst

at higher temperatures there is a risk of the granules of polycarbonate sticking together and then no longer being able to be processed. Dry-air dryers are preferred.

The preferred melt temperature during processing of the polycarbonate according to the invention is 230° to 300°C.

The containers according to the invention can be used for the packaging, storage or transport of liquids, solids or gases. The embodiment as containers which are used for example for the packaging, storage or transport of liquids is preferred. The embodiment as a water bottle which can be used for example for the packaging, storage or transport of water is particularly preferred.

A preferred embodiment of the invention is the one wherein the containers made from branched polycarbonate are characterised in that the branched polycarbonate contains THPE and/or IBC as branching agent and wherein phenol or alkyl phenols are used as chain terminators in the production of the branched polycarbonate and wherein the container is a water bottle.

A particularly preferred embodiment of the invention is the one wherein the container made from branched polycarbonate is characterised in that the branched polycarbonate contains THPE and/or IBC as branching agent and wherein phenol is used in the production of the branched polycarbonate and wherein the polycarbonate has a melt viscosity of 5500 to 7000 Pas at 260°C and a shear rate of 10 s^{-1} and a melt viscosity of 900 to 1100 Pas at 260°C and a shear rate of 1000 s^{-1} and has an MFR (melt flow index, measured according to ISO 1133) of < 3.5 g/10 min and wherein the container is a water bottle.

In a particular embodiment the multilayer products are transparent.

Both the base material and the hydrolysis protection layer(s) in the multilayer moulded articles according to the invention can contain additives.

Depending on the area of application, the hydrolysis protection layer can in particular contain UV stabilisers or mould release agents.

The layers can also contain other conventional processing aids, particularly mould release agents and flow control agents, and the stabilisers conventionally used in polycarbonates, particularly UV stabilisers, heat stabilisers, as well as colorants and optical brighteners and inorganic pigments.

Layers made from all known polycarbonates are suitable as additional layers, in addition to the polyformal and copolyformal layers, particularly as a base layer of the multilayer products according to the invention.

Suitable polycarbonates are e.g. homopolycarbonates, copolycarbonates and thermoplastic polyester carbonates.

They preferably have average molecular weights $\overline{M}_w$ of 18,000 to 40,000, preferably 26,000 to 36,000 and particularly 28,000 to 35,000, 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.

With regard to the manufacture of polycarbonates, reference is made by way of example to "Schnell, Chemistry and Physics of Polycarbonates, Polymer Reviews, Vol. 9, Interscience Publishers, New York, London, Sydney 1964", and to "D.C. PREVORSEK, B.T. DEBONA and Y. KESTEN, Corporate Research Center, Allied Chemical Corporation, Moristown, New Jersey 07960, 'Synthesis of Poly(ester)carbonate Copolymers' in Journal of Polymer Science, Polymer Chemistry Edition, Vol. 19, 75-90 (1980)", and to "D. Freitag, U. Grigo, P.R. Müller, N. Nouvertne, BAYER AG, 'Polycarbonates' in Encyclopedia of Polymer Science and Engineering, Vol. 11, Second Edition, 1988, pages 648-718" and finally to "Drs U. Grigo, K. Kircher and P.R. Müller 'Polycarbonate' in Becker/Braun,

Kunststoff-Handbuch, Volume 3/1, Polycarbonate, Polyacetale, Polyester, Celluloseester, Carl Hanser Verlag Munich, Vienna 1992, pages 117-299".

Production of the polycarbonates is preferably performed by the interfacial polycondensation process or the melt interesterification process and is described below using the interfacial polycondensation process by way of example.

The compounds preferably used as starting compounds are bisphenols having the general formula

HO-Z-OH,

wherein Z is a divalent organic radical having 6 to 30 carbon atoms and containing one or more aromatic groups.

Examples of such compounds are bisphenols belonging to the group of dihydroxydiphenyls, bis(hydroxyphenyl) alkanes, indane bisphenols, bis(hydroxyphenyl) ethers, bis(hydroxyphenyl) sulfones, bis(hydroxyphenyl) ketones and α,α'-bis(hydroxyphenyl) diisopropyl benzenes.

Particularly preferred bisphenols belonging to the previously cited groups of compounds are bisphenol A, tetraalkyl bisphenol A, 1,3-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene (bisphenol M), 1,1-bis-[2-(4-hydroxyphenyl)-2-propyl] benzene, 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane (BP-TMC) and optionally mixtures thereof.

The bisphenol compounds for use according to the invention are preferably reacted with carbonic acid compounds, in particular phosgene, or in the case of the melt interesterification process with diphenyl carbonate or dimethyl carbonate.

Polyester carbonates are preferably obtained by reacting the previously cited bisphenols, at least one aromatic dicarboxylic acid and optionally carbonic acid equivalents. Examples of suitable aromatic dicarboxylic acids are phthalic acid, terephthalic acid, isophthalic acid, 3,3'- or 4,4'-diphenyldicarboxylic acid and benzophenone dicarboxylic acids. A part, up to 80 mol%, preferably from 20 to 50 mol%, of the carbonate groups in the polycarbonates can be replaced by aromatic dicarboxylic acid ester groups.

Examples of inert organic solvents used in the interfacial polycondensation process are dichloromethane, the various dichloroethanes and chloropropane compounds, tetrachloromethane, trichloromethane, chlorobenzene and chlorotoluene, chlorobenzene or dichloromethane or mixtures of dichloromethane and chlorobenzene preferably being used.

The interfacial polycondensation reaction can be accelerated by catalysts such as tertiary amines, in particular N-alkyl piperidines or onium salts. Tributylamine, triethylamine and N-ethyl piperidine are preferably used. In the melt interesterification process the catalysts cited in DE-A 4 238 123 are preferably used.

The polycarbonates can be deliberately branched in a controlled manner by the use of small quantities of branching agents. Some suitable branching agents are: phloroglucinol, 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl) heptene-2; 4,6-dimethyl-2,4,6-tri-(4-hydroxyphenyl) heptane; 1,3,5-tri-(4-hydroxyphenyl) benzene; 1,1,1-tri-(4-hydroxyphenyl) ethane; tri-(4-hydroxyphenyl) phenyl methane; 2,2-bis-[4,4-bis-(4-hydroxyphenyl) cyclohexyl] propane; 2,4-bis-(4-hydroxyphenyl isopropyl) phenol; 2,6-bis-(2-hydroxy-5'-methylbenzyl)-4-methylphenol; 2-(4-hydroxyphenyl)-2-(2,4-dihydroxyphenyl) propane; hexa-(4-(4-hydroxyphenyl isopropyl) phenyl) orthoterephthalic acid ester; tetra-(4-hydroxyphenyl) methane; tetra-(4-(4-hydroxyphenyl isopropyl) phenoxy) methane; α,α,α'-tris-(4-hydroxyphenyl)-1,3,5-triisopropyl benzene; 2,4-dihydroxybenzoic acid; trimesic acid; cyanuric chloride; 3,3-bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole; 1,4-bis-(4',4"-

dihydroxytriphenyl)methyl) benzene and in particular: 1,1,1-tri-(4-hydroxyphenyl) ethane and bis-(3-methyl-4-hydroxyphenyl)-2-oxo-2,3-dihydroindole.

The 0.05 to 2 mol% of branching agents or mixtures of branching agents that can optionally be incorporated, relative to diphenols used, can be added together with the diphenols but can also be added at a later stage of the synthesis.

Phenols such as phenol, alkyl phenols such as cresol and 4-tert-butyl phenol, chlorophenol, bromophenol, cumyl phenol or mixtures thereof are preferably used as chain terminators, in quantities of 1-20 mol%, preferably 2-10 mol%, per mol of bisphenol. Phenol, 4-tert-butyl phenol or cumyl phenol are preferred.

Chain terminators and branching agents can be added to the syntheses either separately or together with the bisphenol.

The production of polycarbonates by the melt interesterification process is described in DE-A 42 38 123 by way of example.

Preferred polycarbonates are the homopolycarbonate based on bisphenol A, the homopolycarbonate based on 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane and the copolycarbonates based on the two monomers bisphenol A and 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethyl cyclohexane and the copolycarbonates based on the two monomers bisphenol A and 4,4'-dihydroxydiphenyl (DOD).

The homopolycarbonate based on bisphenol A is particularly preferred.

All thermoplastics used in the products according to the invention can contain stabilisers. Suitable stabilisers are for example stabilisers containing phosphines, phosphites or Si and other compounds described in EP-A 0 500 496. Triphenyl phosphites, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, tetrakis-(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonite and

triaryl phosphite can be cited by way of example. Triphenyl phosphine and tris-(2,4-di-tert-butylphenyl) phosphite are particularly preferred.

These stabilisers can be present in all layers of the multilayer products according to the invention. In other words both in the so-called base and in the so-called coex layer(s). Different additives or concentrations of additives can be present in each layer.

The multilayer products according to the invention can also include 0.01 to 0.5 wt.% of the esters or partial esters of monohydric to hexahydric alcohols, in particular of glycerol, pentaerythritol or guerbet alcohols.

Monohydric alcohols are for example stearyl alcohol, palmityl alcohol and guerbet alcohols.

An example of a dihydric alcohol is glycol.

An example of a trihydric alcohol is glycerol.

Examples of tetrahydric alcohols are pentaerythritol and mesoerythritol.

Examples of pentahydric alcohols are arabitol, ribitol and xylitol.

Examples of hexahydric alcohols are mannitol, glucitol (sorbitol) and dulcitol.

The esters are preferably the monoesters, diesters, triesters, tetraesters, pentaesters and hexaesters or mixtures thereof, in particular random mixtures, of saturated, aliphatic C_{10} to C_{36} monocarboxylic acids and optionally hydroxy monocarboxylic acids, preferably with saturated, aliphatic C_{14} to C_{32} monocarboxylic acids and optionally hydroxy monocarboxylic acids.

The commercially obtainable fatty acid esters, in particular of pentaerythritol and glycerol, can contain <60% of various partial esters as a consequence of their manufacturing process.

Saturated, aliphatic monocarboxylic acids having 10 to 36 C atoms are for example decanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, stearic acid, hydroxystearic acid, eicosanoic acid, docosanoic acid, tetracosanoic acid, hexacosanoic acid and octacosanoic acids.

Preferred saturated, aliphatic monocarboxylic acids having 14 to 22 C atoms are for example tetradecanoic acid, hexadecanoic acid, stearic acid, hydroxystearic acid, eicosanoic acid and docosanoic acid.

Saturated, aliphatic monocarboxylic acids such as hexadecanoic acid, stearic acid and hydroxystearic acid are particularly preferred.

The saturated aliphatic C_{10} to C_{36} carboxylic acids and the fatty acid esters are either known per se from the literature or can be produced by methods known from the literature. Examples of pentaerythritol fatty acid esters are those of the particularly preferred monocarboxylic acids specified above.

Esters of pentaerythritol and of glycerol with stearic acid and hexadecanoic acid are particularly preferred.

Esters of guerbet alcohols and of glycerol with stearic acid and hexadecanoic acid and optionally with hydroxystearic acid are also particularly preferred.

These esters can be present both in the base and in the coex layer(s). Different additives or concentrations can be present in each layer.

The multilayer products according to the invention can contain antistatics.

Examples of antistatics are cationic compounds, for example quaternary ammonium, phosphonium or sulfonium salts, anionic compounds, for example alkyl sulfonates, alkyl sulfates, alkyl phosphates, carboxylates in the form of alkali-metal salts or alkaline-earth metal salts, non-ionogenic compounds, for example polyethylene glycol esters, polyethylene glycol ethers, fatty acid esters, ethoxylated fatty amines.

These antistatics can be present both in the base and in the coex layer(s). Different additives or concentrations can be present in each layer. They are preferably used in the coex layer(s).

The multilayer products according to the invention can contain organic dyes, inorganic coloured pigments, fluorescent dyes and particularly preferably optical brighteners.

These colorants can be present in both the base and in the coex layer(s). Different additives or concentrations can be present in each layer.

All moulding compositions used for production of the multilayer products according to the invention, feedstocks and solvents therein, can be contaminated with corresponding impurities as a result of manufacture and storage conditions, the objective being to work with the cleanest possible starting materials.

The individual components in the moulding compositions can be mixed by known means, both successively and simultaneously, and at both room temperature and elevated temperature.

The additives, in particular the aforementioned additives, are preferably incorporated into the moulding compositions for the products according to the invention by known means by mixing polymer granules with the additives at temperatures of around 200 to 330°C in conventional units such as internal mixers, single-screw

extruders and double-shaft extruders, for example by melt compounding or melt extrusion or by mixing the polymer solutions with solutions of the additives, followed by evaporation of the solvents by known means. The content of additives in the moulding composition can be varied between broad limits and is governed by the desired properties of the moulding composition. The total content of additives in the moulding composition is preferably up to around 20 wt.%, preferably 0.2 to 12 wt.%, relative to the weight of the moulding composition.

Coextrusion is known per se from the literature (see for example EP-A 0 110 221 and EP-A 0 110 238). In the present case the procedure is preferably performed as follows. Extruders are connected to a coextrusion adapter to produce the core and outer layer(s). The adapter is designed in such a way that the melts forming the outer layer(s) are applied adhesively as a thin layer to the melt of the core. The multilayer melt strand produced in this way is then transferred to the adjacent die in the desired form (multi-wall sheet or solid sheet). The melt is then cooled under controlled conditions by known means by calendering (solid sheet) or vacuum calibration (multi-wall sheet) and then cut into lengths. A conditioning oven can optionally be connected after the calibration stage to eliminate stresses. In place of the adapter connected before the die, the die itself can also be designed in such a way that the melts are brought together there.

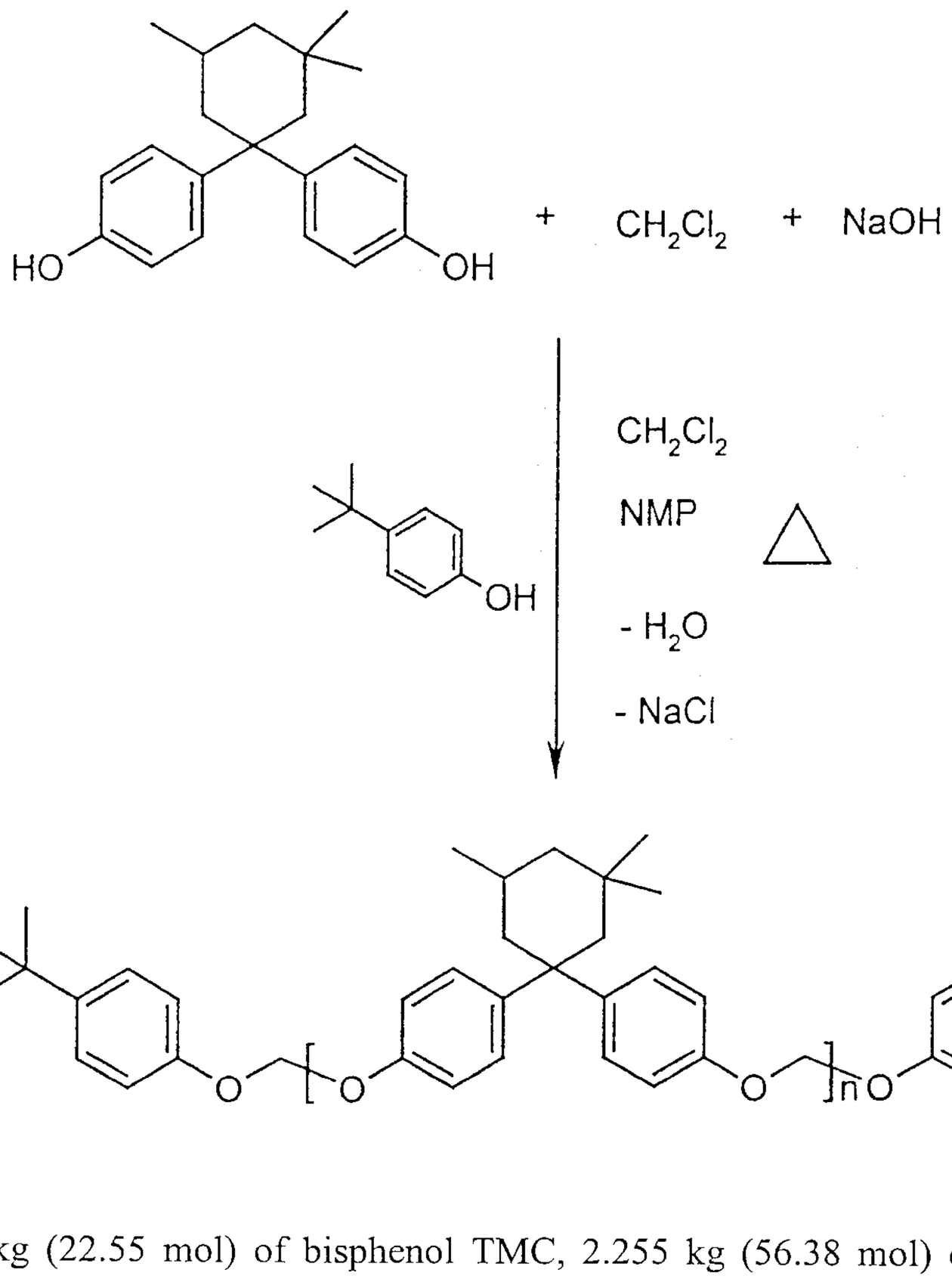
Multilayer composites can also be produced according to the prior art by extrusion coating, coextrusion and coextrusion blow moulding.

The invention is further explained by, without being limited to, the following examples. The examples according to the invention merely describe preferred embodiments of the present invention.

Examples

Example 1

Synthesis of homopolyformal from bisphenol TMC:



7 kg (22.55 mol) of bisphenol TMC, 2.255 kg (56.38 mol) of sodium hydroxide pellets and 51.07 g (0.34 mol) of finely ground p-tert-butyl phenol (Aldrich) in 500 ml of methylene chloride are added to a solvent blend consisting of 28.7 kg of methylene chloride and 40.18 kg of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with 35 l of methylene chloride and 20 l of demineralised water. The batch is

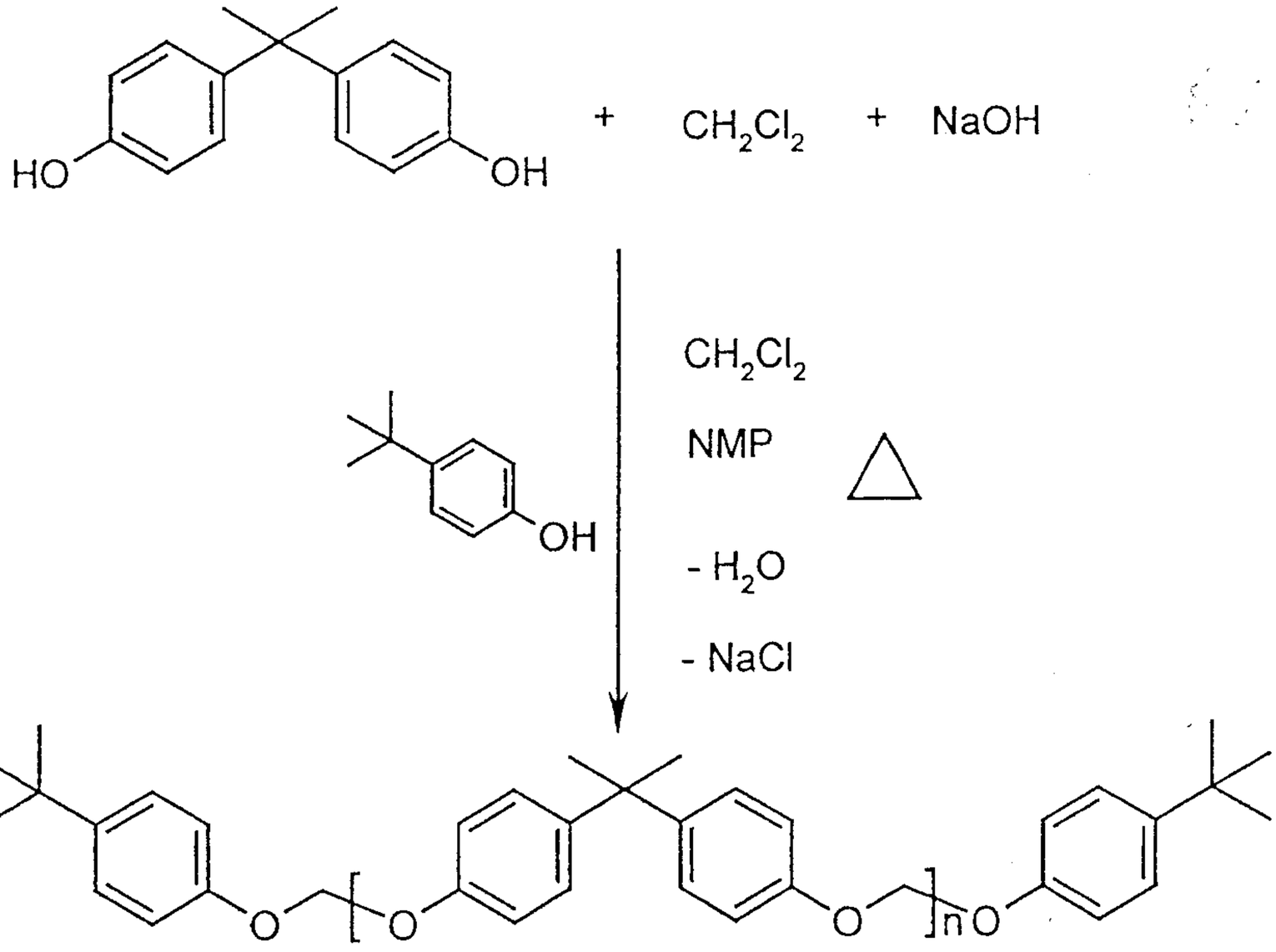
washed with water in a separator until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase from the separator is separated off and the solvent exchange of methylene chloride for chlorobenzene performed in an evaporator. The material is then extruded by means of a ZSK 32 evaporation extruder at a temperature of 270°C with subsequent granulation. This synthesis procedure is performed twice. After discarding the feed material a total of 9.85 kg of polyformal is obtained as transparent granules. This still contains low-molecular-weight cyclic formals as an impurity. The material is divided into two parts and each is swollen overnight with approx. 5 l of acetone. The products obtained are compounded with several portions of fresh acetone until no more cyclic compounds can be detected. After combining the purified material and dissolving it in chlorobenzene it is extruded again through the evaporation extruder at 280°C. After discarding the feed material a total of 7.31 kg of polyformal is obtained as transparent granules.

Analysis:

- Molecular weight Mw = 38345, Mn = 20138, D = 1.90 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 170.8 °C
- Relative solution viscosity in methylene chloride (0.5 g/100 ml solution) = 1.234
- Confirmation of freedom of polymer from cyclic compounds by GPC (oligomers in low-molecular-weight range) and MALDI-TOF (molecular weight of cyclic compounds compared to the molecular weight of open-chain analogues).

Example 2

Homopolyformal from bisphenol A:



7 kg (30.66 mol) of bisphenol A (Bayer AG), 3.066 kg (76.65 mol) of sodium hydroxide pellets and 69.4 g (0.462 mol) of finely ground p-tert-butyl phenol (Aldrich) in 500 ml of methylene chloride are added to a solvent blend consisting of 28.7 kg of methylene chloride and 40.18 kg of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with 20 l of methylene chloride and 20 l of demineralised water. The batch is washed with water in a separator until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase from the separator is separated off and the solvent exchange of methylene chloride for chlorobenzene performed in an evaporator. The material is then extruded by means of a ZSK 32 evaporation extruder at a temperature of 200°C with subsequent granulation. This synthesis procedure is performed twice. After discarding the feed material a total of 11.99 kg of polyformal is obtained as transparent granules.

Analysis:

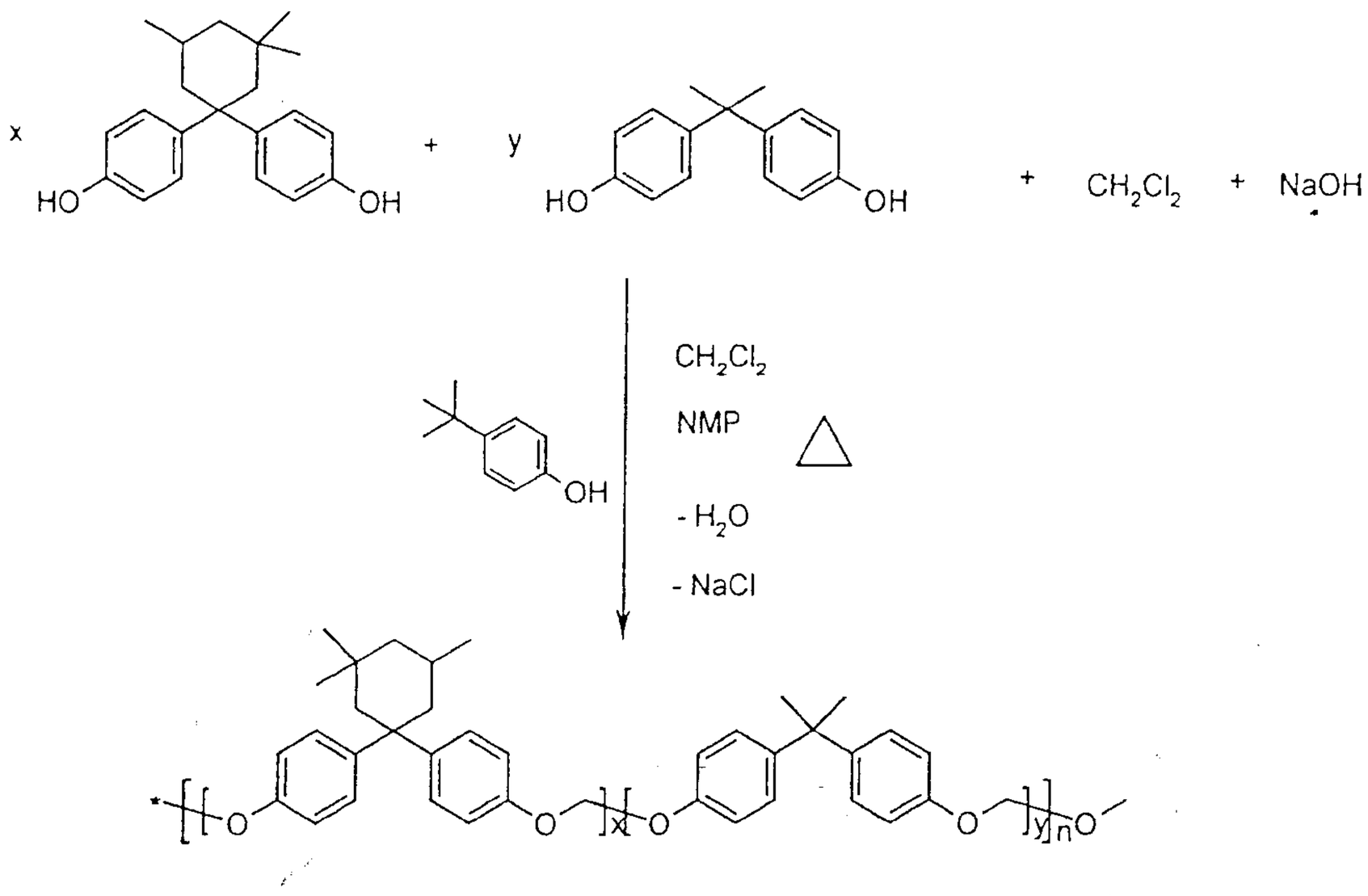
- Molecular weight Mw = 31732, Mn = 3465 by GPC (calibration against polycarbonate). The cyclic compounds were not separated off in this case. Swelling of the material with acetone is not possible, which means that separation of the cyclic compounds is likewise not possible.

- Glass transition temperature Tg = 89°C

- Relative solution viscosity in methylene chloride (0.5 g/100 ml solution) = 1.237/1.239 (double determination)

Example 3

a) Synthesis of copolyformal from bisphenol TMC and bisphenol A:



5.432 kg (17.5 mol) of bisphenol TMC (x=70 mol%), 1.712 kg (7.5 mol) of bisphenol A (y=30 mol%), 2.5 kg (62.5 mol) of sodium hydroxide pellets and

56.33 g (0.375 mol) of finely ground p-tert-butyl phenol (Aldrich) in 500 ml of methylene chloride are added to a solvent blend consisting of 28.7 kg of methylene chloride and 40.18 kg of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with 35 l of methylene chloride and 20 l of demineralised water. The batch is washed with water in a separator until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase from the separator is separated off and the solvent exchange of methylene chloride for chlorobenzene performed in an evaporator. The material is then extruded by means of a ZSK 32 evaporation extruder at a temperature of 280°C with subsequent granulation. After discarding the feed material a total of 5.14 kg of copolyformal is obtained as transparent granules. This still contains low-molecular-weight cyclic compounds as an impurity. The material is swollen overnight with approx. 5 l of acetone. The product obtained is compounded with several portions of fresh acetone until no more cyclic compounds can be detected. The purified material is dissolved in chlorobenzene and extruded again through the evaporation extruder at 270°C. After discarding the feed material 3.11 kg of polyformal are obtained as transparent granules.

Analysis:

- Molecular weight Mw = 39901, Mn = 19538, D = 2.04 by GPC (calibration against polycarbonate).

- Glass transition temperature Tg = 148.2 °C

- Relative solution viscosity in methylene chloride (0.5 g/100 ml solution) = 1.244/1.244 (granules)

- ^{1}H-NMR in $CDCl_3$ shows the expected insertion ratio x/y = 0.7/0.3 of the TMC/BPA monomers (integral of chemical shifts of cyclic aliphatic groups (TMC) to methyl groups (BPA))

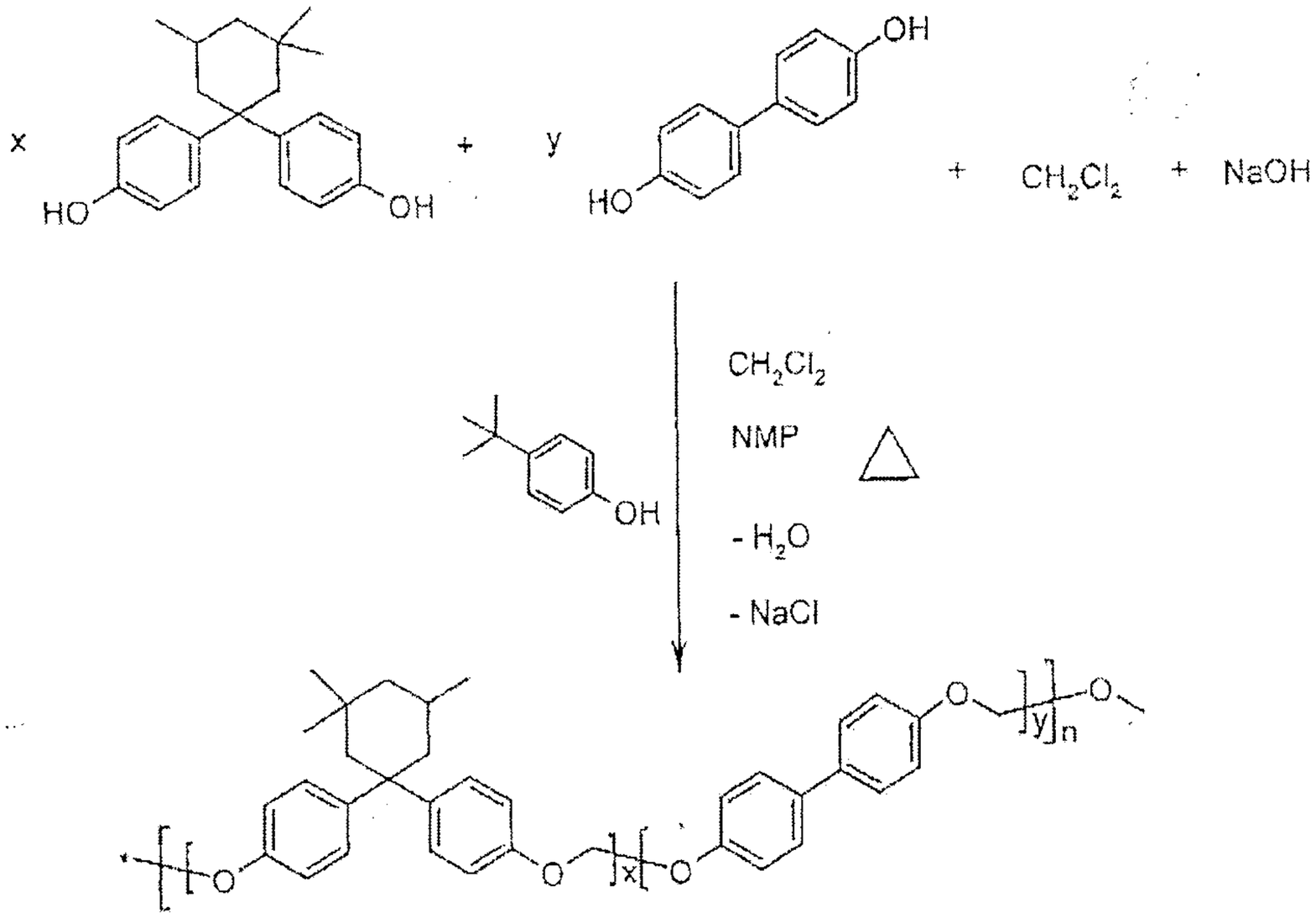
b) to i) Synthesis of copolyformals from bisphenol TMC and bisphenol A with variable composition:

Further copolyformals are produced in the same way as the synthesis in Example 3a) (see Table 1).

Example no.	TMC [mol%]	BPA [mol%]	Tg [°C]
3b)	30	70	115
3c)	35	65	120
3d)	40	60	124
3e)	50	50	132
3f)	55	45	137
3g)	70	30	149
3h)	80	20	158
3i)	90	10	165

Example 4

Synthesis of copolyformal from bisphenol TMC and 4,4'-dihydroxybiphenyl (DOD):



3.749 kg (12.07 mol) of bisphenol TMC (x=90 mol%), 0.2497 kg (1.34 mol) of 4,4'-dihydroxybiphenyl (DOD) (y=10 mol%), 1.339 kg (33.48 mol) of sodium hydroxide pellets and 20.12 g (0.134 mol) of finely ground p-tert-butyl phenol (Aldrich) in 200 ml of methylene chloride are added to a solvent blend consisting of 12.0 l of methylene chloride and 22.25 kg of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with 35 l of methylene chloride and 20 l of demineralised water. The batch is washed with water in a separator until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase from the separator is separated off and the solvent exchange of methylene chloride for chlorobenzene performed in an evaporator. The material is then extruded by means of a ZSK 32 evaporation extruder at a temperature of 280°C with subsequent granulation. After discarding the feed material a total of 2.62 kg of copolyformal is obtained as transparent granules. This

still contains low-molecular-weight cyclic compounds as an impurity. The material is swollen overnight with approx. 5 l of acetone. The product obtained is compounded with several portions of fresh acetone until no more cyclic compounds can be detected. The purified material is dissolved in chlorobenzene and extruded again through the evaporation extruder at 240°C. After discarding the feed material the polyformal is obtained as transparent granules.

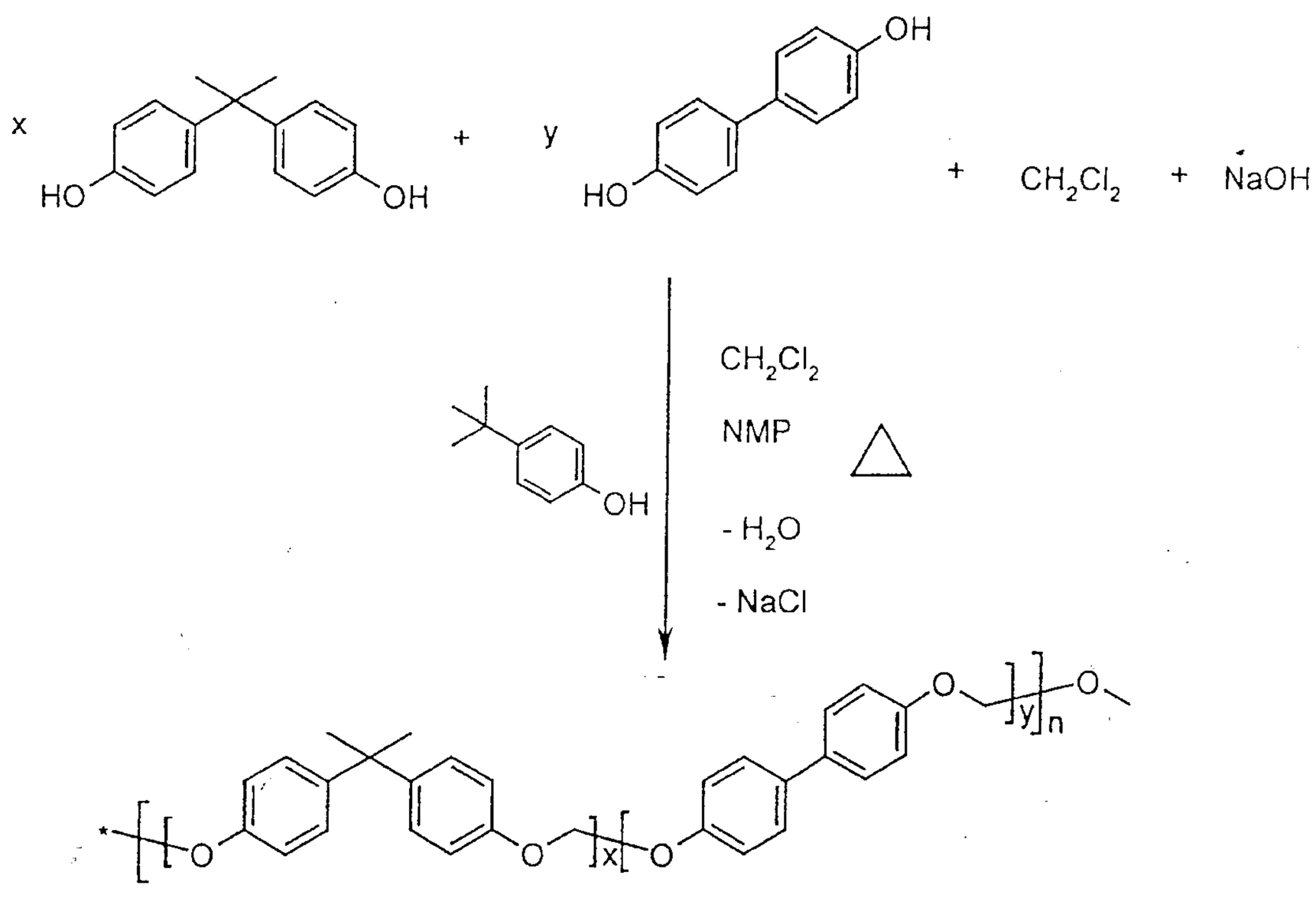
Analysis:

- Molecular weight Mw = 44287, Mn = 17877, D = 2.48 by GPC (calibration against polycarbonate).

- Glass transition temperature Tg = 167 °C

Example 5

Synthesis of copolyformal from bisphenol A and 4,4'-dihydroxybiphenyl (DOD):



22.37 g (0.0098 mol) of bisphenol A (x=70 mol%), 7.82 g (0.0042 mol) of 4,4'-dihydroxybiphenyl (DOD) (y=30 mol%), 14.0 g (0.35 mol) of sodium hydroxide pellets and 0.21 g (0.0014 mol) of finely ground p-tert-butyl phenol (Aldrich) are added to a solvent blend consisting of 125 ml of methylene chloride and 225 ml of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with methylene chloride and demineralised water. And then washed with water until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase is separated off. The polymer is isolated by precipitation in methanol. After washing the product with water and methanol and drying at 80°C, polyformal is obtained as white polymer filaments.

Analysis:

- Molecular weight Mw = 19057, Mn = 4839, D = 3.94 by GPC (calibration against polycarbonate).

Example 6

Hydrolysis test of BPA polyformal from Example 2:

The hydrolysis test is performed by loading with the following hydrolysis media/temperature conditions and determining the molecular weight change over time by measuring the relative solution viscosity in methylene chloride (0.5 g/100 ml solution):

Hydrolysis medium: 0.1 N HCl / 80°C

0.1 N NaOH / 80°C

distilled water / approx. 100°C

The following results are obtained up to a total loading period of 21 days (multiple determinations in each case):

a) Hydrolysis medium: 0.1 N HCl / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.237 / 1.239 (reference sample)
7	1.237 / 1.238 / 1.236 / 1.237 / 1.237 / 1.238
14	1.237 / 1.237 / 1.236 / 1.237 / 1.237 / 1.237
21	1.236 / 1.239 / 1.235 / 1.236 / 1.235 / 1.235

a) Hydrolysis medium: 0.1 N NaOH / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.237 / 1.239 (reference sample)
7	1.237 / 1.238 / 1.237 / 1.237 / 1.236 / 1.237
14	1.237 / 1.237 / 1.236 / 1.236 / 1.236 / 1.236
21	1.236 / 1.236 / 1.236 / 1.236 / 1.236 / 1.235

a) Hydrolysis medium: distilled water / approx. 100°C

Time [days]	Relative solution viscosity η_{rel}
0	1.237 / 1.239 (reference sample)
7	1.238 / 1.237 / 1.238 / 1.237 / 1.237 / 1.237
14	not measured
21	1.238 / 1.237 / 1.237 / 1.237 / 1.237 / 1.235

Example 7

Hydrolysis test of TMC/BPA copolyformal (70/30) from Example 3:

The hydrolysis test is performed by loading with the following hydrolysis media/temperature conditions and determining the molecular weight change over time by measuring the relative solution viscosity in methylene chloride (0.5 g/100 ml solution):

Hydrolysis medium: 0.1 N HCl / 80°C

0.1 N NaOH / 80°C

distilled water / approx. 100°C

The following results are obtained up to a total loading period of 21 days (multiple determinations in each case):

a) Hydrolysis medium: 0.1 N HCl / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.242 / 1.242 (reference sample; after spraying onto the 80x10x4 test piece)
7	1.242 / 1.242 / 1.243 / 1.243 / 1.242 / 1.243
14	1.240 / 1.241 / 1.240 / 1.242 / 1.241 / 1.241
21	1.243 / 1.243 / 1.243 / 1.242 / 1.243 / 1.243

a) Hydrolysis medium: 0.1 N NaOH / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.242 / 1.242 (reference sample)
7	1.243 / 1.242 / 1.243 / 1.243 / 1.243 / 1.243
14	1.240 / 1.241 / 1.241 / 1.241 / 1.242 / 1.242
21	1.242 / 1.242 / 1.243 / 1.242 / 1.243 / 1.242

a) Hydrolysis medium: distilled water / approx. 100°C

Time [days]	Relative solution viscosity η_{rel}
0	1.242 / 1.242 (reference sample)
7	1.242 / 1.243 / 1.242 / 1.243 / 1.243 / 1.242
14	1.241 / 1.241 / 1.241 / 1.242 / 1.241 / 1.241
21	1.242 / 1.243 / 1.242 / 1.241 / 1.244 / 1.243

Example 8

Hydrolysis test of a TMC polyformal:

(same as that from Example 1, but with a higher molecular weight)

- Molecular weight Mw = 50311, Mn = 21637, D = 2.32 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 172°C
- Relative solution viscosity in methylene chloride (0.5 g/100 ml solution) = 1.288/1.290

The hydrolysis test is performed by loading with the following hydrolysis media/temperature conditions and determining the molecular weight change over time by measuring the relative solution viscosity in methylene chloride (0.5 g/100 ml solution):

Hydrolysis medium: 0.1 N HCl / 80°C

0.1 N NaOH / 80°C

distilled water / approx. 100°C

The following results are obtained up to a total loading period of 21 days (multiple determinations in each case):

a) Hydrolysis medium: 0.1 N HCl / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.288 / 1.290 (reference sample; after spraying onto the 80x10x4 test piece)
7	1.291 / 1.290 / 1.289 / 1.288 / 1.288 / 1.290
14	1.288 / 1.288 / 1.289 / 1.289 / 1.288 / 1.288
21	1.288 / 1.288 / 1.289 / 1.289 / 1.289 / 1.289

a) Hydrolysis medium: 0.1 N NaOH / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.288 / 1.290 (reference sample)
7	1.289 / 1.289 / 1.290 / 1.290 / 1.289 / 1.289
14	1.287 / 1.289 / 1.288 / 1.289 / 1.286 / 1.287
21	1.287 / 1.288 / 1.294 / 1.294 / 1.288 / 1.288

a) Hydrolysis medium: distilled water / approx. 100°C

Time [days]	Relative solution viscosity η_{rel}
0	1.288 / 1.290 (reference sample)
7	1.285
14	1.281
21	1.284

Example 9

Hydrolysis test of the polycarbonate Makrolon® 2808, Bayer AG (comparative experiments):

The hydrolysis test is performed by loading with the following hydrolysis media/temperature conditions and determining the molecular weight change over time by measuring the relative solution viscosity in methylene chloride (0.5 g/100 ml solution):

Hydrolysis medium: 0.1 N HCl / 80°C

0.1 N NaOH / 80°C

distilled water / approx. 100°C

The following results are obtained up to a total loading period of 21 days (multiple determinations in each case):

a) Hydrolysis medium: 0.1 N HCl / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.284 / 1.289 (reference sample; after spraying onto the 80x10x4 test piece)
7	1.282 / 1.280 / 1.281 / 1.283 / 1.278 / 1.280
14	1.280 / 1.281 / 1.278 / 1.279 / 1.280 / 1.280
21	1.275 / 1.276 / 1.276 / 1.276 / 1.277 / 1.277

a) Hydrolysis medium: 0.1 N NaOH / 80°C

Time [days]	Relative solution viscosity η_{rel}
0	1.284 / 1.289 (reference sample)
7	1.279 / 1.280 / 1.279 / 1.279 / 1.280 / 1.280
14	1.277 / 1.277 / 1.277 / 1.277 / 1.279 / 1.279
21	1.277 / 1.277 / 1.274 / 1.274 / 1.279 / 1.282

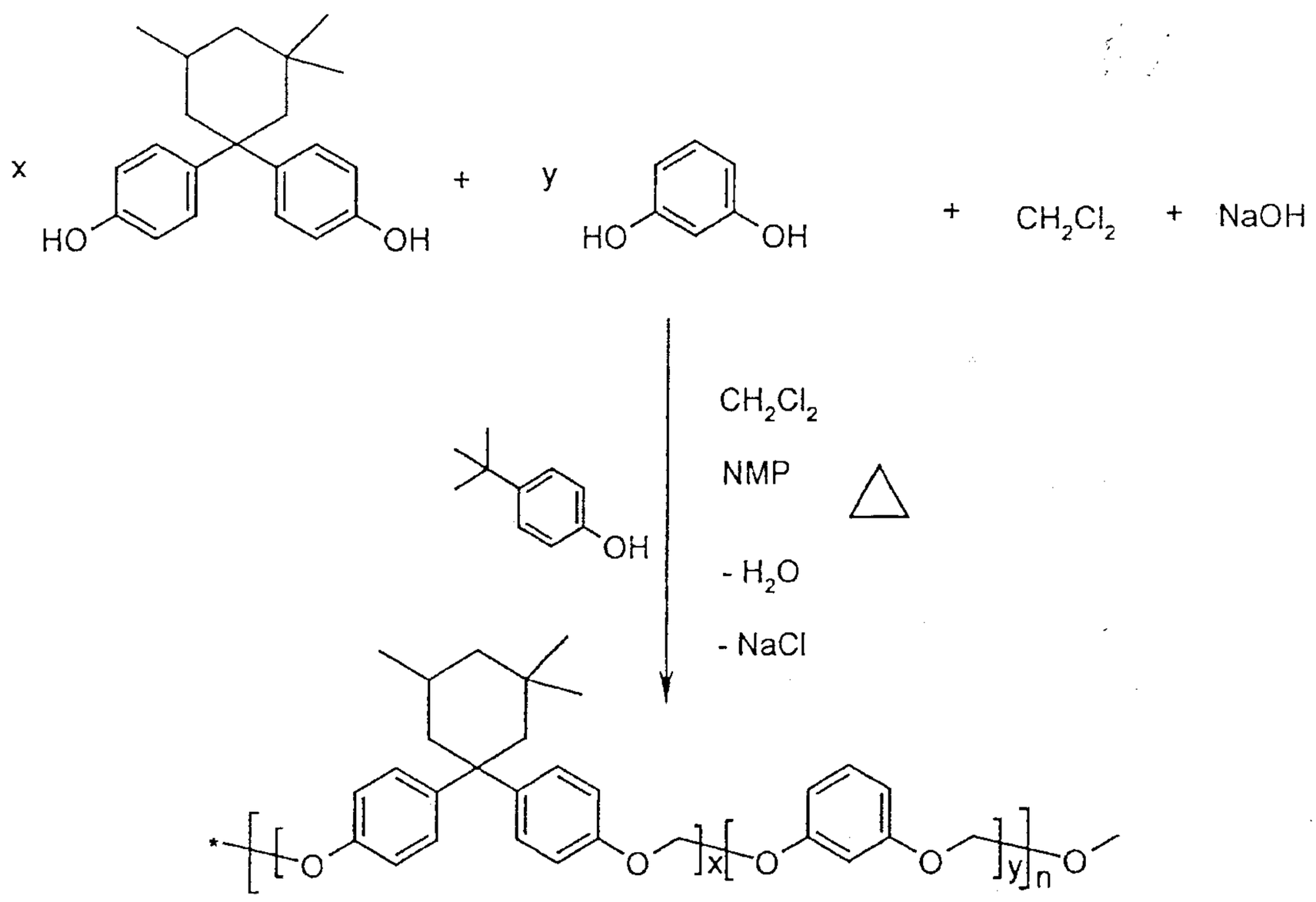
a) Hydrolysis medium: distilled water / approx. 100°C

Time [days]	Relative solution viscosity η_{rel}
0	1.284 / 1.289 (reference sample)
7	1.272
14	1.273
21	1.273

It can clearly be seen that after hydrolysis loading the solution viscosity of polycarbonate falls more sharply than is the case with polyformals. This means that polycarbonate can be degraded more readily, and is therefore less stable, than polyformal. A coextrusion layer made from polyformal thus acts as a protective layer against premature damage of the sheet or container.

Example 10

Synthesis of copolyformal from bisphenol TMC and resorcinol:



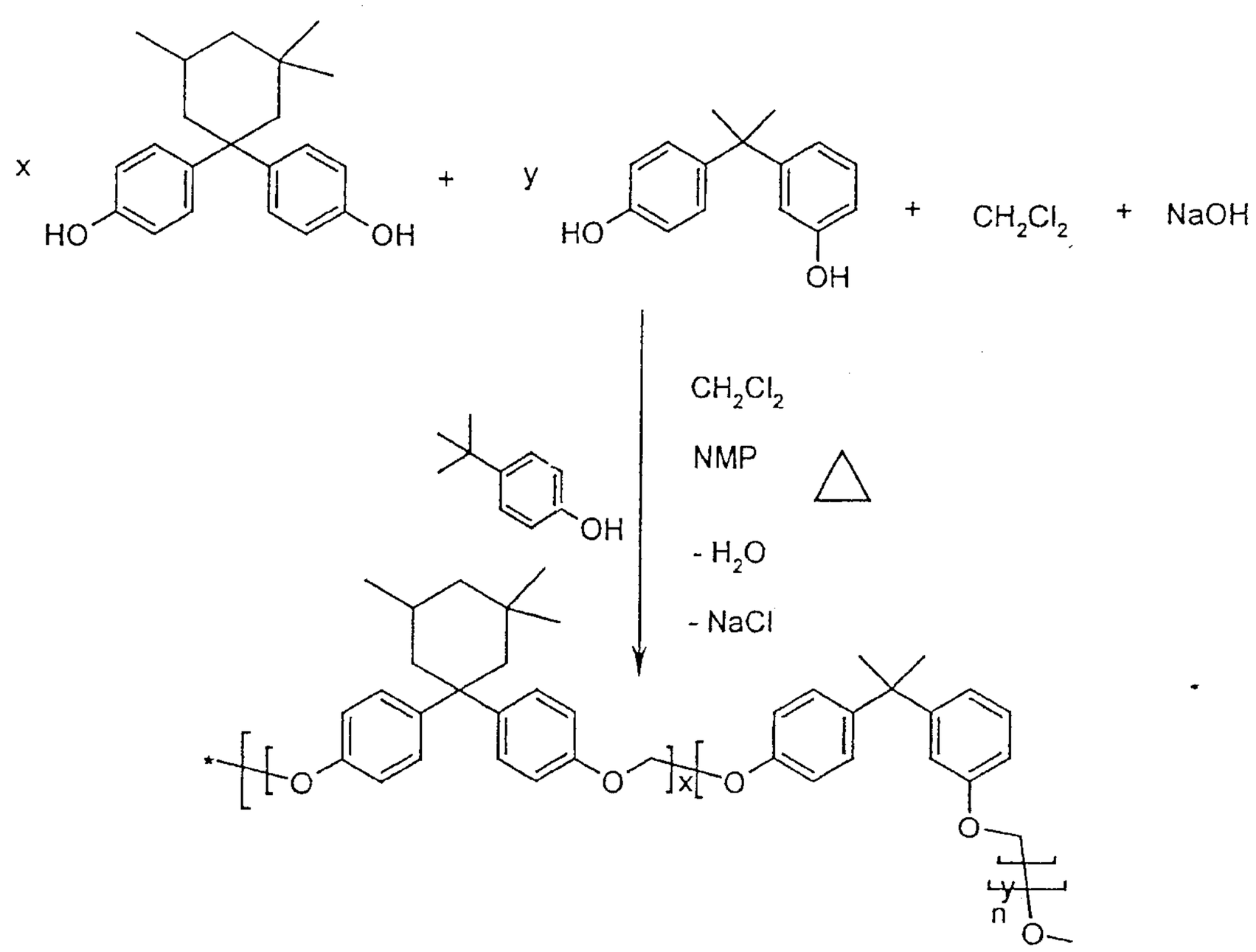
39.1 g (0.126 mol) of bisphenol TMC (x=90 mol%), 1.542 g (0.014 mol) of resorcinol (y=10 mol%), 14.0 g (0.35 mol) of sodium hydroxide pellets and 0.21 g (0.0014 mol) of finely ground p-tert-butyl phenol (Aldrich) are added to a solvent blend consisting of 125 ml of methylene chloride and 225 ml of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with methylene chloride and demineralised water and then washed with water until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase is separated off. The polymer is isolated by precipitation in methanol. After washing the product with water and methanol and separating off the cyclic compounds with acetone and drying at 80°C, polyformal is obtained as white polymer filaments.

Analysis:

- Molecular weight Mw = 32008, Mn = 12251, D = 2.6 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 163 °C

Example 11

Synthesis of copolyformal from bisphenol TMC and m,p-bisphenol A:



14.84 g (0.065 mol) of bisphenol TMC (x=50 mol%), 20.18 g (0.065 mol) of m,p-bisphenol A (3,4-isopropylidene diphenol) (y=50 mol%), 14.0 g (0.35 mol) of sodium hydroxide pellets and 0.21 g (0.0014 mol) of finely ground p-tert-butyl phenol (Aldrich) are added to a solvent blend consisting of 125 ml of methylene chloride and 225 ml of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred

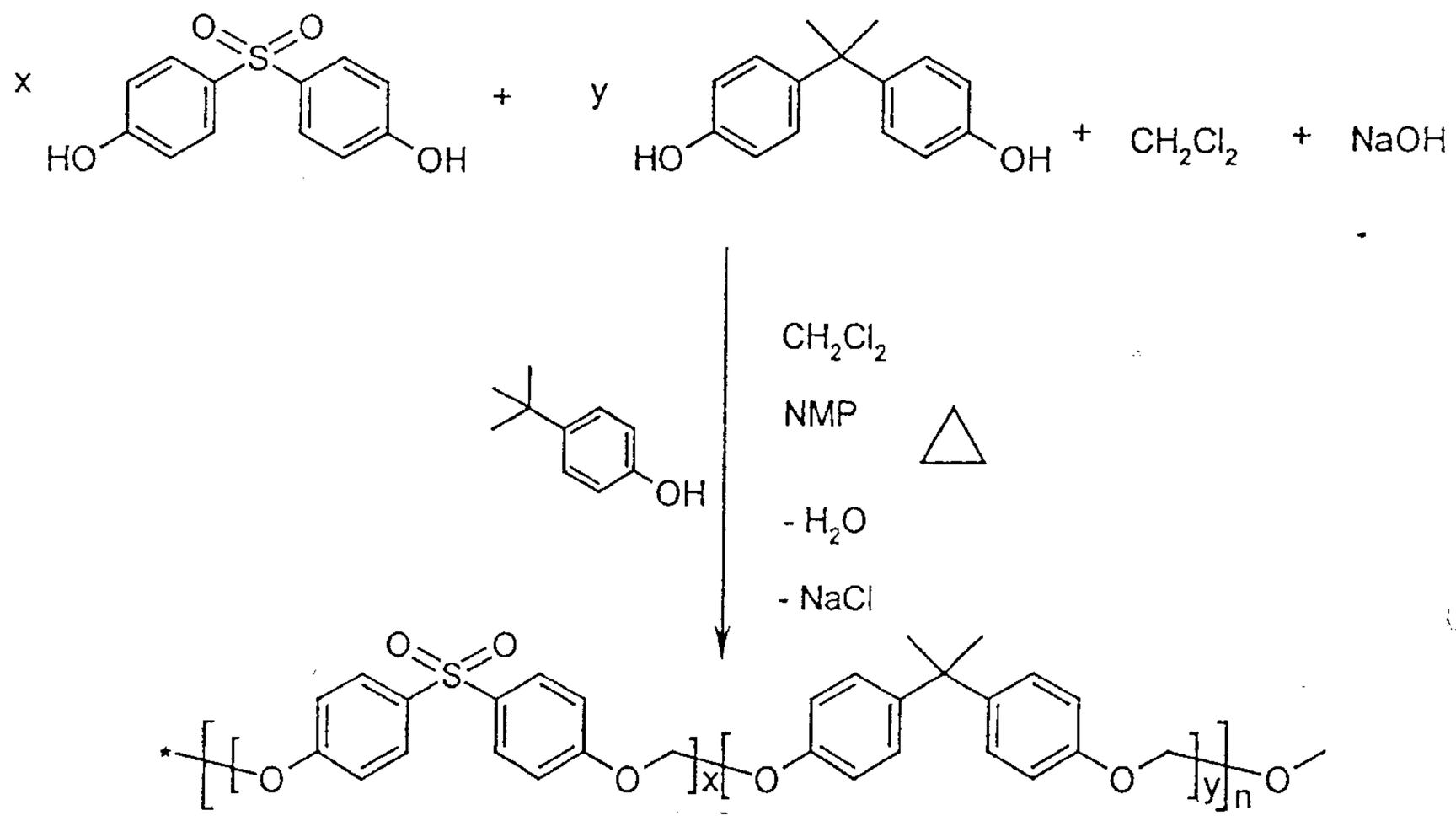
for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with methylene chloride and demineralised water and then washed with water until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase is separated off. The polymer is isolated by precipitation in methanol. After washing the product with water and methanol and separating off the cyclic compounds with acetone and drying at 80°C, polyformal is obtained as white polymer filaments.

Analysis:

- Molecular weight Mw = 28254, Mn = 16312, D = 1.73 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 92 °C

Example 12

Synthesis of copolyformal from bisphenol A and 4,4'-sulfone diphenol:



36.29 g (0.145 mol) of 4,4'-sulfone diphenol (x=50 mol%), 33.46 g (0.145 mol) of bisphenol A (y=50 mol%), 28.8 g (0.72 mol) of sodium hydroxide pellets and 0.436 g (0.0029 mol) of finely ground p-tert-butyl phenol (Aldrich) are added to a

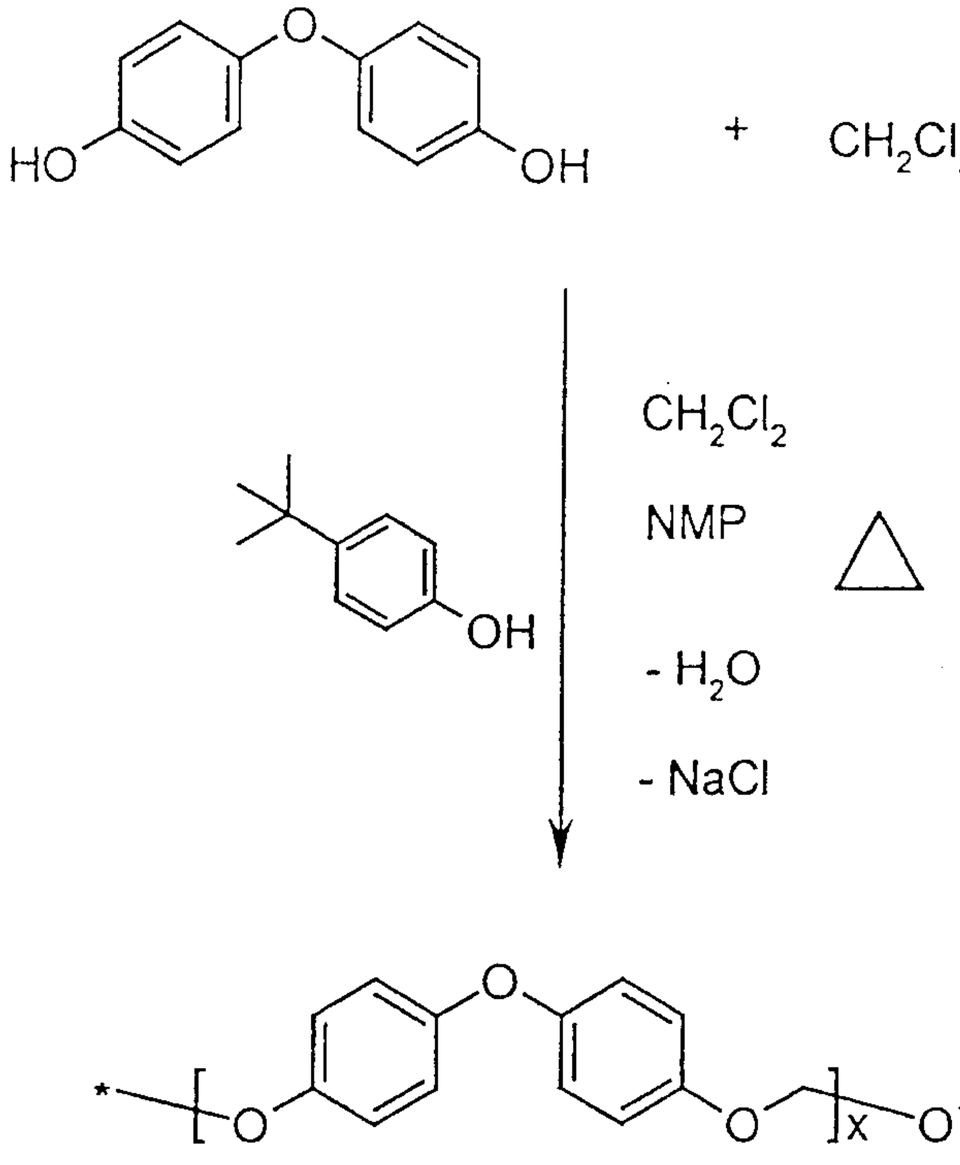
solvent blend consisting of 300 ml of methylene chloride and 570 ml of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with methylene chloride and demineralised water and then washed with water until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase is separated off. The polymer is isolated by precipitation in methanol. After washing the product with water and methanol and separating off the cyclic compounds with acetone and drying at 80°C, polyformal is obtained as white polymer filaments.

Analysis:

- Molecular weight Mw = 21546, Mn = 7786, D = 2.76 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 131°C

Example 13

Synthesis of polyformal from 4,4'-dihydroxyphenyl ether:



28.30 g (0.14 mol) of 4,4'-dihydroxyphenyl ether (Bayer AG), 14.0 g (0.35 mol) of sodium hydroxide pellets and 0.21 g (0.0014 mol) of finely ground p-tert-butyl phenol (Aldrich) are added to a solvent blend consisting of 125 ml of methylene chloride and 225 ml of N-methyl-2-pyrrolidone (NMP) under nitrogen protective gas with stirring. After homogenisation the mixture is refluxed (78°C) and stirred for one hour at this temperature. After cooling to 25°C the reaction batch is diluted with methylene chloride and demineralised water and then washed with water until it is neutral and free from salts (conductivity < 15 $\mu S.cm^{-1}$). The organic phase is separated off. The polymer is isolated by precipitation in methanol. After washing the product with water and methanol and separating off the cyclic compounds with acetone and drying at 80°C, polyformal is obtained as white polymer filaments.

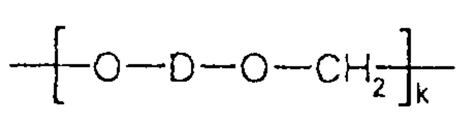
Analysis:

- Molecular weight Mw = 24034, Mn = 9769, D = 2.46 by GPC (calibration against polycarbonate).
- Glass transition temperature Tg = 57 °C

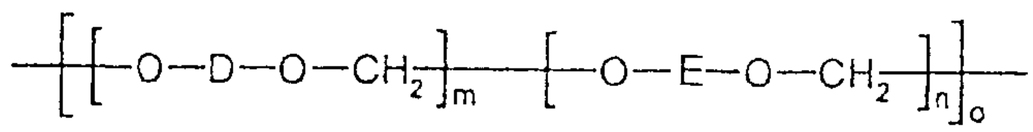
Claims

1. Use of at least one polyformal or copolyformal to produce a hydrolysis protection coating for containers.

2. Use according to claim 1, characterised in that the polyformals or copolyformals having the general formulae (1a) or (1b)



1a



1b

wherein the radicals O-D-O and O-E-O stand for any diphenolate radicals in which -D- and -E- are aromatic radicals having 6 to 40 C atoms, which can contain one or more aromatic or condensed aromatic nuclei, optionally containing heteroatoms, and are optionally substituted with C_1-C_{12} alkyl radicals or halogen and can contain aliphatic radicals, cycloaliphatic radicals, aromatic nuclei or heteroatoms as binding links and in which k stands for a whole number between 1 and 1500 and m stands for a fraction z/o and n for a fraction (o-z)/o, where z stands for numbers between 0 and o, and a part of the radicals -O-D-O- and -O-E-O- mutually independently also stands for a radical derived from one or more trifunctional compounds, as a result of which a third binding site, a branching of the polymer chain, occurs at this point.

3. Containers displaying a hydrolysis protection coating according to claim 1 or 2.

4. Water bottles, baby bottles and medical articles displaying a hydrolysis protection coating according to claim 1 or 2.

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