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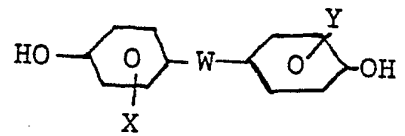
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(54) Title: POLYCARBONATE COMPOSITIONS HAVING IMPROVED BARRIER PROPERTIES

(57) Abstract

Polycarbonate compositions having improved barrier properties; i.e., low water vapor transmission and low gas permeability, are derived from monomers of the general formula



wherein X or Y or both are alkyl, and W is -S-, -O-, -SO<sub>2</sub>-, -SO- or a hydrocarbon radical such as alkylene, alkylidene and cycloalkylidene. They are especially useful for making food and beverage containers.

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DescriptionPolycarbonate Compositions Having Improved  
Barrier Properties

This invention relates to high molecular weight  
5 aromatic polycarbonate compositions having improved  
barrier properties; i.e., low water vapor transmission  
and low gas permeability.

Background Art

Polycarbonate polymers are known as being  
10 excellent molding materials since products made there-  
from exhibit such properties as high impact strength,  
toughness, high transparency, wide temperature limits  
(high impact resistance below -60°C and a UL thermal  
endurance rating of 115°C with impact), good  
15 dimensional stability, good creep resistance, and the  
like.

Dimethylated aromatic polycarbonates are known  
as disclosed in U.S. Patent 3,028,365. Tetra-  
methylated aromatic polycarbonates are also known and  
20 their high heat distortion properties have been  
recognized as disclosed in U.S. Patent 3,879,384.  
It would be desirable to add to this list of  
properties those of low water vapor transmission and  
low gas permeability to enable the aromatic poly-  
25 carbonates to be used to form containers and film  
wraps for foods, beverages, cosmetics, and the like.  
In particular, food and beverage containers made  
from aromatic polycarbonates having these added  
barrier properties would be more economical as they  
30 would be capable of reuse and would thus also help  
reduce the impact of environmental waste occasioned  
by broken glass and discarded, non-reuseable  
containers.



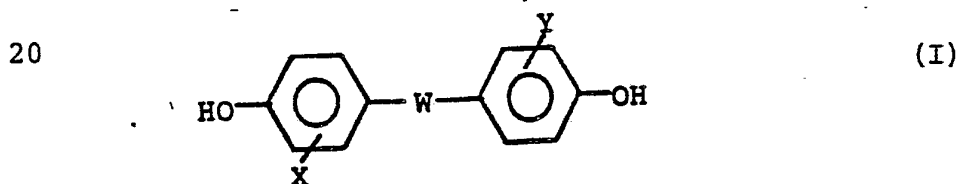
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Summary of the Invention

It has now been found that mono- and di-alkyl substituted, high molecular weight aromatic polycarbonates can be obtained that exhibit improved water vapor transmission and gas barrier properties, as compared to non-alkylated aromatic polycarbonates.

It has been further surprisingly found that mono- and dialkylated aromatic polycarbonates exhibit far superior barrier properties than either non-alkylated or tetramethylated aromatic polycarbonates.

The alkylated aromatic polycarbonates of this invention can be prepared by known techniques using appropriate monomers. The monomers that can be employed can be represented by the following general formula:



25

wherein X and Y can each independently be selected from the group consisting of hydrogen, an alkyl of C<sub>1</sub>-C<sub>10</sub>, and mixtures thereof with the proviso that at least either X or Y is a C<sub>1</sub>-C<sub>10</sub> alkyl; and, W is a member selected from the following group:

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(a)  $\text{---}(\text{CH}_2\text{---})_r$  wherein  $r$  is 0 or an integer from 2-10;

5 (b)  $\begin{array}{c} \text{R} \\ | \\ \text{---C---} \\ | \\ \text{H} \end{array}$  wherein  $R$  is a member selected from

the group consisting of  $\text{C}_1\text{---}\text{C}_{10}$  alkyl,  $\text{C}_5\text{---}\text{C}_{10}$  cycloalkyl and  $\text{C}_6\text{---}\text{C}_{14}$  aryl;

10 (c)  $\begin{array}{c} \text{R} \\ | \\ \text{---C---} \\ | \\ \text{R}' \end{array}$  wherein  $R$  and  $R'$  can each independently be the same as  $R$  in (b) above with the proviso that, when both  $R$  and  $R'$  are each  $\text{CH}_3$ ,  $X$  and  $Y$  are not both symmetrically substituting  $\text{CH}_3$ ;

15 (d)  $\begin{array}{c} \diagup \\ \text{C} \\ \diagdown \\ \text{(CH}_2\text{)}_m \end{array}$  wherein  $m$  is an integer of 4-20;

(e)  $\begin{array}{c} \text{Op} \\ || \\ \text{---S---} \\ || \\ \text{Oq} \end{array}$  wherein  $p$  and  $q$  can each independently

20 be an integer of 0-1; and,

(f)  $\text{---O---}$

25 Typical of some of the monomers that can be employed in this invention are bis(4-hydroxy-3-methylphenyl)methane, 1,6-bis(4-hydroxy-3-ethylphenyl)hexane, 2,2-(4-hydroxyphenyl)(4-hydroxy-3-methylphenyl)propane, 1,1-bis(4-hydroxy-3-methylphenyl)propane, 1,1-bis(4-hydroxy-3-methylphenyl)cyclohexane, bis(4-hydroxy-3-ethylphenyl)sulfone, bis(4-hydroxy-3-isopropylphenyl)ether and the like.

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Of course, it is possible to employ two or more different monomers or a copolymer with a glycol or with hydroxy or acid terminated polyester, or with a dibasic acid in the event a carbonate copolymer or interpolymer rather than a homopolymer is desired for use in preparing the aromatic polycarbonate. Blends of any of these materials can also be used to obtain the aromatic polycarbonates.

These high molecular weight aromatic polycarbonates can be linear or branched homopolymers or copolymers as well as mixtures thereof or polymeric blends and generally have an intrinsic viscosity (IV) of about 0.40-1.0 dl/g as measured in methylene chlororide at 25°C. These high molecular weight aromatic polycarbonates can be typically prepared by reacting a monomer with a carbonate precursor.

The carbonate precursor used can be either a carbonyl halide, a carbonate ester or a haloformate. The carbonyl halides can be carbonyl bromide, carbonyl chloride and mixtures thereof. The carbonate esters can be diphenyl carbonate, di-(halophenyl) carbonates such as di-(chlorophenyl) carbonate, di-(bromophenyl) carbonate, di-(trichlorophenyl) carbonate, di-(tribromophenyl) carbonate, etc., di-(alkylphenyl) carbonates such as di(tolyl) carbonate, etc., di-(naphthyl) carbonate, di-(chloronaphthyl) carbonate, phenyl tolyl carbonate, chlorophenyl chloronaphthyl carbonate, etc., or mixtures thereof. The haloformates that can be used include bis-haloformates of dihydric phenols (bischloroformates of hydroquinone, etc.) or glycols (bishaloformates of ethylene glycol,

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neopentyl glycol, polyethylene glycol, etc.) as well as haloformates of the monomers described above in formula I. While other carbonate precursors will occur to those skilled in the art, carbonyl chloride, 5 also known as phosgene, is preferred.

Also included are the polymeric derivatives of a dihydric phenol, a dicarboxylic acid and carbonic acid such as are disclosed in U.S. Patent 3,169,121 which is incorporated herein by reference.

10 Molecular weight regulators, acid acceptors and catalysts can also be used in obtaining the aromatic polycarbonates of this invention. The useful molecular weight regulators include monohydric phenols such as phenol, chroman-I, paratertiarybutyl-phenol, 15 parabromophenol, primary and secondary amines, etc. Preferably, phenol is employed as the molecular weight regulator.

A suitable acid acceptor can be either an organic or an inorganic acid acceptor. A suitable 20 organic acid acceptor is a tertiary amine such as pyridine, triethylamine, dimethylaniline, tributylamine, etc. The inorganic acid acceptor can be either a hydroxide, a carbonate, a bicarbonate, or a phosphate of an alkali or alkaline earth metal.

25 The catalysts which can be employed are those that typically aid the polymerization of the monomers with phosgene. Suitable catalysts include tertiary amines such as triethylamine, tripropylamine,



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N,N-dimethylaniline, quaternary ammonium compounds such as, for example, tetraethylammonium bromide, cetyl triethyl ammonium bromide, tetra-n-heptylammonium iodide, tetra-n-propyl ammonium bromide, 5 tetramethylammonium chloride, tetramethyl ammonium hydroxide, tetra-n-butyl ammonium iodide, benzyltrimethyl ammonium chloride and quaternary phosphonium compounds such as, for example, n-butyltriphenyl phosphonium bromide and methyltriphenyl phosphonium 10 bromide.

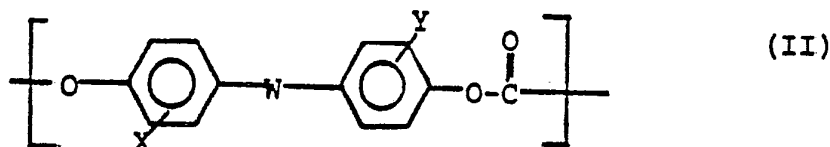
Also included herein are branched polycarbonates wherein a polyfunctional aromatic compound is reacted with the monomer and carbonate precursor to provide a thermoplastic randomly branched polycarbonate. 15 These polyfunctional aromatic compounds contain at least three functional groups which are carboxyl, carboxylic anhydride, haloformyl, or mixtures thereof. Illustrative polyfunctional aromatic compounds which can be employed include trimellitic 20 anhydride, trimellitic acid, trimellityl trichloride, 4-chloroformyl phthalic anhydride, pyromellitic acid, pyromellitic dianhydride, mellitic acid, mellitic anhydride, trimesic acid, benzophenonetetracarboxylic acid, benzophenonetetracarboxylic anhydride, and the 25 like. The preferred polyfunctional aromatic compounds are trimellitic anhydride and trimellitic acid or their acid halide derivatives.



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Accordingly, the mono- and di-alkylated, high molecular weight aromatic polycarbonates of the invention can be represented by the following general formula:

5



10

wherein X, Y and W are the same as in formula I above.

#### Preferred Embodiment of the Invention

The following examples are set forth to more fully and clearly illustrate the present invention and are intended to be, and should be construed as being, exemplary and not limitative of the invention. Unless otherwise stated, all parts and percentages are by weight.

20 The barrier properties for each of the ensuing examples were determined using Modern Controls, Inc. instruments. Water vapor transmission rate (WVTR) measurements were obtained on an IRD-2C instrument pursuant to ASTM F-372-73; carbon dioxide data  
25 (CO<sub>2</sub>TR) were obtained using a Permatran-C instrument; and, oxygen transmission rates (O<sub>2</sub>TR) were determined using an OX-TRAN 100 instrument. The methods used to obtain WVTR and CO<sub>2</sub>TR data are based on infrared analysis whereas the O<sub>2</sub>TR  
30 measurements are based on a coulometric method. The WVTR measurements are expressed in grams/24 hrs./100 in.<sup>2</sup>/mil at 100°F and 90% relative humidity (RH) whereas those of CO<sub>2</sub>TR and O<sub>2</sub>TR are expressed in cc/24 hrs./100 in.<sup>2</sup>/mil/atmosphere.

BUR  
O/  
W.

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Preparation of 4,4'-cyclohexylidenedi-o-cresol (CDC)

To a 22 l. three-necked flask, equipped with stirrer, subsurface gas inlet tube, thermometer and reflux condenser was charged 2180 g (22.2 moles) of cyclohexanone and 12000 g (111 moles) of o-cresol and to the resulting solution was introduced subsurface HCl gas with good stirring. A mildly exothermic reaction ensued; by external cooling, the temperature was not allowed to exceed 55°-60°C.

10 The introduction of HCl was continued until blow-through was observed, when it was stopped. The progress of the reaction was followed by ir (infrared spectroscopy), which indicated that in ca. 1.5-2 hrs. all of the cyclohexanone was consumed, by the

15 disappearance of the carbonyl band at 1710  $\text{cm}^{-1}$ . Crystals started to come out of the warm solution in an additional 1-2 hours, which was facilitated and completed by cooling and stirring.

After the separation of crystals was complete,

20 the reaction mixture was filtered and the filter cake was rinsed on the funnel with methylene chloride. The crystals were then slurried up in methylene chloride, filtered and the cake rinsed again. The crude crystals weighed 4285 g on 76.8% of theory. The cresolic mother

25 liquor typically contained 270 g of the p,p'-product whereas the methylene chloride mother liquors contained an additional 119 g of product, bringing the total conversion of the p,p'-isomer to 83%.

Recrystallization of the 4285 g of crude filter-

30 cake, which had an assay of 98.5% and a mp. of 184-7°C, by dissolution in 9.5 l. or refluxing methanol and subsequent addition of 2.8 l. of water, followed

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by cooling, deposited colorless crystals that, after filtration and airdrying, weighed 3515 g (82% of the crude), and had an assay of 99.8-99.9%, mp. 188-189°C.

5

Example 1

Into a mixture of 74.1 parts of pure 4,4'-cyclohexylidenedi-o-cresol (CDC) (mp 188-189°C; 0.25 parts mole), 300 parts water, 300 parts methylene chloride, 0.47 parts phenol and 0.5 parts triethyl-  
10 amine were introduced, at ambient temperature, 30 parts phosgene over a period of 30 minutes while maintaining the pH of the two-phase system at about 11; i.e., pH 10-12.5, by simultaneously adding a 25% aqueous sodium hydroxide solution. At the end of  
15 the addition period, the pH of the aqueous phase was 11.7 and the CDC content of this phase was less than 1 part per million (ppm) as determined by ultra-violet analysis.

The methylene chloride phase was separated  
20 from the aqueous phase, washed with an excess of dilute (0.01N) aqueous HCl and then washed three times with deionized water. The polymer was precipitated by adding the neutral and salt-free methylene chloride solutions to an excess of  
25 methanol and filtering off the white polymer which was dried at 95°C. The resultant, pure CDC-poly-carbonate had an intrinsic viscosity (IV) in methylene chloride at 25°C of 0.554 dl/g. Its barrier properties are set forth in the Table  
30 following the Examples.

The intrinsic viscosity values mentioned hereinafter were also measured in methylene chloride at 25°C.



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Control Example 1

The procedure of Example 1 was repeated, except that 4,4'-isopropylidenediphenol, (BPA), was substituted, in equivalent amounts, for CDC. The pure BPA-polycarbonate had an IV of 0.560 dl/g. Its barrier properties are listed in the Table.

Control Example 2

Following the procedure of Example 3 of the above-mentioned U.S. Patent 3,879,384, a tetramethylated polycarbonate was prepared from 2,2-bis(3,5-dimethyl-4-hydroxyphenyl) propane. Its barrier properties are listed in the Table.

Example 2

The procedure of Example 1 was repeated, except that an equivalent amount of a 75 weight % C D C/25 weight % BPA mixture was used in place of only CDC. A copolycarbonate was obtained having an IV of 0.55 dl/g and that yielded colorless, transparent moldings or film. Its barrier properties are listed in the Table.

Example 3

The procedure of Example 1 was repeated, except that an equivalent amount of a 55 weight % C D C/45 weight % BPA mixture was used in place of CDC. The resultant copolycarbonate, which yielded tough, transparent test objects and films, had an IV of 0.54 dl/g. Its barrier properties are listed in the Table.

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Preparation of 4,4'-cyclohexylidenediphenol (CDP)

The above-described procedure for the preparation of CDC was repeated, except that 10500 g (111.6 moles) of phenol was substituted for o-cresol. The crude crystals that separated out were rinsed with methylene chloride; after airdrying they weighed 5170 g or 87% of theoretical. Recrystallization from methanol-water yielded pure CDP, mp 188-189°C, that was 99.8% pure by gas chromatography.

<sup>10</sup>Preparation of 4,4'-(1-methylethylidene)bis-o-cresol (MEC)

The above-described procedure for the preparation of CDC was repeated except that 645 g (11.1 moles) of acetone was substituted for the cyclohexanone and heat was applied during the introduction of HCl to maintain the reaction temperature between 50°-70°C. The progress of the reaction was conveniently monitored by gas chromatography, which indicated that most of the 2,2'- and 2,4'-isomers formed at the beginning of the reaction rearranged to the 4,4'-isomer. When the concentration of this latter in the product had increased from an initial 63% to 93% (with only 7% of the 2,4'-isomer and no detectable amount of the 2,2'-isomer being present), the hydrochloric acid catalyst and the excess of o-cresol were removed by heating and distillation under water aspirator vacuum. The distillation residue, after recrystallization from chlorobenzene, yielded 2333 g (9.1 mole) or 82% of MEC, mp 135-7°C, that was 98.5% pure by gas chromatography.



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Preparation of 4,4'-(1-methylpropylidene)bis-o-Cresol (MPC)

The above-described procedure for the preparation of CDC was repeated, except that 800 g (11.1 moles) of 2-butanone was substituted for acetone and the reaction temperature was kept at or below 50°C. Purification was effected by extracting the solid distillation residue twice with methylene chloride, which left behind the 4,4'-isomer as white crystals, mp 144° - 146°C, 99.1% purity and 1840 g or 61.3% yield. This monomer, MPC, is believed to be novel.

Preparation of 4,4'-(1-ethylpropylidene)bis-o-cresol (EPC)

The above-described procedure for the preparation of CEC, was repeated, except that 956 g (11.1 moles) of 3-pentanone was substituted for acetone. EPC was obtained in 99.2% purity, after recrystallization from cyclohexane, with a melting point of 119° - 120°C. This monomer, EPC, is a dimethylated bisphenol-A (dimethyl BPA) and is believed to be novel.

Preparation of 2-methyl-4,4'-(1-methylethylidene)bisphenol (MMEP)

Anhydrous HCl was introduced, with adequate cooling, into a mixture of 134 g (1.0 mole) of freshly prepared 4-isopropenyl phenol (made by thermally cracking BPA in the presence of catalytic amounts of sodium hydroxide and separating it from the co-product phenol by fractional vacuum distillation) and 540 g (5.0 moles) of o-cresol, while

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maintaining the temperature of the ensuing exothermic reaction below 50°C. After 4 hours, the red colored reaction mixture was stripped of HCl and excess cresol under water aspirator vacuum and the resultant straw colored melt was purified by recrystallization from cyclohexane. The 98.7% pure MMEP had a melting point of 112°-113°C. This monomer, MMEP, is a monomethyl bisphenol-A.

Example 4 - 6

10 The preparation of polycarbonates by the procedure of Example 1 was repeated by substituting equivalent amounts of the following diphenols for CDC:

15 Example 4: MEC (4,4'-(1-methylethylidene)bis-o-cresol)

Example 5: MPC (4,4'-(1-methylpropylidene)bis-o-cresol)

Example 6: EPC (4,4'-(1-ethylpropylidene)bis-o-cresol)

20 The barrier properties of the resultant polycarbonates are listed in the Table.

Examples 7 - 10

The preparation of copolycarbonates with BPA by the procedure of Example 3 was repeated by substituting equivalent amounts of the following diphenols for CDC:

Reference Example CDP (4,4'-cyclohexylidene-diphenol)

30 Example 7: MEC (4,4'-(1-methylethylidene)bis-o-cresol)

Example 8: MPC (4,4'-(1-methylpropylidene)bis-o-cresol)



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Example 9: EPC (4,4'-1-ethylpropylidene)bis-o-cresol)

Example 10: MMEP (2-methyl-4,4'-(1-methyl-ethylidene bisphenol)

5       The barrier properties of the resultant copoly-carbonates are listed in the Table wherein the Reference Example, the BPA-polycarbonate, is used as the comparative standard.

10       Some of the test specimens from which the barrier properties were obtained were made by extruding the polycarbonates and copolycarbonates in an extruder operated at about 265°C and, comminuting the extrudate into pellets. Thereafter, the pellets were compression molded into films having an average  
15       thickness of 10 mils. Other test specimens were obtained by film casting the polycarbonates and copolycarbonates directly from a methylene chloride solution to provide film specimens also having an average thickness of about 10 mils.



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TABLEBarrier Properties of Polycarbonates and Copoly-  
carbonates

Example	IV, dl/g	WVTR	CO <sub>2</sub> TR	O <sub>2</sub> TR	
5					
1	0.554	0.7	20.4	10.2	
control 1	0.560	10.0	875	200	
control 2	-	8.3	-	-	
2	0.550	1.6	148	34	
10	3	0.540	2.7	-	56
4	0.548	2.7	-	33	
5	0.526	2.0	-	34	
6	0.555	1.4	-	28	
Reference	0.547	6.2	-	110	
15	7	0.542	4.8	-	122
8	0.552	5.5	-	140	
9	0.538	5.2	-	132	
10	0.544	5.6	-	-	

20 A comparison of the measured values of the water vapor transmission rates for the polycarbonate derived from bisphenol-A (control Example 1) and tetramethylated BPA (Control Example 2) with the values measured for the polycarbonates derived

25 from the monomethylated (Example 10) and dimethylated (Example 5) homologs of bisphenol-A, shows that the mono- and di-methylated polycarbonates have surprisingly superior barrier properties, as is dramatically illustrated in the following list.



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<u>Monomer</u>	<u>WVTR</u>	<u>% decrease *</u>
BPA	10	0
monomethyl BPA	5.6	44
dimethyl BPA	2.0	80
tetramethyl BPA	8.3	17

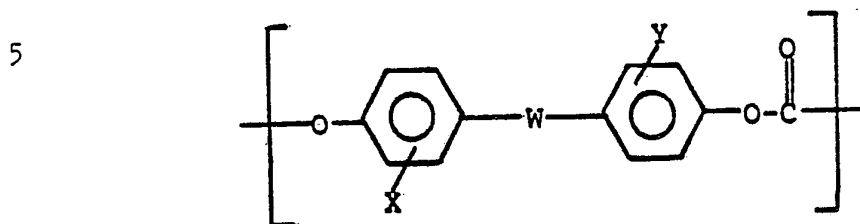
\* with respect to BPA polycarbonate



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Claims

1. A high molecular weight aromatic polycarbonate composed of repeating units of the following general formula:



10 wherein X and Y are each independently selected from hydrogen, an alkyl of C<sub>1</sub>-C<sub>10</sub> and mixtures thereof, with the proviso that at least either X or Y is a C<sub>1</sub>-C<sub>10</sub> alkyl; and, W is selected from the following group:

15 (a)  $\left( \text{---CH}_2 \right)_R$  wherein R is 0 or an integer from

2-10;

(b)  $\begin{array}{c} \text{R} \\ | \\ \text{---C---} \\ | \\ \text{H} \end{array}$  wherein R is C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>5</sub>-C<sub>10</sub>

cycloalkyl or C<sub>6</sub>-C<sub>14</sub> aryl;

20 (c)  $\begin{array}{c} \text{R} \\ | \\ \text{---C---} \\ | \\ \text{R}' \end{array}$  wherein R and R' are the same as R in

(b) above with the proviso that when both R and R' are each CH<sub>3</sub>, X and Y are not both

25 symmetrically substituting CH<sub>3</sub>;

(d)  $\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{(CH}_2\text{)}_m \end{array}$  wherein m is an integer of 4-20;

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(e)  $\frac{Op}{-s-}$  wherein p and q can each be an integer

of 0-1; and,

(f) -0-.



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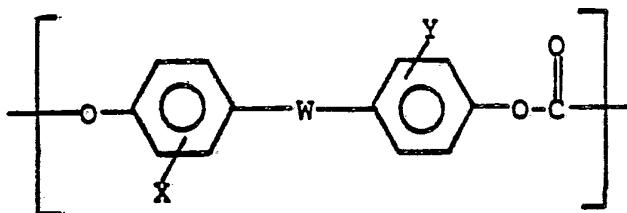
2. The polycarbonate of claim 1 wherein X and Y are each a C<sub>1</sub>-C<sub>10</sub> alkyl.
3. The polycarbonate of claim 1 wherein X is a C<sub>1</sub>-C<sub>10</sub> alkyl and Y is hydrogen.
4. The polycarbonate of claim 1 wherein W is cyclohexylidene, 1-methyl-propylidene, 1-ethyl-propylidene or 1-methyl-ethylidene, and X and Y are both methyl groups ortho to the respective oxygens.
5. The polycarbonate of claim 1, further comprising units in which X and Y are both hydrogen.
6. The monomer, 4,4'-(1-methylpropylidene)bis-o-cresol.
7. The monomer, 4,4'-(1-ethylpropylidene)bis-o-cresol.



## AMENDED CLAIMS

(received by the International Bureau on 3 December 1979 (03.12.79))

1. A halogen-free high molecular weight aromatic polycarbonate having an intrinsic viscosity of about 0.40-1.0 dl/g in methylene chloride at 25°C and composed of repeating units of the following general formula:



wherein X and Y are each independently selected from hydrogen, an alkyl of C<sub>1</sub>-C<sub>10</sub>, and mixtures thereof, with the proviso that at least either X or Y is a C<sub>1</sub>-C<sub>10</sub> alkyl; and, W is selected from the following group:

(a)  $\left( \text{CH}_2 \right)_R$  wherein R is 0 or an integer from 2-10;

(b)  $\begin{array}{c} \text{R} \\ | \\ -\text{C}- \\ | \\ \text{H} \end{array}$  wherein R is C<sub>1</sub>-C<sub>10</sub> alkyl, C<sub>5</sub>-C<sub>10</sub> cycloalkyl or C<sub>6</sub>-C<sub>14</sub> aryl;

(c)  $\begin{array}{c} \text{R} \\ | \\ -\text{C}- \\ | \\ \text{R}' \end{array}$  wherein R and R' are the same as R in

(b) above with the proviso that when both R and R' are each CH<sub>3</sub>, X and Y are not both symmetrically substituting CH<sub>3</sub>;

(d)  $\begin{array}{c} \text{C} \\ / \quad \backslash \\ \text{---} \quad \text{---} \\ \text{(CH}_2\text{)}_m \end{array}$  wherein m is an integer of 4-20;

(e)  $\begin{matrix} Op \\ | \\ -S- \\ | \\ Oq \end{matrix}$  wherein p and q can each be an integer  
of 0-1; and,  
(f) -O-.




2. The polycarbonate of claim 1 wherein X and Y are each a C<sub>1</sub>-C<sub>10</sub> alkyl.
3. The polycarbonate of claim 1 wherein X is a C<sub>1</sub>-C<sub>10</sub> alkyl and Y is hydrogen.
4. The polycarbonate of claim 1 wherein W is cyclohexylidene, 1-methyl-propylidene, 1-ethyl-propylidene or 1-methyl-ethylidene, and X and Y are both methyl groups ortho to the respective oxygens.
5. The polycarbonate of claim 1, further comprising units in which X and Y are both hydrogen.
6. The monomer, 4,4'-(1-methylpropylidene)bis-o-cresol.
7. The monomer, 4,4'-(1-ethylpropylidene)bis-o-cresol.



# INTERNATIONAL SEARCH REPORT

WO 80/00348

International Application No PCT/US79/00547

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>3</sup>				
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL: Co8G 63/62; C07C 37/20; C07C 39/06 US CL. 568/727, 568/171				
<b>II. FIELDS SEARCHED</b>				
Minimum Documentation Searched <sup>4</sup>				
Classification System	Classification Symbols			
U.S.	260/463 528/171 528/196 528/219 568/722			
	568/723 568/727 568/728			
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched <sup>5</sup>				
CHEMICAL ABSTRACTS - FORMULAE: C <sub>18</sub> H <sub>22</sub> O <sub>2</sub> , C <sub>20</sub> H <sub>27</sub> O <sub>2</sub> , 4,4'-(1 methylpropylidene) bis-o-cresol- to date.				
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> <sup>14</sup>				
Category <sup>*</sup>	Citation of Document, <sup>16</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>18</sup>		
X	U S, A 3,367,980 PUBLISHED 06 FEBRUARY 1968, col. 11, line 47; example 3, Zaweski	6, 7		
X	U S, A 2,936,272 PUBLISHED 10 MAY 1960, col. 2, lines 43-67. BENDER ET AL.	6, 7		
X	U S, A 3,422,065 PUBLISHED 14 JANUARY 1969 col. 2, lines 1-35, WULFF ET AL.	1-5		
X	U S, A 3,398,120 PUBLISHED 20 AUGUST 1968 col. 2, lines 1-22, HINDERSINN ET AL.	1-6		
X	A CHEMICAL ABSTRACTS, VOLUME 64, NO. 4 ISSUED 14 FEBRUARY 1966, ABST. NO. 6832d, SANDLER ET AL.	6		
<p><sup>*</sup> Special categories of cited documents: <sup>15</sup></p> <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> </td> <td style="width: 50%; border: none;"> <p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p> </td> </tr> </table>			<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>
<p>"A" document defining the general state of the art</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document cited for special reason other than those referred to in the other categories</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p>	<p>"P" document published prior to the international filing date but on or after the priority date claimed</p> <p>"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance</p>			
<b>IV. CERTIFICATION</b>				
Date of the Actual Completion of the International Search <sup>2</sup>	Date of Mailing of this International Search Report <sup>2</sup>			
2 NOVEMBER 1979	14 NOV 1979			
International Searching Authority <sup>1</sup>	Signature of Authorized Officer <sup>20</sup>			
ISA/U.S.	 THEODORE PERTILLA			

## FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V.  OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE <sup>10</sup>

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.  Claim numbers \_\_\_\_\_, because they relate to subject matter <sup>12</sup> not required to be searched by this Authority, namely:

2.  Claim numbers \_\_\_\_\_, because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out <sup>13</sup>, specifically:

VI.  OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING <sup>11</sup>

This International Searching Authority found multiple inventions in this international application as follows:

I. CLAIMS 1-5, DRAWN TO POLYCARBONATES.

II. CLAIMS 6; 7, DRAWN TO CRESOL MONOMERS.

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

## Remark on Protest

The additional search fees were accompanied by applicant's protest.

No protest accompanied the payment of additional search fees.