Polycarbonates
Recent Developments
1970

Keith Johnson

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Thirty-Five Dollars

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FOREWORD

The detailed, descriptive information in this book is based on U.S. Patents relating to the production of polycarbonates. Only recent developments are included, based on U.S. patent technology from January 1967.

This book serves a double purpose in that it supplies detailed technical information and can be used as a guide to the U.S. Patent literature in this field. By indicating only information that is significant, this book then becomes an advanced review of polycarbonate technology.

The U.S. Patent literature is the largest and most comprehensive collection of technical information in the world. There is more practical, commercial timely process information assembled here than is available from any other source. The technical information obtained from a patent is extremely reliable and comprehensive; sufficient information must be included to avoid rejection for "insufficient disclosure".

The patent literature covers a substantial amount of information not available in the journal literature. The patent literature is a prime source of basic commercially utilizable information. This information is overlooked by those who rely primarily on the periodical journal literature. It is realized that there is a lag between a patent application on a new process development and the granting of a patent, but it is felt that this may roughly parallel or even anticipate the lag in putting that development into commercial practice.

Many of these patents are being utilized commercially. Whether used or not, they offer opportunities for technological transfer. Also, a major purpose of this book is to describe the number of technical possibilities available, which may open up profitable areas of research and development.

These publications are bound in paper in order to close the time gap between "manuscript" and "completed book". Industrial technology is progressing so rapidly that hard cover books do not always reflect the latest developments in a particular field, due to the longer time required to produce a hard cover book.

The Table of Contents is organized in such a way as to serve as a subject index. Other indexes by company, inventor, and patent number help in providing easily obtainable information.

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I. AROMATIC POLYCARBONATES

SYNTHESIS AND POLYMERIZATION OF INTERMEDIATES

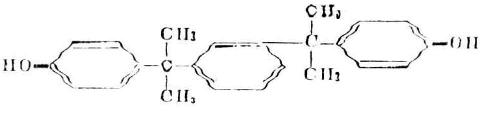
BISPHENOL DERIVATIVES

Bis(p-Hydroxycumyl)Benzene

G.F. Broderick, B.C. Oxenrider and J. Vitrone (U.S. Patent 3,393,244; July 16, 1968; assigned to Allied Chemical Corporation) describe a process for the production in high yield of 1,4-bis(p-hydroxycumyl)benzene and 1,3-bis(p-hydroxycumyl)benzene.

1,4-bis(p-hydroxycumyl)benzene, a white crystalline solid having a MP of about 190° to 192°C., has the following structural formula:

1,3-bis(p-hydroxycumyl)benzene, a white crystalline solid having a MP of about 138° to 140°C., possesses the following structural formula:

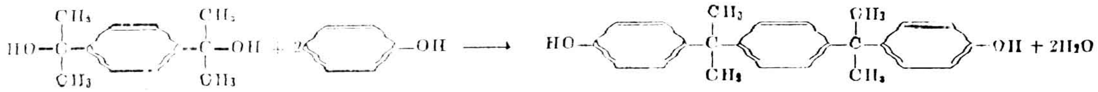


When p-diisopropylbenzene-α,α'-diol (referred to as the dicarbinol of 1,4-diisopropyl benzene) or m-diisopropylbenzene-α,α'-diol (referred to as the dicarbinol of 1,3-diisopropyl benzene) is reacted with phenol in the presence of sulfuric acid as catalyst, even at elevated temperatures of 70° to 130°C., little or no yield of 1,4-bis(p-hydroxycumyl)-benzene or 1,3-bis(p-hydroxycumyl)benzene is obtained.

It has been found that 1,4-bis(p-hydroxycumyl)benzene or 1,3-bis(p-hydroxycumyl)benzene may be prepared in high yield by reacting the dicarbinol of 1,4-diisopropyl benzene or the dicarbinol of 1,3-diisopropyl benzene with at least a stoichiometric amount of phenol at a temperature of about 40° to 100°C. in the presence of anhydrous hydrogen chloride as catalyst. The resulting reactions are represented by the equations on the following page.

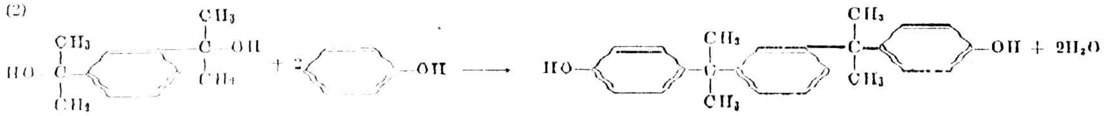
Synthesis and Polymerization of Intermediates

(1)



1,4-bis(p-hydroxycumyl)benzene

(2)



1,3-bis(p-hydroxycumyl)benzene

Although the reaction may be carried out using the stoichiometric quantities of the dicarbinol of the diisopropyl benzene and phenol, it has been discovered that greated efficiency and higher yield of product are obtained when about 8 to 13 mols of phenol per mol of the dicarbinol of diisopropyl benzene are employed.

The amount of anhydrous hydrogen chloride catalyst employed is not critical and is conveniently introduced by saturating the phenol with gaseous hydrogen chloride. The reaction may be carried out at a temperature within the range of 40° to 100°C. However, particularly outstanding results are obtained when the reaction temperature is maintained within the range of about 40° to 70°C.

The desired product may be recovered from the reaction mass by any convenient means. For example, the reaction mass may be slurried with hot water and the 1,4-bis(p-hydroxycumyl)benzene or 1,3-bis(p-hydroxycumyl)benzene filtered off.

In preferred operation, phenol heated to the desired temperature is saturated with gaseous hydrogen chloride. The dicarbinol of 1,4-diisopropyl benzene or 1,3-diisopropyl benzene is then added gradually, for example, over a period of about 1/2 to 2 1/2 hours, until the desired mol ratio is realized. This preferred procedure possesses the advantage of securing maximum mol ratio of phenol to the dicarbinol of diisopropyl benzene in the initial step of the reaction. Further, since the reaction is exothermic in nature, the use of heat dissipating equipment is minimized or avoided.

When 1,4-bis(p-hydroxycumyl)benzene and 1,3-bis(p-hydroxycumyl)benzene are produced by the process, high yields of product are obtained. For example, in the production of 1,4-bis(p-hydroxycumyl)benzene, the resulting yields are in the order of at least 90% of theory.

1,4-bis(p-hydroxycumyl)benzene and 1,3-bis(p-hydroxycumyl)benzene are of particular utility in the production of polycarbonate resins. A polycarbonate resin may be prepared, for example, by reacting 1,4-bis(p-hydroxycumyl)benzene or 1,3-bis(p-hydroxycumyl)benzene with phosgene in an emulsion system containing aqueous caustic and a nonpolar solvent such as ethylene chloride. The resulting resin has been found to have an unusually high glass transition temperature; for example, 154°C. in the case of 1,4-bis(p-hydroxycumyl)-benzene. Due to such high glass transition temperature, the polycarbonate possesses a high dimensional stability and, thus, is suitable for the preparation of molded articles which are capable of retaining their shapes at elevated temperatures up to the glass transition temperature. The resulting resin has also been found to form a film having outstanding tensile properties.

Example 1: 1,100 parts of phenol were heated to a temperature of 50° to 60°C. in a vessel provided with a stirrer. The phenol was then saturated with gaseous hydrogen chloride. 194 parts of the dicarbinol of 1,4-diisopropyl benzene were then added to the reaction mass over a one hour period. The reaction mass was maintained at a temperature of 50° to 60°C. for an additional period of 2 1/2 hours. The resulting product was slurried with about 10 times its weight of hot water and filtered off. The product was then purified by recrystallization twice from acetone to give 313 parts of a white crystalline solid having a MP of 190° to 192°C., identified as 1,4-bis(p-hydroxycumyl)benzene. This amount of product corresponded to a yield of 90% of theory based upon the dicarbinol charged.

Elemental analysis of the product gave 7.36% hydrogen and 83.3% carbon (theory — 7.52% hydrogen and 83.3% carbon). Analysis for the hydroxyl group gave 9.85% against theory of 9.82% for 1,4-bis(p-hydroxycumyl)benzene. The infrared spectrum of the product showed the characteristic bonds for the hydroxyl group, the aromatic nuclei and the methyl groups and also that the substituents on the aromatic rings were predominantly para.

Example 2: 135 parts of phenol were heated to a temperature of about 45° to 50°C. for a period of 1 hour in a vessel provided with a stirrer. The phenol was then saturated by the continuous addition of gaseous hydrogen chloride. The temperature was increased to about 55° to 60°C., and 30 parts of the dicarbinol of 1,3-diisopropyl benzene were added with constant stirring over a period of 10 minutes.

After addition of the dicarbinol, the continuous stirring and gaseous hydrogen chloride addition were maintained at a temperature of 55° to 60°C. for 1 hour. The resulting product was then slurried with 10 times its volume of warm (60°C.) water and was agitated for several minutes. A two-phase system resulted and the upper aqueous layer was removed by decantation and discarded. The remaining organic layer was slurried with 10 times its volume of warm water. The resulting reaction product was then filtered off and washed several times with water to effect removal of residual phenol.

The solid product was then dissolved in 113 parts of toluene at 75°C., filtered to remove solid impurities, cooled to about 30°C. and then filtered again. The product was recrystallized once more from 150 parts of toluene and dried in a rotary steam drier under vacuum conditions to give 25.5 parts of a white crystalline solid have a MP of about 138° to 140°C., identified as 1,3-bis(p-hydroxycumyl)benzene. This amount of product corresponded to a yield of 48% of theory based upon the dicarbinol charged.

The preparation of polycarbonates from 1,4-bis(p-hydroxycumyl)benzene (BHCB) is described by L.C. Bostian, T.M. Cawthon and B.C. Oxenrider (U.S. Patent 3,466,260;

September 9, 1969; assigned to Allied Chemical Corporation). The following examples illustrate the process.

Example 1: A solution was prepared by dissolving 34.6 parts of 1,4-BHCB in 503 parts of ethylene chloride and 77.8 parts of tributylamine. An inert atmosphere was provided by maintaining a slow stream of nitrogen over the reaction system. 14.85 parts of phosgene were slowly added to the solution over a 3 hour period at a temperature of 30°C. The reaction mixture was allowed to stand for an extended period at room temperature, whereupon it was washed with a dilute aqueous solution of hydrochloric acid and the water until wash water of a pH 7 was obtained. The resulting 1,4-BHCB polycarbonate was then precipitated by slowly adding the reaction mixture to 750 parts of rapidly agitated methanol. The precipitated polycarbonate was dried at a temperature of 70°C. and under vacuum (about 150 mm. Hg). 50.7 parts of polycarbonate were obtained.

A portion of the polycarbonate was dissolved in ethylene chloride and fractionated by increment addition of methanol. About 40% of the polycarbonate precipitated as the first fraction. After drying, this polycarbonate possessed an inherent viscosity of 0.43 (corresponding to a molecular weight of about 15,000) and a flow point of 200° to 215°C. A tough, flexible film was prepared from the polycarbonate by pressing it between platens of a Carver Press.

Example 2: 34.6 parts of 1,4-BHCB were slurried in a dispersion of 100 parts of 1,4-dioxane, 377 parts of ethylene chloride and 300 parts of water containing 10.8 parts of sodium hydroxide, while maintaining a nitrogen atmosphere over the reaction system. The slurry was heated for a period of 25 minutes at a temperature of 30°C. 9.5 parts phosgene were slowly added to the slurry over a period of 33 minutes, while maintaining a reaction temperature at 30°C. 0.9 part triethylbenzylammonium chloride in the form of a 10% by weight aqueous solution was then added to the reaction mixture in order to facilitate molecular growth, and the phosgenation was continued. A total of 7 parts of phosgene were added over a period of 20 minutes. Throughout the entire reaction, a pH of 11 was maintained by adding a 5% aqueous solution of sodium hydroxide.

The organic phase was separated and was washed with a dilute aqueous hydrochloric acid solution and water as in Example 1. The resulting polycarbonate was finally isolated by slowly adding the organic phase to 1,000 parts of rapidly agitated acetone, followed by filtration and drying procedure at a temperature of 80°C. under vacuum. 21.4 parts of 1,4-BHCB polycarbonate having an inherent viscosity of 0.88 (corresponding to a molecular weight of about 40,000) were recovered.

Example 3: 34.6 parts of 1,4-BHCB were slurried in a dispersion of 377 parts of ethylene chloride and 400 parts of water containing 10 parts of sodium hydroxide, while maintaining a nitrogen atmosphere over the reaction system. While maintaining the reaction system at a temperature of 30°C., 13.5 parts phosgene were slowly added over a 37 minute period until the pH of the system decreased to 7. 0.28 part of p-cumylphenol and 0.18 part of benzyltriethylammonium chloride were then added to the reaction mixture, and the mixture was stirred for 1 1/2 hours, while adding 1 normal aqueous sodium hydroxide solution, as needed, to maintain a pH of 11. The organic phase was separated, washed with dilute hydrochloric acid and then successive portions of water until the wash water had a pH of about 7. The polycarbonate was precipitated by addition of the washed polymer solution to 1,000 parts of rapidly agitated acetone. 33 parts of 1,4-BHCB polycarbonate possessing an inherent viscosity of 0.70 (corresponding to a molecular weight of about 30,000) and a flow point of 240° to 250°C. were recovered.

The infrared spectra of the 1,4-BHCB polycarbonate showed strong absorption bands at the following wave lengths: 5.65, 6.65, 8.05, 8.38, 8.60, 9.85 and 12.02 microns. These spectra are in agreement with that which would be expected from theoretical considerations of the molecule.

The physical and mechanical properties of 1,4-BHCB polycarbonate having an inherent viscosity of 0.61 (corresponding to a molecular weight of about 25,000) are set forth below. All testing procedures employed are those of the American Society for Testing Materials.

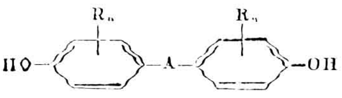
Physical and Mechanical Properties of 1,4-bis(p-Hydroxycumyl)Benzene Polycarbonate

Property	ASTM method	Value
Specific gravity, 23° C	D792	1.1414
Glass transition temp., ° C	D1043	154
Elastic modulus, p.s.i	D747	480,000
Compressive strength, p.s.i	D695	11,500
Flexural strength, p.s.i	D790	15,000
Heat distortion, ° C	D648	152
Rockwell hardness, R scale	D785	117
Water absorption, percent 24 hrs	D570	0.14

Bis(Hydroxyphenyl)Cyclododecane

C. Wulff, H. Schnell and L. Bottenbruch (U.S. Patent 3,422,065; January 14, 1969; assigned to Farbenfabriken Bayer AG, Germany) describe a method for preparing linear high molecular weight polycarbonates by the reaction of bis(hydroxyphenyl)cyclododecane either alone or in a mixture with other aromatic and/or aliphatic and/or cycloaliphatic dihydroxy compounds with carbonate group yielding derivatives of carbonic acid and rendering them insoluble by heating in the presence of a cross-linking agent.

The bis-(hydroxyphenyl)cyclododecane which can be used in the production of the polycarbonate resins is represented by the formula



$$HO-C_6H_{4-n}(R_n)-A-C_6H_{4-n}(R_n)-OH$$

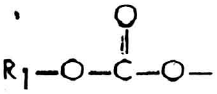
where A represents a cyclododecylene radical, R is an alkyl, cycloalkyl, aryl, or alkoxy group or halogen atom, and n is an integer of from 0 to 4. In addition, other dihydroxy compounds may be combined with the bis(hydroxyaryl)cyclododecane.

These polycarbonates can be produced in the same way as the known polycarbonates, that is is to say, bis(hydroxyphenyl)cyclododecane, either alone or in admixture with other aromatic and/or aliphatic and/or cycloaliphatic dihydroxy compounds can be reacted with derivatives of carbonic acids selected from the group consisting of carbonic diesters, especially diaryl esters, phosgene, and bis-chloro carbonic acid esters of dihydroxy compounds.

A process particularly suitable for producing polycarbonates consists of introducing phosgene into an aqueous solution or suspension of alkali or alkaline earth metal salts such as lithium, sodium, potassium, and calcium salts with the dihydroxy compounds, preferably in the presence of an excess of a base such as lithium, sodium, potassium or calcium hydroxide or carbonate. The polycarbonate then precipitates out from the aqueous solution.

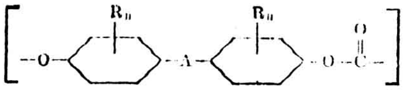
The conversion in the aqueous solution is promoted by the addition of reaction inert solvents of the kind mentioned above which are capable of dissolving phosgene and eventually the produced polycarbonate. The phosgene may be used in an equivalent amount, generally, however, it is preferred to use an excess of the phosgene. Suitable temperatures range from about 0°C. up to about 100°C.

The polycarbonates which are obtained by the process are high molecular weight linear copolycarbonates consisting of repeating units X and Y, the units being distributed at random in the chain, the ratio of the units X:Y amounting from about 5:95, preferred from about 10:90, to about 100:0, the chains having end groups selected from the group consisting of HO— and

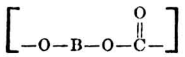


$$R_1-O-\overset{O}{\overset{\|}{C}}-O-$$

and a molecular weight more than about 10,000, preferably more than about 20,000, and up to about 150,000, X being

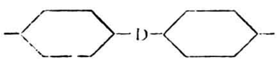


and Y being



$$\left[-O-B-O-\overset{O}{\overset{\|}{C}}-\right]$$

where A represents a cyclododecylene radical, R is alkyl, cycloalkyl, aryl, or alkoxy groups or halogen atoms, n is an integer of from 0 to 4, B is an alkylidene, cycloalkylidene or arylene radical and R_1 is alkyl up to 4 carbon atoms, cycloalkyl up to 6 carbon atoms or phenyl. Preferred products are such where n is O, B is



D being an alkylidene radical, preferably the isopropylidene radical, and R_1 is phenyl. These polycarbonates possess improved physical properties such as, for example, increased tensile strength, an exceptionally high transition point of the second order, reduced permeability to steam, and increased electric insulation and surface resistance.

In addition, these polycarbonates when heated at moderately elevated temperatures, i.e., in the range between about 100° and 250°C., preferably between about 100° and 200°C. in the presence of a cross-linking agent become substantially insoluble in a relatively short period of time. Cross-linking agents which promote cross-linking of these polycarbonates are for example, oxygen or radical forming catalysts such as, dibenzyl peroxide and dicumyl peroxide.

These polycarbonates are especially suitable in the formation of films, fibers, bristles, foils, coatings, pressed and injection molding bodies which become insoluble by tempering. The 1,1-bis(4-hydroxyphenyl)cyclododecane may be prepared in the following manner.

A mixture containing about 1,190 parts of cyclododecanone, about 3,100 parts of phenol and about 8 parts of thioglycollic acid is saturated with hydrogen chloride at room temperature. The reaction mixture is left to stand overnight, heated to from about 40° to 50°C. the next day, with the addition of hydrogen chloride gas. This procedure is repeated for three days. The mass which is finally completely crystalline is mixed with methylene chloride to form a viscous mass and filtered off with suction. It is slurried once with hot water and the crystalline slurry filtered off with suction. After drying, the colorless product is recrystallized from ethylene chloride. Approximately 1,500 parts 1,1-bis(4-hydroxyphenyl)cyclododecane, 60% of theory, were recovered, which had a MP of about 211°C. and a BP of about 235° to 242°C./0.2 mm. Hg. Analysis — Calculated: C, 81.77%; H, 9.15%. Found: C, 81.28%; H, 8.90%.

Example 1: Approximately 30.2 parts of phosgene are introduced over a period of about 1 hour and 50 minutes into a solution containing about 98 parts of 1,1-bis(4-hydroxyphenyl)-cyclododecane (Bisphenol Cy), about 75 parts of dry pyridine and about 150 parts of dry methylene chloride. After about 1 hour and 40 minutes, the solution becomes so highly viscous that an additional 280 parts of methylene chloride must be added. After the addition of the phosgene is complete, the reaction mixture is stirred for an additional 15 minutes. The solution is then poured into a mixture of concentrated hydrochloric acid and ice where it separated into layers. The methylene chloride phase is washed neutral with water and, after drying with sodium sulfate, the solvent is evaporated. A polycarbonate having a relative viscosity (5 g./1,000 cc methylene chloride at 25°C.) of 1.925 is recovered.

Example 2: Approximately 57 parts of 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A) and about 27 parts of Bisphenol Cy are slurried with about 400 parts water. A solution consisting of about 37 parts of sodium hydroxide and about 85 parts of water is added slowly to this mixture. It is slightly heated in order to obtain a clear solution. After cooling, about 175 parts of methylene chloride are added and approximately 38.5 parts of phosgene are introduced over a period of about an hour. Subsequently, with further stirring, about 1 part of a wetting agent and 3 parts of a 4% triethylamine solution are added. After about 2 hours of additional stirring, the organic phase becomes highly viscous. Enough methylene chloride is then added to form a thin, clear organic phase. This is then washed first with acid and subsequently with water until neutral. After evaporation of the methylene chloride, the resulting polycarbonate is dried in a vacuum at 100°C. A product having a relative viscosity of about 2.01 (measured on a solution of 5 g./1,000 cc methylene chloride at 25°C.) is thus obtained.

Example 3: A mixture of 57 parts of Bisphenol A and 9 parts of Bisphenol Cy is slurried with 290 parts of water. A solution consisting of 31 parts of sodium hydroxide in 70 parts of water is added slowly into this slurry, followed by 145 parts of methylene chloride. 32.5 parts of phosgene are then introduced in the course of about 1 hour, with agitation. With continued agitation, 0.85 parts of a wetting agent and 2.5 parts of a 4% triethylamine solution are subsequently added. After stirring for an additional 2 hours, the organic phase becomes very viscous. The product is worked up as described in Example 2. The polycarbonate thus obtained possesses a relative viscosity of 1.50 (5 g./1,000 cc at 25°C.).

Example 4: Polycarbonate foils were prepared and heated in an aerated drying cabinet. The results of this experiment are illustrated below.

	Temperature of the tempering	
Polycarbonate from—	150° C.	195° C.
Bisphenol A	Soluble after 10½ weeks.	Soluble after 24 hours.
Bisphenol Z	Soluble after 10½ weeks, strong decomposition.	Do.
Bisphenol Cy	Insoluble after 18 hours.	Partially insoluble after 1 hour, completely insoluble after 2 hours.
Bisphenol Cy—2.5+ DBP.	Insoluble after 8 hours.	
Bisphenol A 100 parts, bisphenol Cy 10 parts.	....	Insoluble after 24 hours.
Bisphenol A 100 parts, parts.	....	Do.

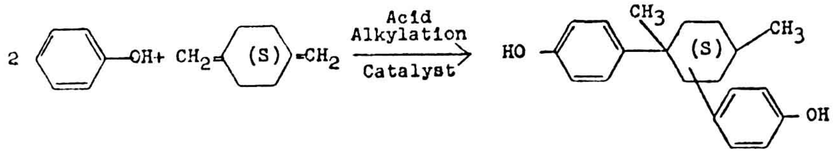
Bisphenol A = 2,2-bis(4-hydroxyphenyl)propane
Bisphenol Z = 1,1-bis(4-hydroxyphenyl)cyclohexane
Bisphenol Cy = 1,1-bis(4-hydroxyphenyl)cyclododecane
DBP = dibenzoyl peroxide
Solvent = methylene chloride

In comparing the results of Example 4, the polycarbonates prepared from the reaction of phosgene with 1,1-bis(4-hydroxyphenyl)cyclododecane are rendered insoluble by heating at a temperature between about 150° and 195°C., while polycarbonates prepared from the reaction of phosgene with either Bisphenol Z [1,1-bis(4-hydroxyphenyl)cyclohexane] or Bisphenol A [2,2-bis(4-hydroxyphenyl)propane] remain soluble even after prolonged heating at these temperatures. In fact, polycarbonates obtained from 1,1-bis(4-hydroxyphenyl)-cyclododecane were rendered insoluble in methylene chloride after 18 hours at 150°C., whereas polycarbonates obtained from Bisphenol A or Bisphenol Z were still soluble even after 10.5 weeks.

In addition, heating Bisphenol Z at a temperature of 150°C. resulted in the formation of decomposition products. Furthermore, polycarbonates prepared from a mixture of 1,1-bis-(4-hydroxyphenyl)cyclododecane and Bisphenol A were rendered insoluble when heated to a temperature of about 195°C. for 24 hours, whereas polycarbonates prepared from Bisphenol A alone were soluble even after 24 hours. It was found that the polycarbonates of this process when used either alone or in combination with other polycarbonates undergo cross-linking at temperatures substantially below polycarbonates prepared from bis(hydroxyaryl)alkanes or cycloalkanes.

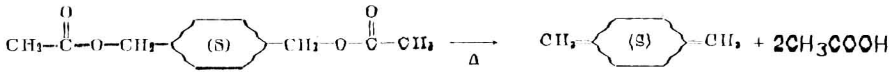
1,4-Dimethylene Cyclohexane

M. Matzner and L.B. Conte Jr. (U.S. Patent 3,395,186; July 30, 1968 and U.S. Patent 3,437,637; April 8, 1969; both assigned to Union Carbide Corporation) have found that bisphenols having phenolic portions on different carbon atoms are prepared by contacting together 1,4-dimethylene cyclohexane and at least a stoichiometric amount of a phenol with an acidic alkylation catalyst. The reaction shown for phenol and 1,4-dimethylene cyclohexane proceeds, in general, as follows:



A substantial molar excess of phenol over 1,4-dimethylene cyclohexane is desirable. Thus, molar ratios of from 3 to 20 and more mols of the phenol per mol of 1,4-dimethylene cyclohexane are completely suitable. Molar ratios of from 6 to 12 mols of phenol per mol of 1,4-dimethylene cyclohexane provide good reaction rates and are easily handled, and hence, are preferred.

The preparation of 1,4-dimethylene cyclohexane has been described in the technical literature using the diacetate of 1,4-cyclohexanedimethanol as the starting material. Pyrolysis of the latter at 625°C., followed by refractionation of the crude pyrolyzate affords pure 1,4-dimethylene cyclohexane, BP 121.5° to 122°C./730 mm., $n_D^{20} = 1.4719$.



Phenols which can be reacted with 1,4-dimethylene cyclohexane to form the bisphenols of this process are hydroxy substituted aryl compounds having a replaceable hydrogen attached to a ring carbon atom in a position preferably either ortho or para to a phenolic hydroxyl.

Among the phenols having replaceable hydrogen in the position ortho and para to a phenolic hydroxyl, some of these deserving of special mention are: hydroxy substituted benzenes, e.g., phenol, catechol, pyrogallol, resorcinol, phloroglucinol and unsymmetrical trihydroxy substituted benzenes.

The acidic alkylation catalyst used in the reaction of the above phenols with 1,4-dimethylene cyclohexane comprises a Friedel-Crafts catalyst including the hydrogen form (H^+) of a cation exchanging resin, i.e., an "acidic" cation exchanging resin. These resins are insoluble in the reaction mixture and hence, there is no problem of catalyst separation from the reaction zone effluent or need of removal of small amounts of impurities in the product.

Throughout the reaction and product recovery the catalyst remains in the reaction zone. The service life of the acidic cation exchanging resin in this method is nearly infinite and hence, the resin does not of necessity have to be regenerated, if care is exercized in preventing the introduction of basic metal ions such as sodium, potassium, calcium, etc., or other contaminants which inactivate the cation exchanging groups of the resin. The use of this insoluble catalyst confers the additional advantages of (1) eliminating the need for acid corrosion resistant equipment which is otherwise essential, and (2) making unnecessary any neutralization steps.

Among the cation exchanging resins which are highly deserving of special mention are: sulfonated styrene-divinylbenzene copolymers, sulfonated cross-linked styrene polymers, phenol formaldehyde sulfonic acid resins, benzene-formaldehydesulfonic acid resins, and the like. Most of these resins and many others are available commercially under trade names such as Amberlite XE-100, Dowex 50-X-4, Permutit QH and Chempro C-20.

It has been found that condensation polymers can be synthesized from the bisphenols of this process which exhibit in addition to other physical properties, high glass transition temperatures, tensile strengths and tensile moduli. The following examples illustrate the process.

Example 1: The preparation of the bisphenol of 1,4-dimethylene cyclohexane is carried out in the following way. To a three-necked, round bottom flask equipped with a mechanical stirrer, thermometer, reflux condenser, dropping funnel and heating mantle, was added 188 g. (2 mols) of freshly distilled, molten phenol and 125 g. (about 0.5 hydrogen equivalent) of the acid form of Dowex 50 X-4 (sulfonated styrene-divinylbenzene copolymer) which has had essentially all of the water displaced by phenol.

The resultant slurry was heated to 70° to 75°C. and heating then discontinued. Then 22 g. of 1,4-dimethylene cyclohexane (0.2 mol) was added dropwise while the exotherm was controlled with cooling water to maintain the temperature at 70° to 75°C. As the exotherm diminished, heat was applied. At the end of the 22 hour reaction period, the mixture was filtered and the catalyst washed with 250 ml. of freshly distilled molten phenol. The combined filtrate and washings were distilled to remove the fraction boiling up to 200°C. at 1 to 10 mm. The yield of crude bisphenol of 1,4-dimethylene cyclohexane remaining in the distillation pot as residue was 55 g. or 90% based on the weight of 1,4-dimethylene cyclohexane charged. A sample crystallized from toluene for analysis had a MP of 195°C., an hydroxyl value of 11.34% (theoretical value 11.49%) and a molecular weight of 290 (theoretical 296).

The infrared spectrum of the crystalline product obtained from toluene showed an intense band at 12 microns indicative of a p-alkylphenol. The nuclear magnetic resonance (NMR) spectrum of this crystalline product verified by a count of the relative number of aromatic and aliphatic hydrogen atoms that this was the product of 2 mols of phenol and 1 mol of dimethylene cyclohexane and that it was a true bisphenol. The NMR spectrum also suggested that this product was a mixture (approximately 1 : 1) of two isomers, viz., 1,4-dimethyl-1,2-bis(p-hydroxyphenyl)cyclohexane and 1,4-dimethyl-1,3-bis(p-hydroxyphenyl)-cyclohexane. This conclusion was confirmed by thin layer chromatography which also revealed the presence of other bisphenol isomers in the toluene mother liquor after removal of the crystalline isomers.