

Description

This invention relates to monomers and copolymers of polyfunctional vinylbenzyl ethers of polyhydric halogenated phenolic compounds.

5 Vinyl-terminated compounds are useful in preparing a variety of both thermoset and thermoplastic resins. Additionally, such compounds are useful comonomers in a variety of resin systems. The vinyl moieties are useful polymerization sites in free-radical induced and thermal-initiated polymerization reactions.

10 Aromatic nuclei are desirably included in the backbone of thermoset and thermoplastic resins because they provide both chemical and structural stability. Other useful moieties included in the backbones of such resins are halogens, such as bromine. The halogens are known to promote fire-resistance to compounds containing them.

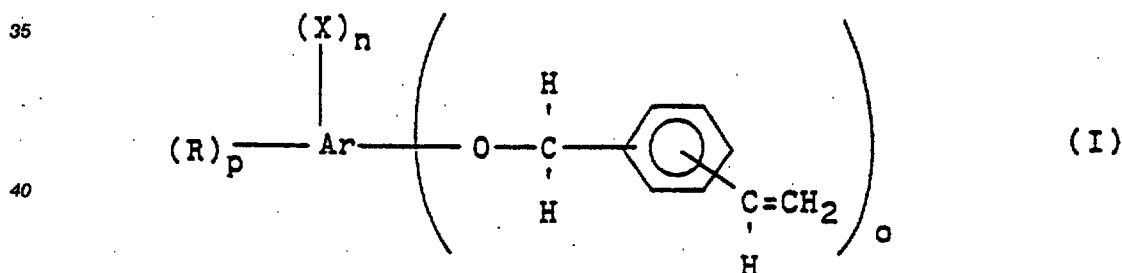
In the U.S. Patent 3,058,953, polymers and methods of preparing vinylbenzyl phenol ethers are disclosed. However, the monomers are monofunctional (i.e., they have only one vinyl moiety). In U.S. Patent 15 4,116,936, polymers of polyvinylbenzyl ethers of polyphenols are disclosed which compounds being excluded from the present invention by use of a disclaimer. However, the compounds which are halogenated require a glycidyl bridging group between aromatic rings. In U.S. Patent 4,180,680, methods for preparing halophenolvinylbenzyl ethers are disclosed. Unfortunately, the monomers are monofunctional.

20 An especially desirable family of thermoset resins is disclosed in U.S. Patent 4,528,366. These resins are aromatic polycyanate resins which can exhibit a dielectric constant of below 3 at 10 kHz. Therefore, these resins are desirably employed in preparing laminates for electronic circuit boards. Such polycyanates have been copolymerized with ethylenically unsaturated monomers in U S-A-4,581,425 and 4,559,399. Other polycyanates have been copolymerized with maleimides and ethylenically unsaturated monomers, as described in U.S. Patents 4,371,689; 4,393,195; 4,396,745; and 4,469,859. Unfortunately, such compositions 25 require expensive and complicated processing steps and fail to provide a polycyanate resin which exhibits the desired degree of fire retardancy.

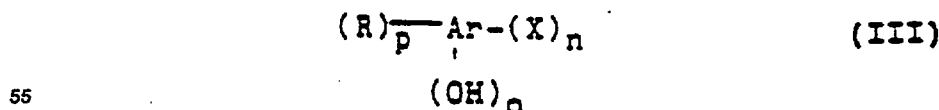
In U.S. Patent 4,094,861, a non-inflammable polytriazene is disclosed. Unfortunately, such compounds do not exhibit as desirable physical properties of triazenes prepared with other polycyanates.

30 It would be desirable to have polyfunctional vinylbenzyl ethers of polyhydric halogenated phenolic compounds. It would further be desirable if such compounds could be copolymerized with other monomers, especially poly(arylcyanate) ester resins to impart fire-resistance to the cured compositions.

The present invention concerns a polyfunctional vinylbenzyl ether of the formula:

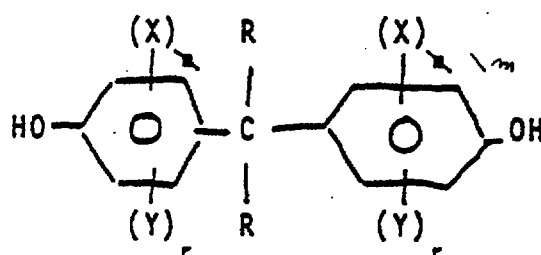


45 wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety; said vinyl benzyl 50 ether comprising a reaction product of a polyhydric halogenated phenolic compound of the formula:



wherein Ar, X, R, n and o are as defined in formula I; p is the remaining number of sites available on the

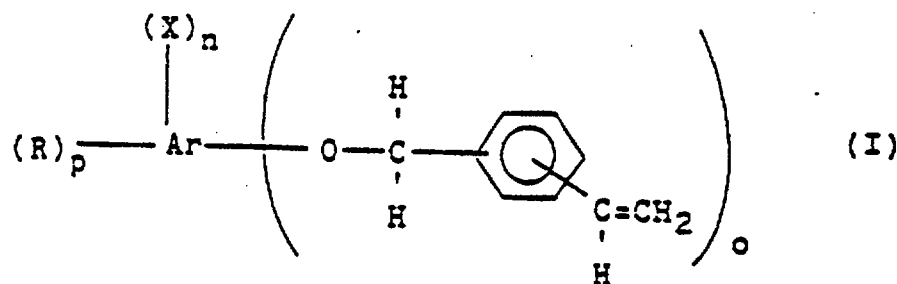
aromatic nucleus which are not substituted with the halogen or hydroxyl moieties, with the proviso that the polyhydric halogenated phenolic compounds of the formula



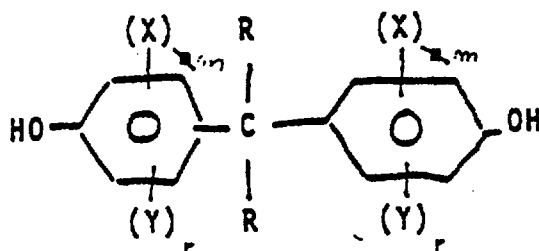
- wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of m + r is not greater than 2, are excluded; and an amount of vinylbenzyl chloride sufficient to provide at least 2 vinylbenzyl ether moieties per polyhydric phenolic compound.

Another aspect of this invention is a process for preparing polyfunctional vinylbenzyl ethers of polyhydric halogenated phenolic compounds corresponding to the above Formula (I). The process comprises contacting, under suitable reaction conditions, a polyhydric halogenated phenolic compound of Formula (III) with an amount of vinylbenzyl chloride sufficient to provide a reaction product having at least 2 vinylbenzyl ether moieties per phenolic compound.

In yet another aspect, this invention is a copolymer composition comprising a reaction product of an ethylenically polymerizable comonomer and of a polyfunctional vinylbenzyl ether of the formula:

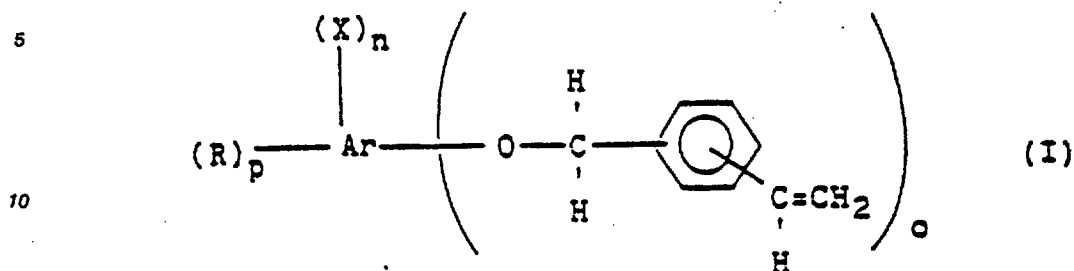


wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moieties, with the proviso if the ethylenically polymerizable comonomer is styrene or an acrylate that polyfunctional vinylbenzyl ethers of the formula I which are the reaction product of vinylbenzylchloride and polyhydric halogenated phenolic compounds of the formula

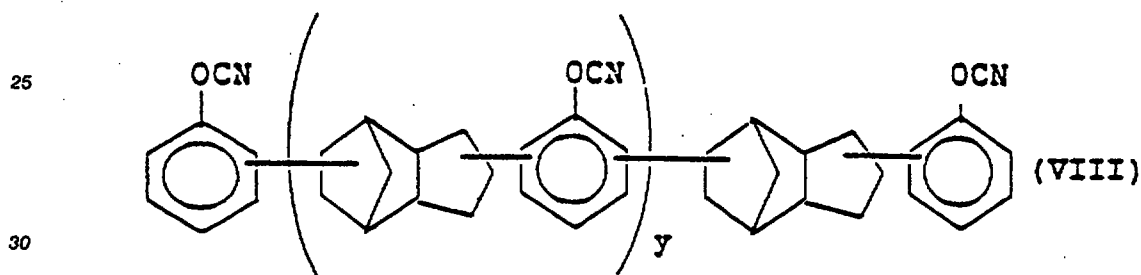


wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of m + r is not greater than 2, are excluded.

In still yet another aspect, this invention is a copolymer composition comprising a reaction product of an aromatic polycyanate ester compound and a polyfunctional vinylbenzyl ether of the formula:



wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety. Preferably the aromatic polycyanate ester compound in this copolymer composition is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula



wherein y is greater than or equal to zero, more preferably wherein y in formula VIII is 0.2.

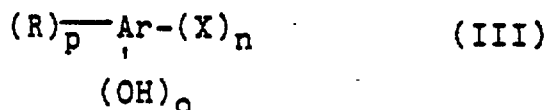
This invention provides polyfunctional vinylbenzyl ether compounds which are halogenated, and special copolymers of such compounds. The vinylbenzyl ethers are useful for promoting certain properties in resins, such as fire-resistance. The copolymers of the vinylbenzyl ethers and aromatic polycyanate ester compounds are useful in fabricating laminates useful for preparing electronic circuit boards. The neat resin employed in preparing the laminates exhibits a dielectric constant below 3, and a V-O rating in the UL-94 test.

The polyhydric halogenated phenolic compounds useful in this invention are comprised of an aromatic nucleus substituted with at least 2 hydroxyl moieties (i.e., a polyhydric compound) and a halogen moiety which aromatic nucleus contains from 6 to 24 carbons and which comprises a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety. In addition to being substituted with the halogen and the hydroxyl moieties, the aromatic moieties can be substituted with a variety of substituents provided such substituents do not interfere with the etherification reaction or detract from the physical properties of the polymers or the copolymers. Examples of suitable moieties include alkyl moieties which are of a non-plasticizing length. Typically, alkyl chains of from 1 to 6 carbon atoms do not contribute a plasticizing effect and are suitable. Preferably, the aromatic nucleus is comprised of two aromatic rings connected by a direct bond or an alkyl group, however, taking care of the above mentioned proviso.

Additionally, the aromatic nucleus is substituted with a halogen moiety. Preferred halogens are chlorine and bromine, with bromine being most preferred. Enough of the halogen is contained in the aromatic nucleus to provide the desired degree of fire retardancy to a copolymer composition containing the compounds of this invention. Typically, if the aromatic nucleus has a low halogen content, more of the comonomer will be required to provide the degree of fire retardancy. Contrariwise, if the aromatic nucleus contains a high halogen content less of the comonomers need to be employed. Preferably, such halogen amount provides a halogen content of at least 5 weight percent in the cured copolymer composition. Preferably, the aromatic nucleus is a polyhalogenated aromatic nucleus (i.e., contains more than one

halogen moiety). Preferably, when the aromatic nucleus contains 2 bromine moieties per aromatic moiety, the bromine moieties are in a meta position on the aromatic moiety because the meta substituted bromines tend to provide a more stable compound.

The polyhydric halogenated phenolic compound can correspond to the formula:



wherein

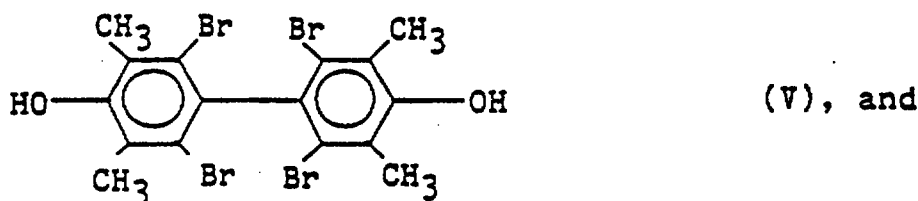
Ar, X, R, n and o are as defined in Formula I;

and

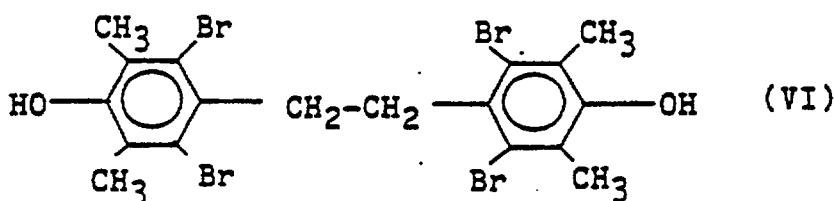
p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties, observing the above mentioned proviso.

Preferred polyhydric halogenated phenolic compounds are polyhalogenated biphenols.

Preferred halogenated biphenol compounds include 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula:

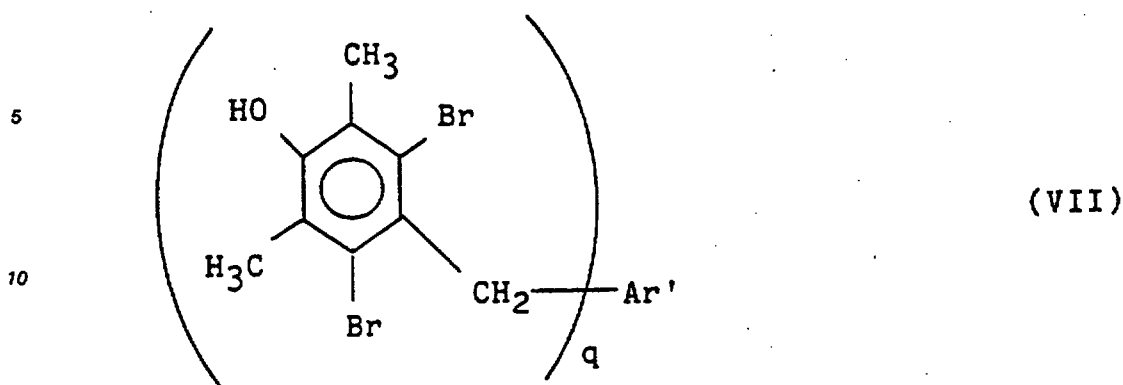


1,2-bis(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)-ethane which corresponds to the formula



These compounds can be prepared by contacting bromine and the respective poly(alkyl)polyhydroxy aromatic compound in the presence of a suitable brominating medium, such as using a Friedel-Crafts catalyst.

Still yet other preferred phenolic compounds are alkylated halogenated mesitols which correspond to the formula



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wherein Ar' is an aromatic nucleus of C₆-C₂₄ carbon atoms which can be the same or different as Ar of Formula I and q is an integer of at least 2. A suitable method for preparing such a compound is a Friedel-Crafts alkylation wherein tribromomesitol is contacted with the desired aromatic compound in the presence of a suitable catalyst. Examples of such catalysts are Lewis and Bronsted acids such as AlCl₃, AlBr₃, and FeCl₃. Other suitable reaction conditions are temperatures ranging from 20° to 150° C, with higher temperatures producing a quicker reaction. The reaction is conducted at ambient pressures for any suitable time, which typically can range from 10 minutes to 14 hours. An inert diluent to solubilize the tribromomesitol can be employed. Haloalkanes such as dichloromethane can be employed. Tribromomesitol can be prepared according to the methods described in K. Auweis and F. Rapp, Ann., 302, 153-71 (1898); O. Jacobsen, Ann., 195, 265-92 (1879); and K. Fries and E. Brandes, Ann., 542, 48-77 (1939).

25 Preferred polyhydric halogenated phenolic compounds are disclosed in and prepared by the methods described in U.S. Patent No. 4,621,159 issued November 4, 1986.

Vinylbenzyl chloride is readily available from The Dow Chemical Company and can be prepared according to known methods. Suitable methods are disclosed in U.S. Patents 2,780,604; 2,981,758; 30 3,311,602; Czechoslovakian Patent 83,721; British Patent 792,859; and Russian Patent 318, 560.

The polyfunctional vinylbenzyl ethers of the polyhydric halogenated phenolic compounds of this invention are prepared by contacting the polyhydric halogenated phenolic compounds with an amount of vinylbenzyl chloride sufficient to provide at least 2 vinylbenzyl ether moieties per phenolic compound. By "polyfunctional vinylbenzyl ethers" is meant that at least 2 vinylbenzyl ether moieties are provided per 35 compound. The amount of vinylbenzyl chloride can be as much as one, and preferably is an excess of one vinylbenzyl chloride equivalent per hydroxyl equivalent in the phenolic compound. It is most advantageous to cap all the hydroxyl groups with vinylbenzyl groups because residual hydroxyl groups can detract from the polymer's and copolymer's properties. Preferably, the compounds of this invention are the reaction products (i.e., the isomeric mixture) of contacting only the vinylbenzyl chloride and 1 or more polyhydric 40 halogenated phenolic compounds.

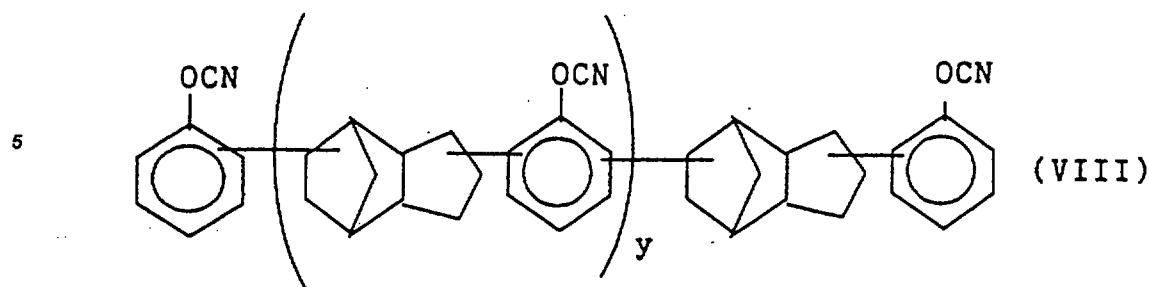
In one method, the polyhydric halogenated phenolic compound can be mixed with a solvent. An amount of base, for example potassium hydroxide, or sodium hydroxide, sufficient to initiate the reaction is added, and the mixture can then be heated. Finally, the desired amount of vinylbenzyl chloride is added, and the reaction product is recovered after cooling.

45 The vinylbenzyl ether compounds of this invention can be subjected to suitable polymerization conditions to provide polymeric compositions. Such suitable polymerization conditions include polymerizing in the presence of a suitable free-radical catalyst, or treating at suitable polymerization temperatures. Conventional vinyl polymerization reactions are suitable.

The polyfunctional vinylbenzyl ether of this invention can be copolymerized with other comonomers. Preferred comonomers include monomers which undergo ethylenically unsaturated polymerization reactions. For example, such comonomers include styrene, acrylates and acrylic acid, ethylenically unsaturated hydrocarbons, maleimide compounds and the like. Other comonomers include the epoxy resins and the vinyl ester analogs of the epoxy resins.

50 A preferred comonomer useful in copolymerizing with the polyfunctional vinylbenzyl ethers of this invention are the aromatic polycyanate ester compounds described in U.S. Patent 4,528,366. An especially preferred aromatic polycyanate ester is the polyphenol cyanate ester bridged by a dicyclopentadiene moiety which corresponds to the formula

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wherein y is greater than or equal to zero and is preferably 0.2.

The copolymers of the aromatic polycyanate ester and polyfunctional vinylbenzyl ether of this invention are prepared by melting the comonomers together and heating in the presence of a suitable trimerization catalyst. Examples of suitable catalysts are the cobalt salts. Especially preferred cobalt salts are cobalt naphthenate and cobalt acetylacetonate (CoAcAc).

The amount of the comonomers employed in preparing the copolymer can vary according to the types of properties desired in the copolymer. Increasing the amount of vinylbenzyl ether copolymer can increase the degree of fire resistance, but can be restricted by economical considerations. Typically, at least 8 weight percent, preferably at least 10 weight percent of the vinylbenzyl ether comonomer is employed. An especially preferred copolymer contains 12.2 weight percent of vinylbenzyl ether. Such a cured neat copolymer can exhibit a dielectric constant of below 3 at 10 kHz and a V-0 rating in a UL-94 test.

Laminates can be prepared by copolymerizing the aromatic polycyanate ester and the polyfunctional vinylbenzyl ether of this invention in the presence of suitable fillers. Examples of such fillers are organic and inorganic fibers and powders, such as glass fibers, Kevlar® fibers, and ceramic powders. The laminates are useful in preparing electronic circuit boards. The laminates prepared from the copolymers can exhibit a synergistic dielectric constant because the dielectric constant of the neat cured copolymerization product is lower than the dielectric constants of either of the cured homopolymers. Additionally, due to the presence of the bromine of the vinylbenzyl ether component, the laminates can provide a V-0 rating in the UL-94 test.

The following examples are provided to illustrate the invention.

Example 1 - The Preparation of Vinylbenzyl Ether of Tetrabromobisphenol A

A 1-liter 3-necked round bottom flask was fitted with a reflux condensor, a dropping funnel, and a mechanical stirrer. To this flask was added 12.85 g (0.32 moles) of sodium hydroxide and 400 ml of methanol. The mixture was stirred until the solid had dissolved. Tetrabromobisphenol A (87.34 g, 0.16 moles) was added to the flask and the material heated to 55°C. Vinylbenzyl chloride (54.10 g, 0.35 moles) was added dropwise over a period of 20 minutes. The mixture was maintained at 55°C for 400 minutes. The mixture was cooled and filtered to remove the solid which was a mixture of the reaction product and sodium chloride. The solid was slurried in 1,400 ml of a 1:1 mixture of methanol and water for 50 minutes and then filtered. The solid was rinsed with water and methanol and then dried in vacuo at 40°C to give 107 g of a white solid (86 percent yield). The product had a bromine content of 41 weight percent.

Example 2- Copolymerizing the Vinylbenzyl Ether of Tetrabromobisphenol A with Polycyanate Esters

An amount of the polycyanate ester of dicyclopentadiene was warmed to 100°C and poured into beakers. Different amounts of the vinylbenzyl ether of tetrabromobisphenol A were added and the mixture was stirred while heating to 90°C. A 1 percent, based on weight of cobalt, solution of cobalt acetylacetonate in acetonitrile (100 parts per million cobalt) was added and the mixture was stirred well at 90°C. The mixture was degassed in a vacuum at 150°C for 10 minutes using carborundum boiling stones to aid in degassing. The material was poured into stainless steel parallel plate molds which were preheated to 125°C. The material was cured at 125°C for 1 hour, 175°C for 1 hour, 225°C for 1 hour and 250°C for 1 hour. The molds were allowed to cool slowly to 100°C and the plaques were removed.

Six samples of the copolymer composition having different amounts of the vinylbenzyl ether and aromatic polycyanate were prepared, and the degrees of fire resistance were measured according to the UL-94 test. The results are provided at Table I.

TABLE I

Sample	VBE ⁽¹⁾ Content (Percent)	Br ⁽²⁾ Content (Percent)	Burn Time	UL-94 Rating
1	24.3	10	0	V-O
2	18.2	7.5	0	V-O
3 ⁽³⁾	12.2	5	23 sec.	V-O
4	9.7	4	67 Sec.	V-1
5	7.3	3	>300 sec.	HB
6	4.9	2	>300 sec.	HB

(1) Weight percent of bis(vinylbenzyl) ether of tetrabromobisphenol A in the copolymer.

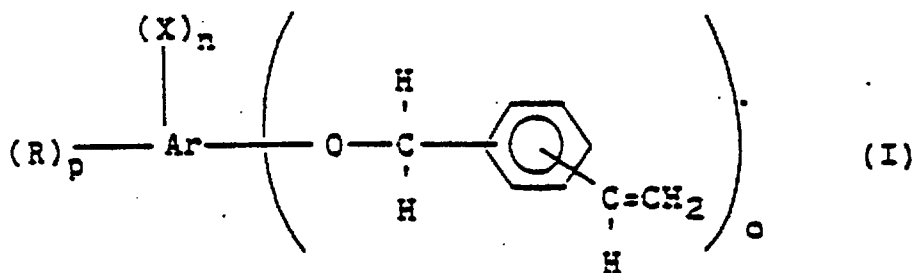
(2) Weight percent of bromine in the copolymer.

(3) The dielectric constant of this sample, Sample 3, is 2.75, measured dry at 10 kHz.

Claims

Claims for the following Contracting States : BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. A polyfunctional vinylbenzyl ether of the formula:



wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety; said vinyl benzyl ether comprising a reaction product of a polyhydric halogenated phenolic compound of the formula:



wherein Ar, X, R, n and o are as defined in formula I; p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties, with the proviso that the polyhydric halogenated phenolic compounds of the formula

TABLE I

Sample	VBE ⁽¹⁾ Content (Percent)	Br ⁽²⁾ Content (Percent)	Burn Time	UL-94 Rating
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4	9.7	4	67 Sec.	V-1
5	7.3	3	>300 sec.	HB
6	4.9	2	>300 sec.	HB

(1) Weight percent of bis(vinylbenzyl) ether of tetrabromobisphenol A in the copolymer.

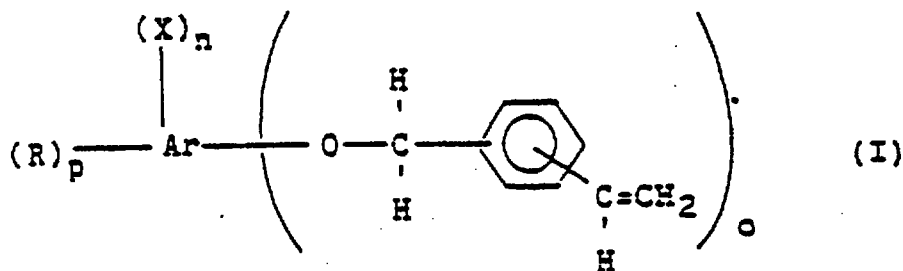
(2) Weight percent of bromine in the copolymer.

(3) The dielectric constant of this sample, Sample 3, is 2.75, measured dry at 10 kHz.

Claims

Claims for the following Contracting States : BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. A polyfunctional vinylbenzyl ether of the formula:

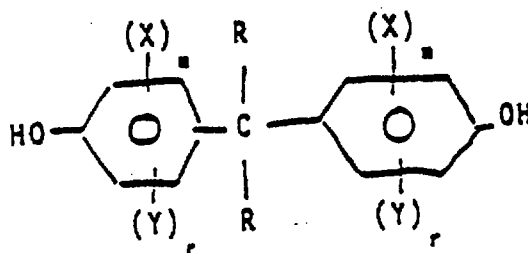


wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety; said vinyl benzyl ether comprising a reaction product of a polyhydric halogenated phenolic compound of the formula:



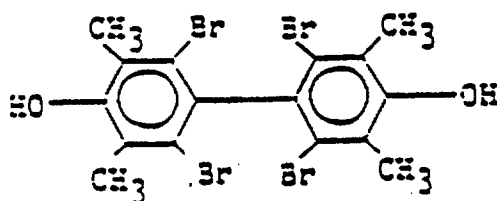
wherein Ar, X, R, n and o are as defined in formula I; p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties, with the proviso that the polyhydric halogenated phenolic compounds of the formula





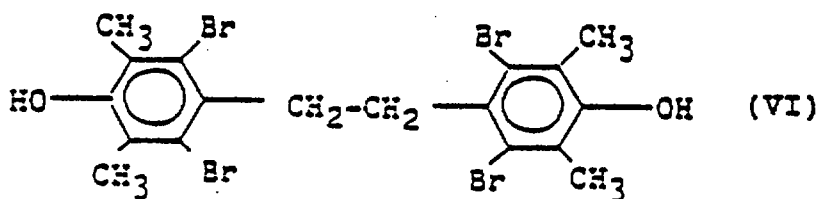
wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of m+r is not greater than 2, are excluded; with an amount of vinylbenzyl chloride sufficient to provide a reaction product having at least 2 vinylbenzyl ether moieties per polyhydric phenolic compound.

2. The vinylbenzyl ether of claim 1, wherein the used polyhydric halogenated phenolic compound is a polyhalogenated biphenol.
3. The vinylbenzyl ether of claim 2 wherein the used polyhalogenated biphenol is 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula



(V)

4. The vinylbenzyl ether of Claim 2 wherein the polyhalogenated biphenol is 1,2-bis-(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



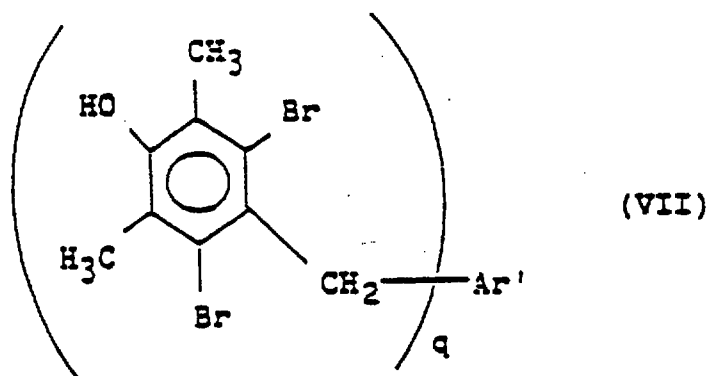
(VI)

5. The vinylbenzyl ether of Claim 1 wherein the polyhydric halogenated phenolic compound is an alkylated halogenated mesitol which corresponds to the formula



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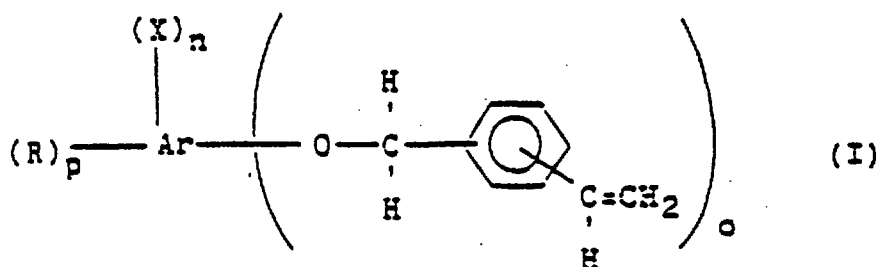


15 wherein Ar' is an aromatic nucleus of C₆-C₂₄ carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, which Ar' can be the same or different as Ar of formula I and q is an integer of at least 2.

- 20 6. A copolymer composition comprising a reaction product of an aromatic polycyanate ester compound and a polyfunctional vinylbenzyl ether of the formula:

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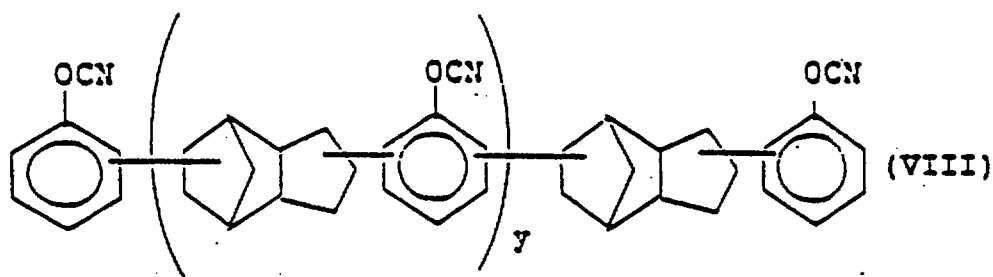


35 wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety.

- 40 7. The copolymer composition of claim 6, wherein the aromatic polycyanate ester compound is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula

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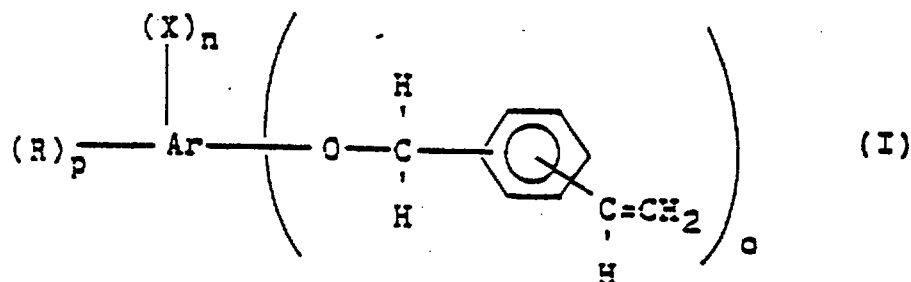
55 wherein y is greater than or equal to zero.

8. The copolymer composition of claim 7, wherein y in formula VIII is 0.2.

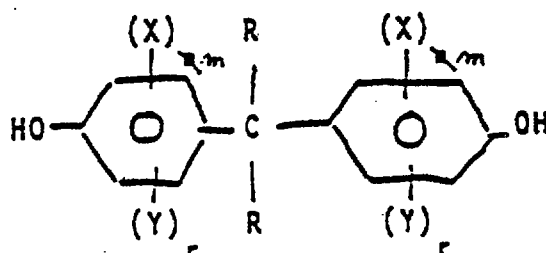
9. A copolymer composition comprising a reaction product of an ethylenically polymerizable comonomer



and of a polyfunctional vinylbenzyl ether of the formula:

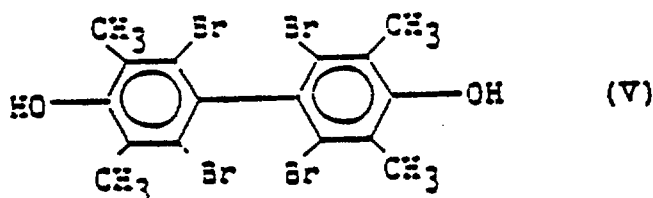


wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moieties, with the proviso if the ethylenically polymerizable comonomer is styrene or an acrylate that polyfunctional vinylbenzyl ethers of the formula I which are the reaction product of vinylbenzylchloride and polyhydric halogenated phenolic compounds of the formula



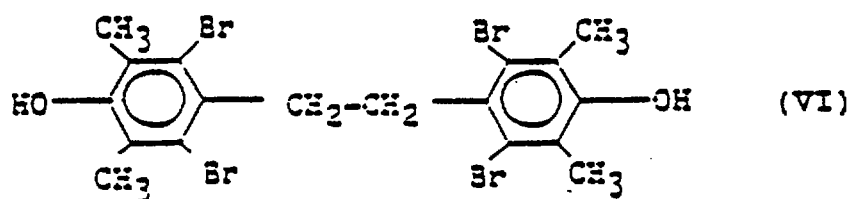
wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of m+r is not greater than 2, are excluded.

10. The copolymer composition of claims 7 or 8, wherein the copolymer composition exhibits a dielectric constant of less than 3 at 10 kHz, and a V-O rating in a UL-94 test.
11. The copolymer composition of claim 9, wherein the polyhydric halogenated phenolic compound is a polyhalogenated biphenol.
12. The Copolymer composition of claim 11, wherein the polyhalogenated biphenol is 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenol which corresponds to the formula

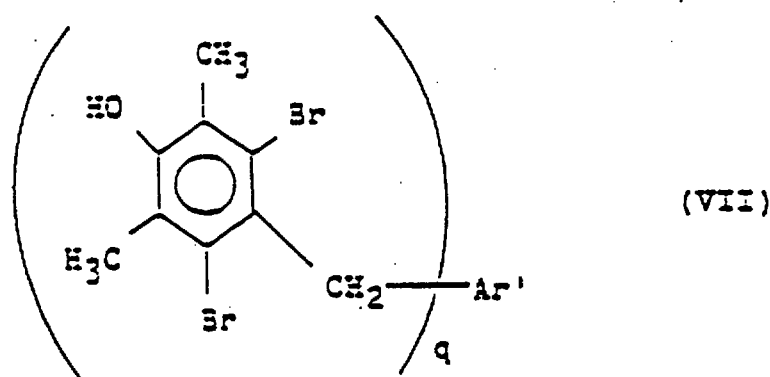


13. The copolymer composition of claim 11, wherein the polyhalogenated biphenol is 1,2-bis(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula





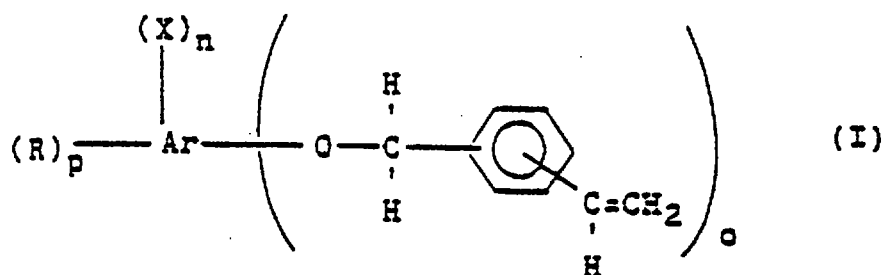
14. The copolymer composition of claim 6 wherein the polyhydric halogenated phenolic compound is an alkylated halogenated mesitol which corresponds to the formula



wherein Ar' is an aromatic nucleus of C₆ to C₂₄ carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, which Ar' can be the same or different as Ar of formula I and q is an integer of at least 2.

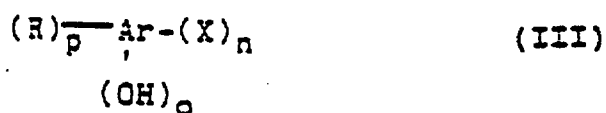
Claims for the following Contracting States : AT, ES

1. A process for the preparation of a polyfunctional vinylbenzyl ether of the formula:

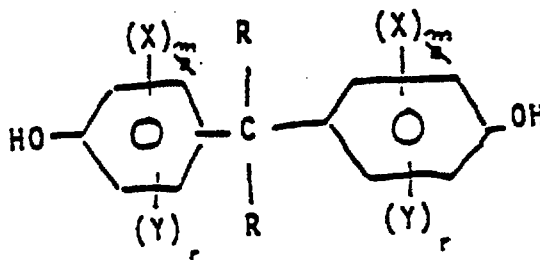


wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety; by contacting under suitable reaction conditions a polyhydric halogenated phenolic compound of the formula:



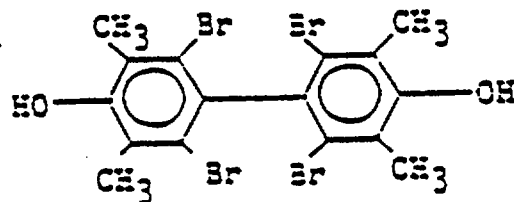


wherein Ar, X, R, n and o are as defined in formula I; p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or hydroxyl moieties, with the proviso that the polyhydric halogenated phenolic compounds of the formula

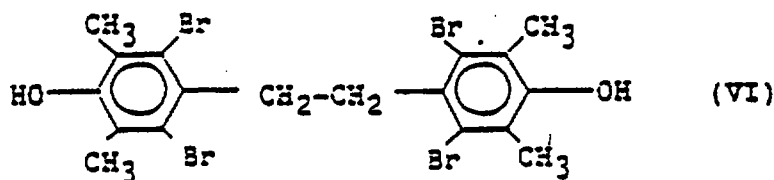


wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of m+r is not greater than 2, are excluded; with an amount of vinylbenzyl chloride sufficient to provide a reaction product having at least 2 vinylbenzyl ether moieties per polyhydric phenolic compound.

2. The process of claim 1, wherein the used polyhydric halogenated phenolic compound is a polyhalogenated biphenol.
3. The process of claim 2 wherein the used polyhalogenated biphenol is 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenyl which corresponds to the formula

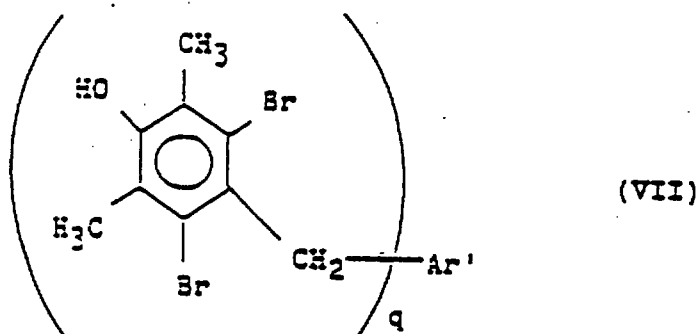


or 1,2-bis-(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



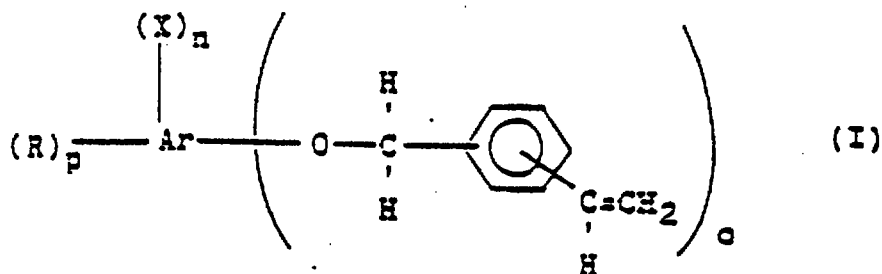
4. The process of claim 1 wherein the used polyhydric halogenated phenolic compound is an alkylated halogenated mesitol which corresponds to the formula





15 wherein Ar is an aromatic nucleus of from 6-24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety which Ar' can be the same or different as Ar of formula I and q is an integer of at least 2.

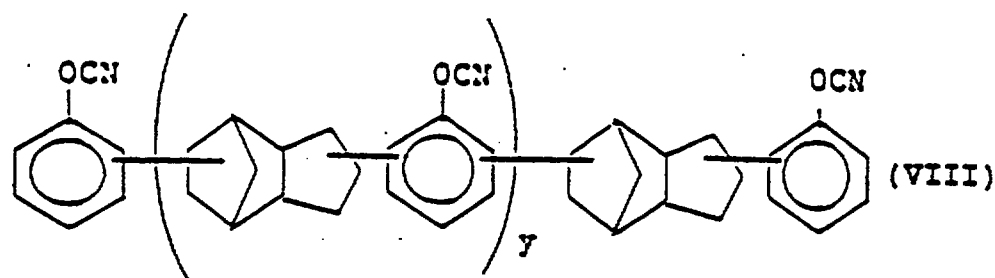
- 20 5. The process of any one of claims 1 to 4 which is conducted in the presence of a solvent.
6. The process of any one of claims 1 to 4 which is conducted in the presence of a suitable base.
7. The process of any one of claims 1 to 4 which is conducted at temperatures ranging from 20° C to 150° C.
- 25 8. A process for the preparation of a copolymer composition by heating in the presence of a suitable trimerization catalyst an aromatic polycyanate ester compound with a polyfunctional vinylbenzyl ether of the formula



40 wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moiety.

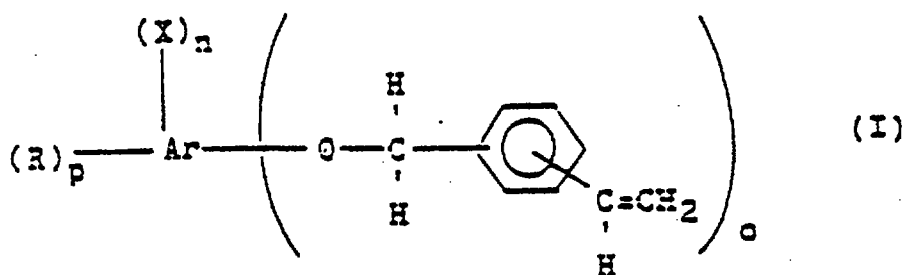
- 45 9. The process of claim 8, wherein the used aromatic polycyanate ester compound is a dicyclopentadiene bridged polycyanate ester which corresponds to the formula



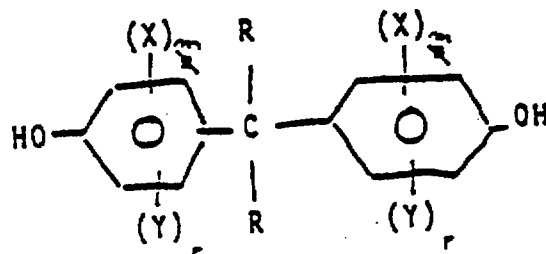


wherein y is greater than or equal to zero, and the catalyst is cobalt naphthanate or cobalt acetylacetonate.

10. The process of claim 8 wherein y in the formula (VIII) is 0.2.
11. The process of claims 9 or 10, wherein the copolymer composition exhibits a dielectric constant of less than 3 at 10 kHz, and a V-O rating in a UL-94 test.
12. A process for the preparation of a copolymer composition by copolymerizing an ethylenically polymerizable comonomer and a polyfunctional vinylbenzyl ether of the formula:



wherein Ar is an aromatic nucleus of from 6 to 24 carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, X is a halogen moiety, R is hydrogen or an alkyl group of from 1 to 6 carbon atoms, n is an integer of at least 1; o is an integer of at least 2 and p is the remaining number of sites available on the aromatic nucleus which are not substituted with the halogen or oxygen containing moieties, with the proviso if the ethylenically polymerizable comonomer is styrene or an acrylate that polyfunctional vinylbenzyl ethers of the formula I which are the reaction product of vinylbenzylchloride and polyhydric halogenated phenolic compounds of the formula



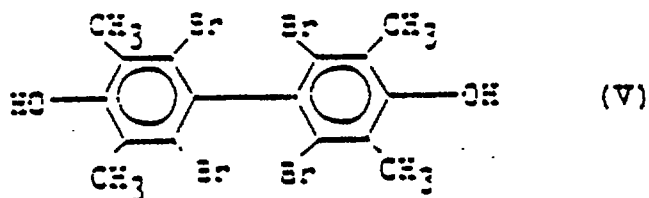
wherein R and X are as defined in formula I, Y is an alkyl group of from 1 to 6 carbon atoms and m is an integer of 1 or 2 and r is an integer of 0 or 1 and the sum of $m+r$ is not greater than 2, are excluded.

13. The process of claim 12 wherein the polyhydric halogenated phenolic compound used to prepare the

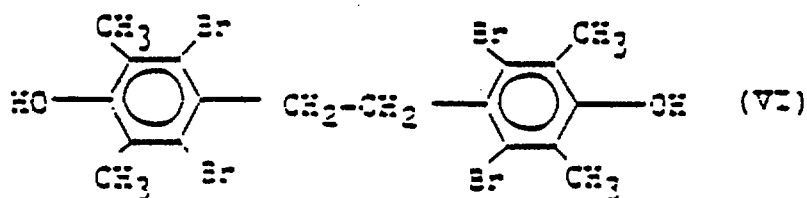


polyfunctional vinylbenzylester is a polyhalogenated biphenol.

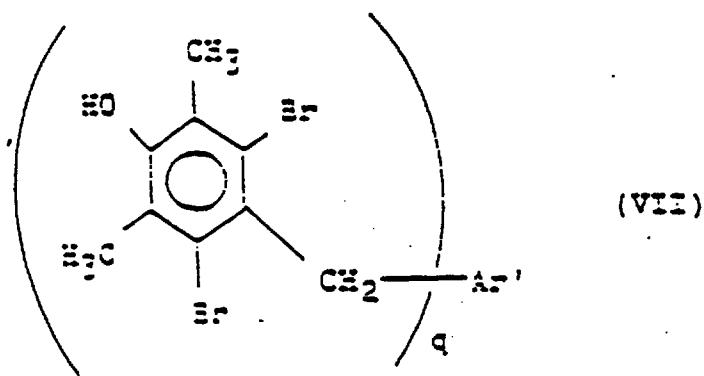
14. The process of claim 13 wherein the polyhalogenated biphenol used is 3,3',5,5'-tetramethyl-2,2',6,6'-tetrabromo-4,4'-dihydroxy biphenol which corresponds to the formula



15. The process of claim 13, wherein the polyhalogenated biphenol is 1,2-bis(2,6-dibromo-3,5-dimethyl-4-hydroxyphenyl)ethane which corresponds to the formula



16. The process of claim 12 wherein the polyhydric halogenated phenolic compound used to prepare the polyfunctional vinylbenzyl ether is an alkylated halogenated mesitol which corresponds to the formula



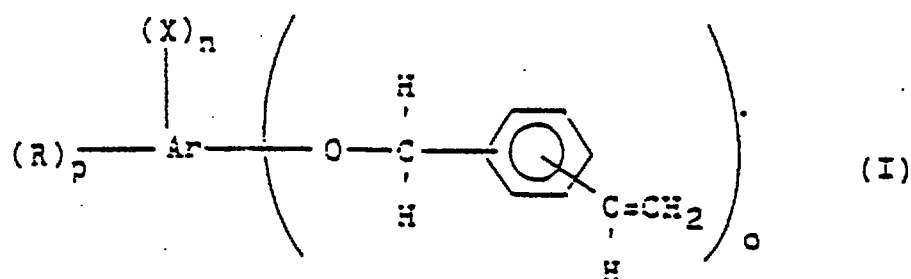
wherein Ar' is an aromatic nucleus of C₆ to C₂₄ carbon atoms comprising a single aromatic ring or multiple aromatic rings which are fused together, or are connected by a direct bond or a hydrocarbon bridging moiety, which Ar' can be the same or different as Ar of formula I and q is an integer of at least 2.

Revendications

Revendications pour les Etats contractants suivants : BE, CH, DE, FR, GB, GR, IT, LI, NL, SE.

- 55 1. Ether vinylbenzylique polyfonctionnel de formule :

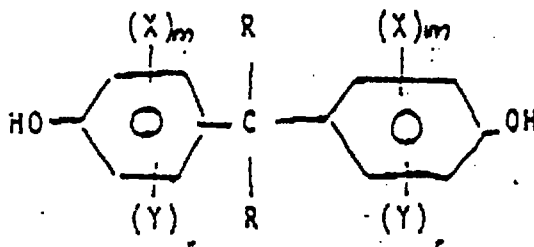




dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1, o est un nombre entier valant au moins 2 et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par le fragment contenant l'atome d'halogène ou d'oxygène ; ledit éther vinylbenzylique comprenant le produit de réaction d'un composé phénolique halogéné polyhydroxylé de formule :



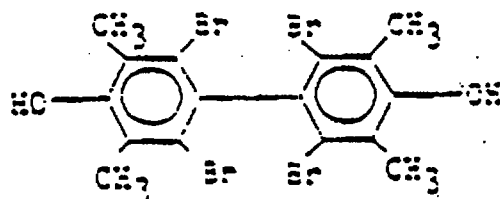
dans laquelle Ar, X, R, n et o sont tels que définis dans la formule (I), p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par les fragments halogène ou hydroxyle, à la condition que les composés phénoliques halogénés polyhydroxylés de formule



dans laquelle R et X sont tels que définis dans la formule I, Y est un groupe alkyle avec de 1 à 6 atomes de carbone et m est un nombre entier valant 1 ou 2 et r est un nombre entier valant 0 ou 1 et la somme m + r n'est pas supérieure à 2, soient exclus ; et d'une quantité de chlorure de vinylbenzyle suffisante pour fournir au moins 2 fragments éther vinylbenzyliques par composé phénolique polyhydroxylé.

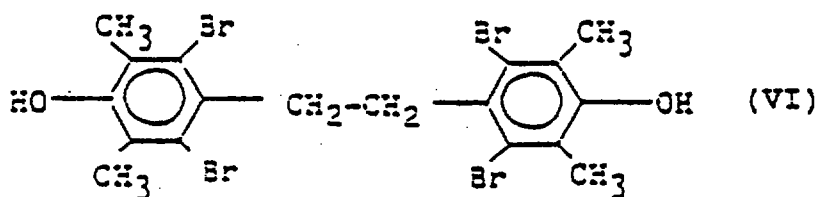
2. Ether vinylbenzylique selon la revendication 1, dans lequel le composé phénolique halogéné polyhydroxylé est un biphenol polyhalogéné.
3. Ether vinylbenzylique selon la revendication 2, dans lequel le biphenol polyhalogéné est le 3,3',5,5'-tétraméthyl-2,2',6,6'-tétrabromo-4,4'-dihydroxybiphényle qui correspond à la formule





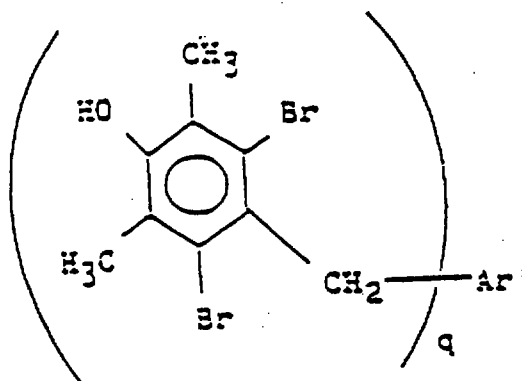
(V)

4. Ether vinylbenzylique selon la revendication 2, dans lequel le bisphénol polyhalogéné est le 1,2-bis-(2,6-dibromom-3,5-diméthyl-4-hydroxyphényl)éthane qui correspond à la formule



(VI)

5. Ether vinylbenzylique selon la revendication 1, dans lequel le composé phénolique halogéné polyhydroxylé est un mésitol halogéné alkylé qui correspond à la formule

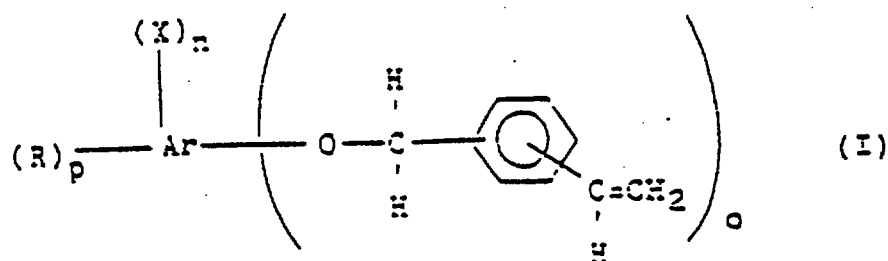


(VII)

dans laquelle Ar' est un noyau aromatique avec 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, Ar' pouvant être identique à ou différent de Ar de la formule I, et q est un nombre entier valant au moins 2.

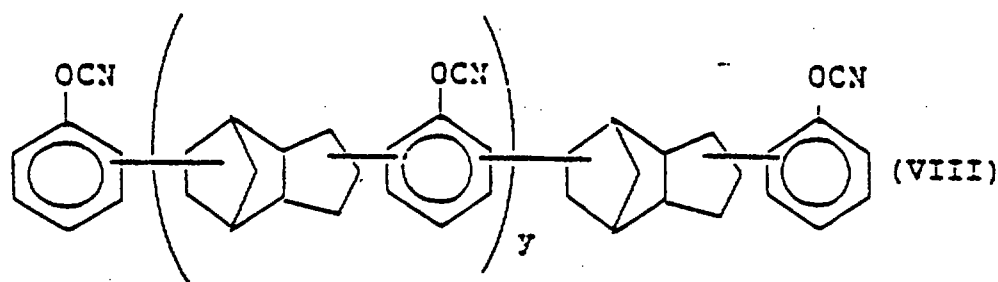
6. Composition copolymère comprenant un produit de réaction d'un composé ester polycyanate aromatique et d'un éther vinylbenzylique polyfonctionnel de formule :





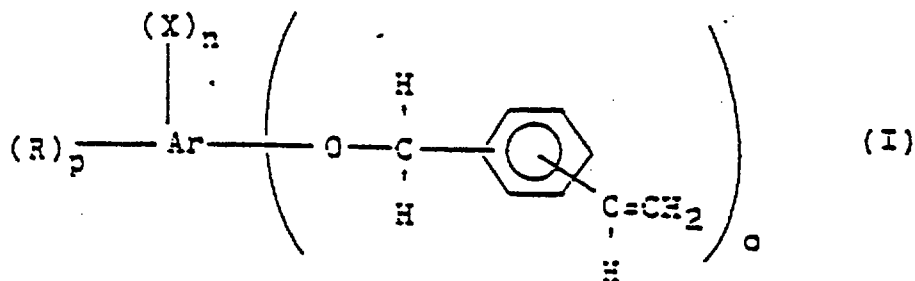
dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1, o est un nombre entier valant au moins 2 et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par le fragment contenant l'atome d'halogène ou d'oxygène.

7. Composition copolymère selon la revendication 6, dans laquelle le composé ester polycyanate aromatique est un ester polycyanate ponté par un dicyclopentadiène, qui correspond à la formule



dans laquelle y est supérieur ou égal à zéro.

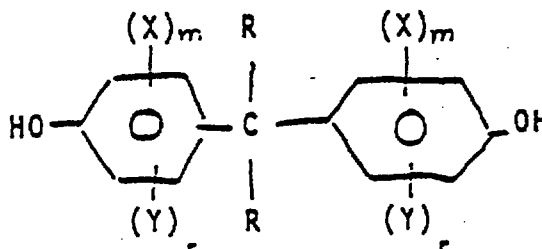
8. Composition copolymère selon la revendication 7, dans laquelle y dans la formule (VIII) vaut 0,2.
9. Composition copolymère qui comprend un produit de réaction d'un comonomère éthyléniquement polymérisable et d'un éther vinylbenzylique polyfonctionnel de formule



dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone, qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1, o est un nombre entier valant au moins 2 et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par les fragments contenant un atome d'halogène ou d'oxygène,

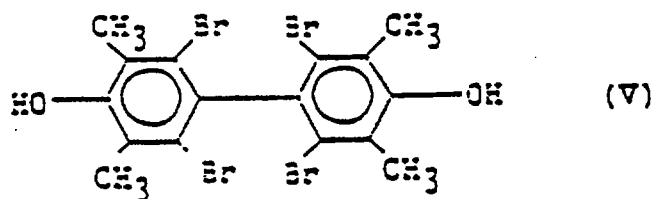


à la condition que, si le comonomère éthyléniquement polymérisable est le styrène ou un acrylate, les éthers vinylbenzyliques polyfonctionnels de formule I qui sont les produits de réaction du chlorure de vinylbenzyle et des composés phénoliques halogénés polyhydroxylés de formule

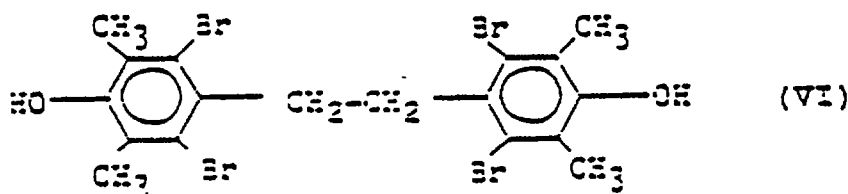


dans laquelle R et X sont tels que définis dans la formule I, Y est un groupe alkyle avec de 1 à 6 atomes de carbone, et n est un nombre entier valant 1 ou 2 et r est un nombre entier valant 0 ou 1, et la somme $m + r$ n'est pas supérieure à 2, soient exclues.

10. Composition copolymère selon les revendications 7 ou 8, la composition copolymère présentant une constante diélectrique inférieure à 3 à 10 kHz, et un classement V-O dans un essai UL-94.
11. Composition copolymère selon la revendication 9, dans laquelle le composé phénolique halogéné polyhydroxylé est un biphenol polyhalogéné.
12. Composition copolymère selon la revendication 11, dans laquelle le biphenol polyhalogéné est le 3,3',5,5'-tétraméthyl-2,2',6,6'-tétrabromo-4,4'-dihydroxybiphenol qui correspond à la formule

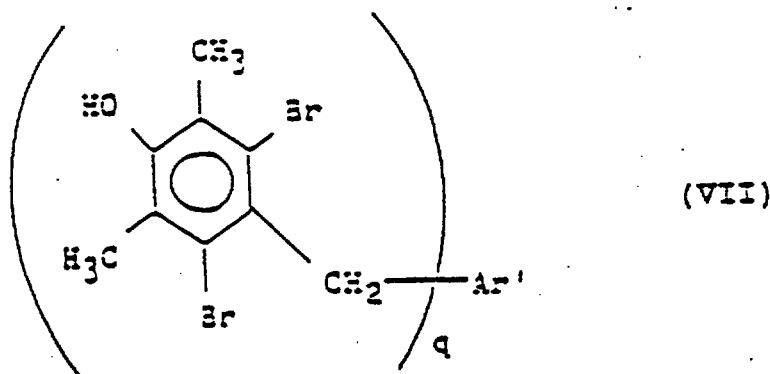


13. Composition copolymère selon la revendication 11, dans laquelle le biphenol polyhalogéné est le 1,2-bis(2,6-dibromo-3,5-diméthyl-4-hydroxyphényl)éthane qui correspond à la formule



14. Composition copolymère selon la revendication 6, dans laquelle le composé phénolique halogéné polyhydroxylé est un mésitol halogéné alkylé qui correspond à la formule

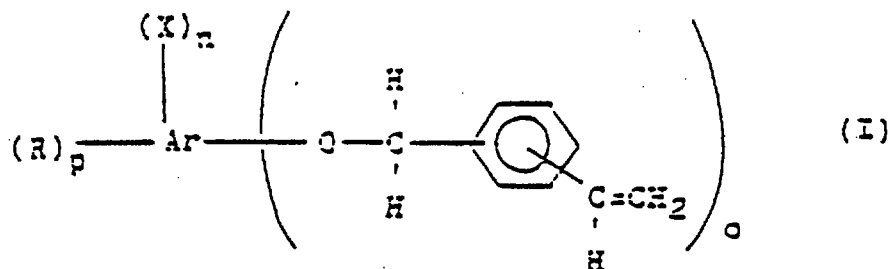




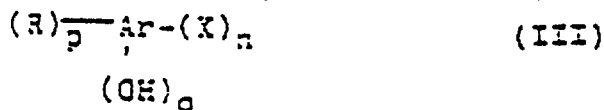
dans laquelle Ar' est un noyau aromatique avec 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, Ar' pouvant être identique ou différent à Ar dans la formule I et q est un nombre entier valant au moins 2.

Revendications pour les Etats contractants suivants : AT, ES.

1. Procédé pour la préparation d'un éther vinylbenzylique polyfonctionnel de formule :

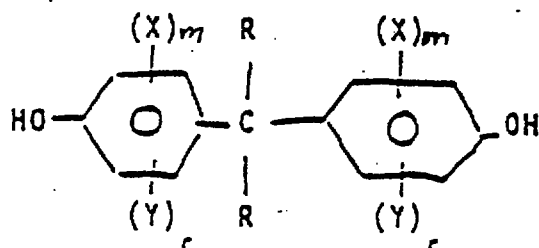


dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1 ; o est un nombre entier valant au moins 2 et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par le fragment contenant un atome d'halogène ou d'oxygène ; par la mise en contact, dans des conditions convenables de réaction, d'un composé phénolique halogéné polyhydroxylé de formule :



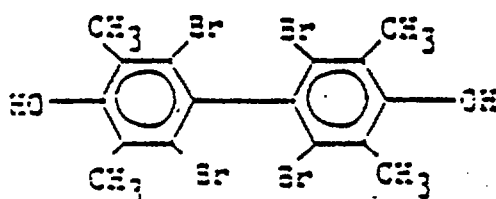
dans laquelle Ar, X, R, n et o sont tels que définis dans la formule I ; p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par les fragments halogène ou hydroxyle, à la condition que les composés phénoliques halogénés polyhydroxylés de formule





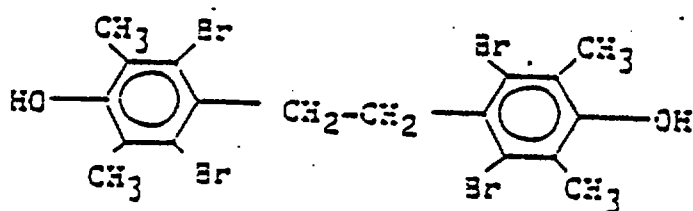
dans laquelle R et X sont tels que définis dans la formule I, Y est un groupe alkyle avec de 1 à 6 atomes de carbone et m est un nombre entier valant 1 ou 2 et r est un nombre entier valant 0 ou 1 et la somme de m + r n'est pas supérieure à 2, soient exclus ; et d'une quantité de chlorure de vinylbenzyle suffisante pour fournir un produit de réaction ayant au moins 2 fragments éther vinylbenzylique par composé phénolique polyhydroxylé.

2. Procédé selon la revendication 1, dans lequel le composé phénolique halogéné polyhydroxylé utilisé est un biphenol polyhalogéné.
3. Procédé selon la revendication 2, dans lequel le biphenol polyhalogéné utilisé est le 3,3',5,5'-tétraméthyl-2,2',6,6'-tétrabromo-4,4'-dihydroxybiphényle qui correspond à la formule



(V)

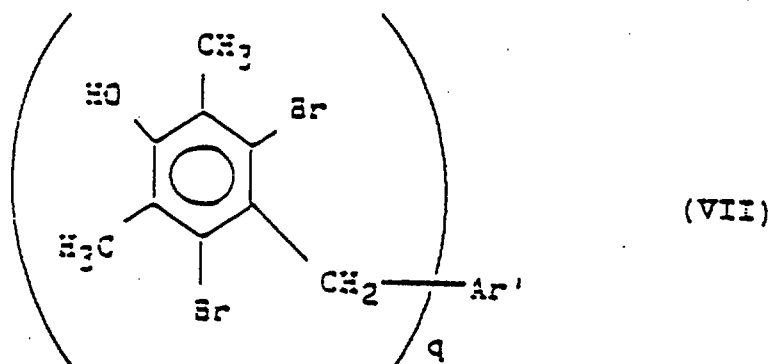
ou le 1,2-bis(2,6'dibromo-3,5-diméthyl-4-hydroxyphényl)éthane qui correspond à la formule



(VI)

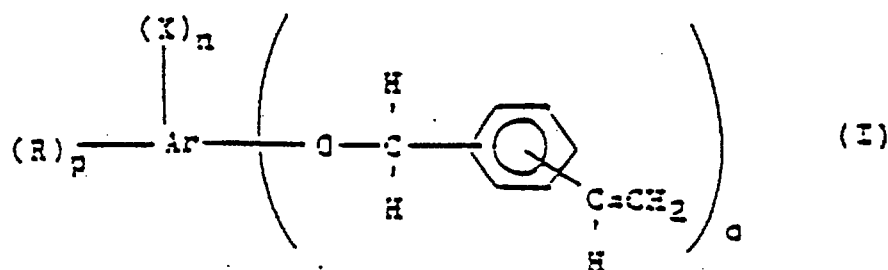
4. Procédé selon la revendication 1, dans lequel le composé phénolique halogéné polyhydroxylé utilisé est un mésitol halogéné alkylé qui correspond à la formule





dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, Ar' pouvant être identique ou différent de Ar dans la formule I, et q est un nombre entier valant au moins 2.

- 20
- 25
- 30
5. Procédé selon l'une quelconque des revendications 1 à 4, que l'on effectue en présence d'un solvant.
 6. Procédé selon l'une quelconque des revendications 1 à 4, que l'on effectue en présence d'une base convenable.
 7. Procédé selon l'une quelconque des revendications 1 à 4, que l'on effectue à des températures comprises entre 20°C et 150°C.
 8. Procédé pour la préparation d'une composition copolymère par chauffage, en présence d'un catalyseur convenable de trimérisation, d'un composé ester polycyanate aromatique avec un éther vinylbenzylique polyfonctionnel de formule



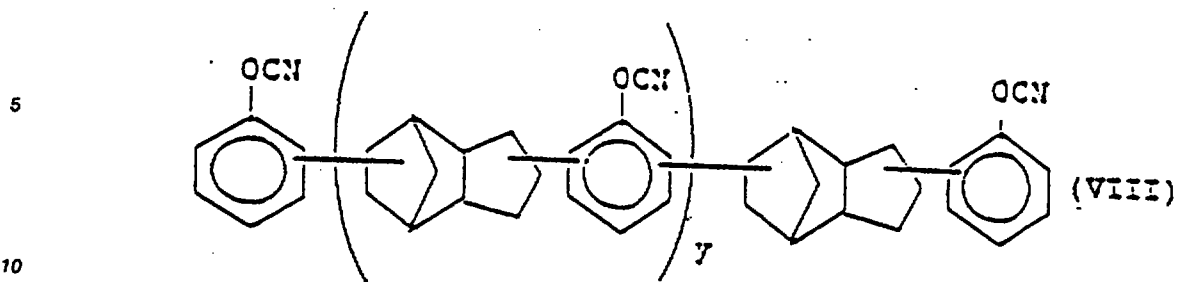
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dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone, qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1 ; o est un nombre entier valant au moins 2, et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par le fragment contenant un atome d'halogène ou d'oxygène.

- 55
9. Procédé selon la revendication 8, dans lequel le composé ester polycyanate aromatique utilisé est un ester polycyanate ponté par un dicyclopentadiène qui correspond à la formule



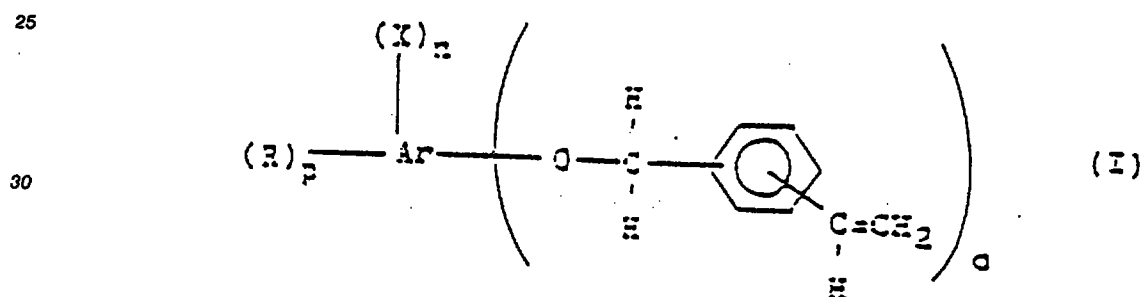


15 dans laquelle y est supérieur ou égal à zéro, et le catalyseur est le naphtéate de cobalt ou l'acétylacétonate de cobalt.

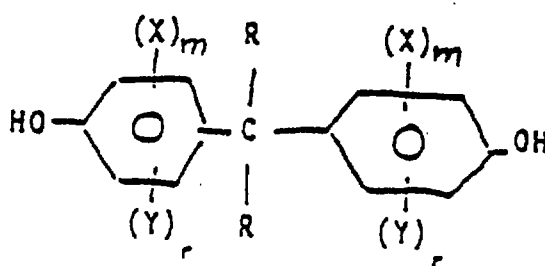
10. Procédé selon la revendication 9, dans lequel y dans la formule (VIII) vaut 0,2.

11. Procédé selon la revendication 9 ou 10, dans lequel la composition copolymère présente une constante diélectrique inférieure à 3 à 10 kHz et un classement V-O dans un essai UL-94.

12. Procédé pour la préparation d'une composition copolymère par copolymérisation d'un comonomère éthyléniquement polymérisable et d'un éther vinylbenzylique polyfonctionnel de formule :



35 dans laquelle Ar est un noyau aromatique avec de 6 à 24 atomes de carbone, qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, X est un fragment halogène, R est un atome d'hydrogène ou un groupe alkyle avec de 1 à 6 atomes de carbone, n est un nombre entier valant au moins 1 ; o est un nombre entier valant au moins 2 et p est le nombre restant de sites disponibles sur le noyau aromatique qui ne sont pas substitués par les fragments contenant un atome d'halogène ou d'oxygène, à la condition que, si le comonomère éthyléniquement polymérisable est le styrène ou un acrylate, les éthers vinylbenzyliques polyfonctionnels de formule I qui sont les produits de réaction du chlorure de vinylbenzyle et des composés phénoliques halogénés polyhydroxylés de formule



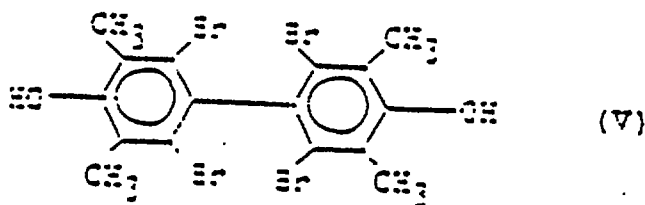
dans laquelle R et X sont tels que définis dans la formule I, Y est un groupe alkyle avec de 1 à 6 atomes de carbone et m est un nombre entier valant 1 ou 2 et r est un nombre entier valant 0 ou 1 et



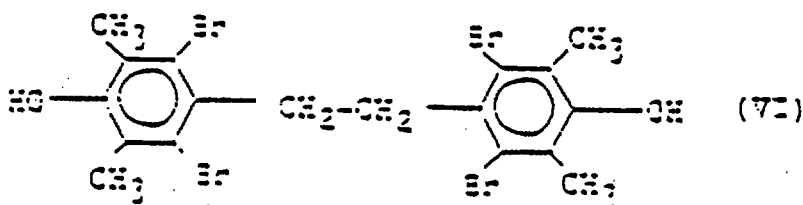
la somme $m + r$ n'est pas supérieure à 2, soient exclus.

13. Procédé selon la revendication 12, dans lequel le composé phénolique halogéné polyhydroxylé utilisé pour préparer l'éther vinylbenzylique polyfonctionnel est un biphenol polyhalogéné.

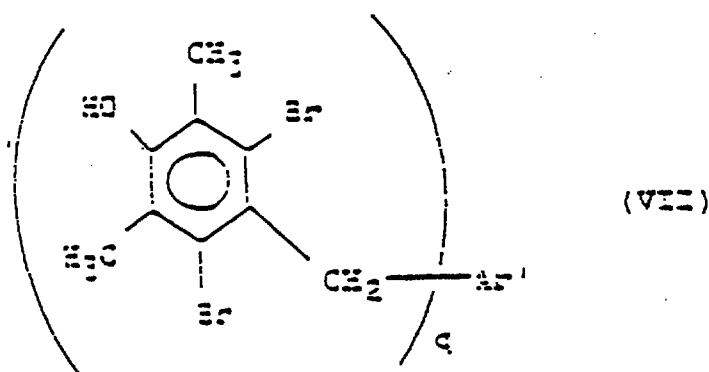
14. Procédé selon la revendication 13, dans lequel le biphenol polyhalogéné utilisé est le 3,3',5,5'-tétraméthyl-2,2',-6,6'-tétrabromo-4,4'-dihydroxybiphenol qui correspond à la formule



15. Procédé selon la revendication 13, dans laquelle le biphenol polyhalogéné est le 1,2-bis(2,6-dibromo-3,5-diméthyl-4-hydroxyphényl)éthane qui correspond à la formule



16. Procédé selon la revendication 12, dans lequel le composé phénolique halogéné polyhydroxylé utilisé pour préparer l'éther vinylbenzylique polyfonctionnel est un mésitol halogéné alkylé qui correspond à la formule



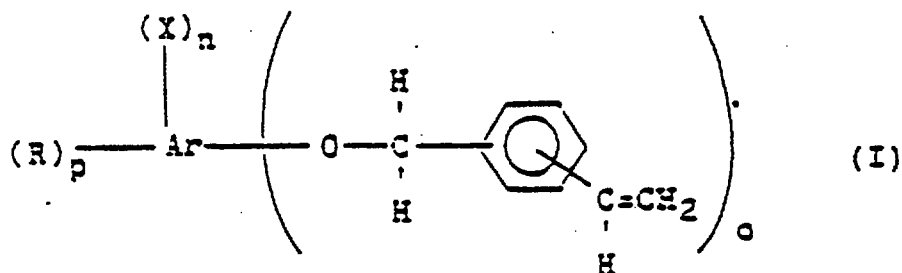
dans laquelle Ar' est un noyau aromatique avec de 6 à 24 atomes de carbone qui comprend un noyau aromatique unique ou plusieurs noyaux aromatiques qui sont condensés ou reliés par une liaison directe ou un fragment pontant hydrocarboné, Ar' pouvant être identique ou différent de Ar dans la formule I, et q est un nombre entier valant au moins 2.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten: BE, CH, DE, FR, GB, GR, IT, LI, NL, SE



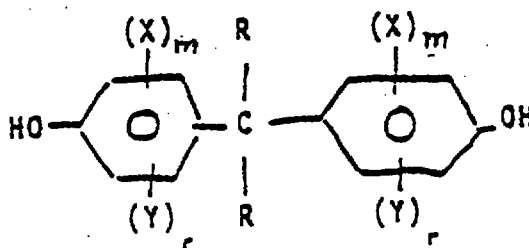
1. Polyfunktioneller Vinylbenzylether der Formel:



in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe durch eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogengruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder Sauerstoff enthaltender Gruppe besetzt sind, wobei der Vinylbenzylether ein Reaktionsprodukt enthält von einer mehrwertigen, halogenierten, phenolischen Verbindung der Formel:



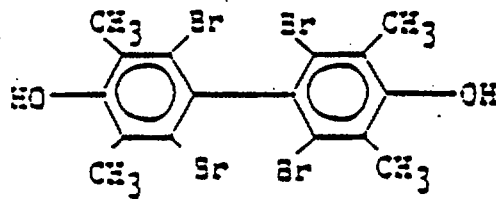
in der Ar, X, R, n und o die für Formel I angegebene Bedeutung haben, p ist die verbleibende Zahl von Stellen am aromatischen Kern, die nicht mit Halogen oder Hydroxylgruppen besetzt sind, mit der Bedingung, daß die mehrwertigen, halogenierten, phenolischen Verbindungen der Formel



in der R und X die für Formel I angegebene Bedeutung haben, Y eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist und m eine ganze Zahl von 1 oder 2 ist und r eine ganze Zahl von 0 oder 1 ist und die Summe von m + r nicht größer als 2 ist, ausgeschlossen sind, wobei die Menge an Vinylbenzylchlorid ausreichend ist, um ein Reaktionsprodukt zu ergeben, das mindestens 2 Vinylbenzylethergruppen pro mehrwertiger, phenolischer Verbindung aufweist.

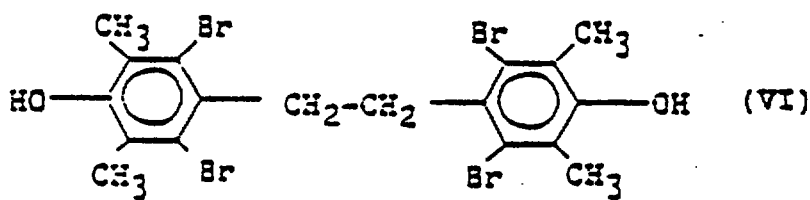
2. Vinylbenzylether nach Anspruch 1, dadurch gekennzeichnet, daß die verwendete mehrwertige, halogenierte, phenolische Verbindung ein polyhalogeniertes Biphenol ist.
3. Vinylbenzylether nach Anspruch 2, dadurch gekennzeichnet, daß das verwendete polyhalogenierte Biphenol 3,3',5,5'-Tetramethyl-2,2',6,6'-tetrabrom-4,4'-dihydroxybiphenyl ist, das der Formel entspricht





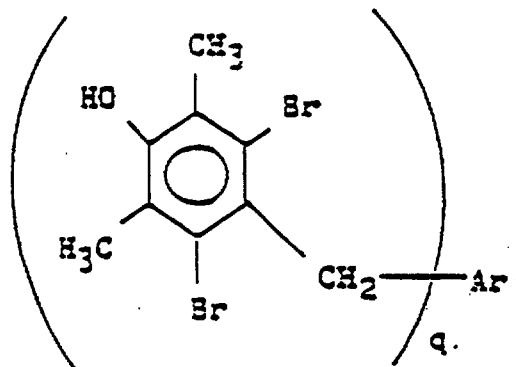
(V)

4. Vinylbenzylether nach Anspruch 2, dadurch gekennzeichnet, daß das polyhalogenierte Biphenol 1,2-bis-(2,6-Dibrom-3,5-dimethyl-4-hydroxyphenyl)ethan ist, das der Formel entspricht



(VI)

5. Vinylbenzylether nach Anspruch 1, dadurch gekennzeichnet, daß die mehrwertige, halogenierte, phenolische Verbindung ein alkyliertes, halogeniertes Mesitol der folgenden Formel ist

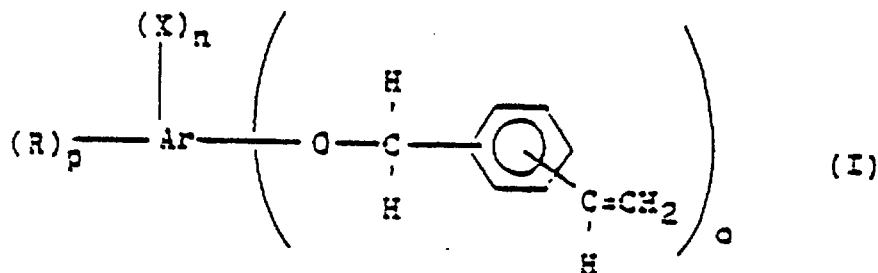


(VII)

in der Ar' ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte aromatische Ringe oder die aromatischen Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, wobei Ar' die gleiche oder unterschiedliche Bedeutung wie Ar der Formel I haben kann und q eine ganze Zahl von mindestens 2 ist.

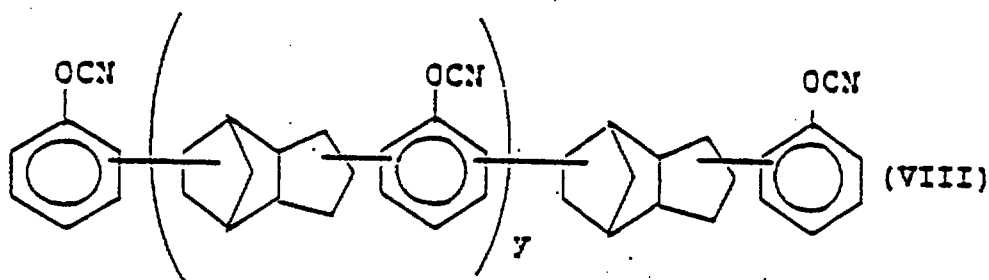
6. Copolymerzusammensetzung, enthaltend ein Reaktionsprodukt einer aromatischen Polycyanatesterbindung und eines polyfunktionellen Vinylbenzylethers der Formel





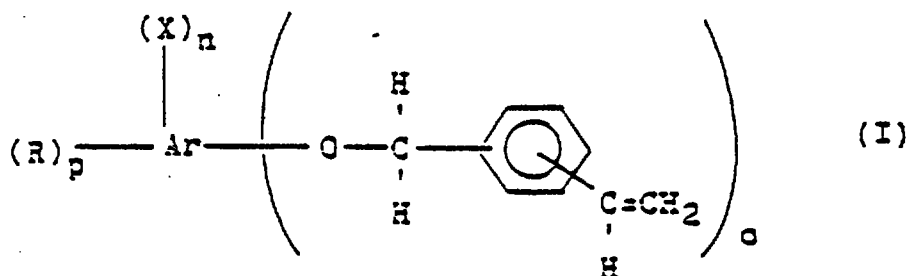
in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogengruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder einer Sauerstoff enthaltenden Gruppe besetzt sind.

7. Copolymerzusammensetzung nach Anspruch 6, dadurch gekennzeichnet, daß die aromatische Polycyanatesterverbindung ein Polycyanatester ist mit Dicyclopentadienbrücke, der der Formel entspricht



in der y größer als oder gleich Null ist.

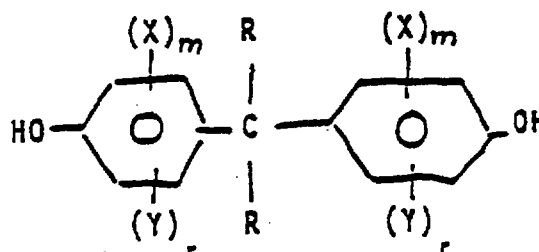
8. Copolymerzusammensetzung nach Anspruch 7, dadurch gekennzeichnet, daß y in der Formel VIII 0,2 ist.
9. Copolymerzusammensetzung, enthaltend ein Reaktionsprodukt eines ethylenisch polymerisierbaren Comonomeren und eines polyfunktionellen Vinylbenzylethers der Formel



in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe durch eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogengruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o

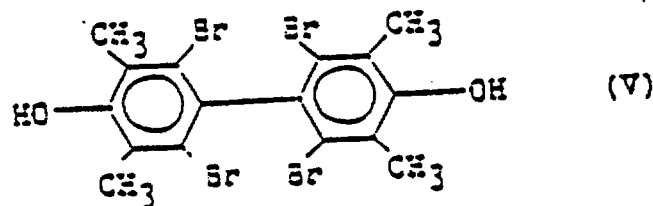


eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder Sauerstoff enthaltender Gruppe besetzt sind, mit der Bedingung, daß, wenn das ethylenisch polymerisierbare Comonomer Styrol oder ein Acrylat ist, die polyfunktionellen Vinylbenzylether der Formel I, die das Reaktionsprodukt von Vinylbenzylchlorid und einer mehrwertigen, halogenierten, phenolischen Verbindung der Formel sind

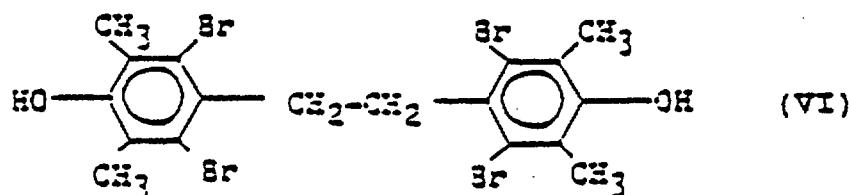


in der R und X die für Formel I angegebene Bedeutung haben, Y eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist und m eine ganze Zahl von 1 oder 2 ist und r eine ganze Zahl von 0 oder 1 ist und die Summe von m + r nicht größer als 2 ist, ausgeschlossen sind.

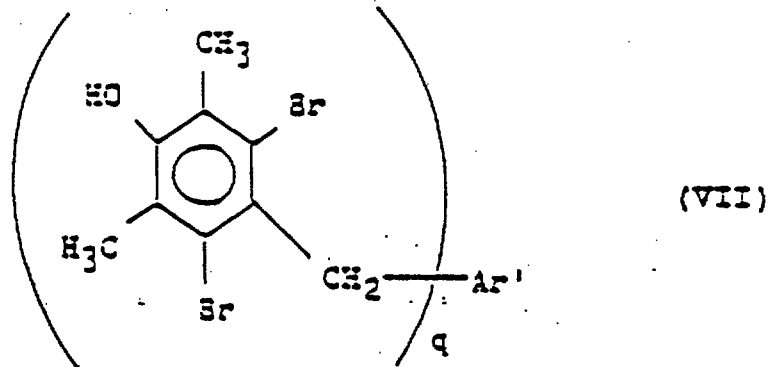
10. Copolymerzusammensetzung nach Ansprüchen 7 oder 8, dadurch gekennzeichnet, daß die Copolymerzusammensetzung eine Dielektrizitätskonstante von kleiner 3 bei 10 kHz und eine V-O Leistung in einer UL-94 Prüfung aufweist.
11. Copolymerzusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß die mehrwertige, halogenierte, phenolische Verbindung ein polyhalogeniertes Biphenol ist.
12. Copolymerzusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das polyhalogenierte Biphenol 3,3',5,5'-Tetramethyl-2,2',6,6'-tetrabrom-4,4'-dihydroxybiphenol ist, das der Formel entspricht



13. Copolymerzusammensetzung nach Anspruch 11, dadurch gekennzeichnet, daß das polyhalogenierte Biphenol 1,2-bis(2,6-Dibrom-3,5-dimethyl-4-hydroxyphenyl)ethan ist, das der Formel entspricht



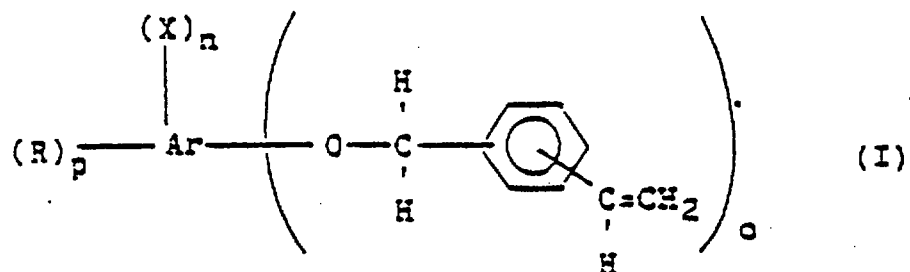
14. Copolymerzusammensetzung nach Anspruch 6,
dadurch gekennzeichnet,
daß die mehrwertige, halogenierte, phenolische Verbindung ein alkyliertes, halogeniertes Mesityl ist,
das der Formel entspricht



in der Ar' ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, wobei Ar' gleich oder unterschiedlich zu Ar von Formel I sein kann und q eine ganze Zahl von mindestens 2 ist.

Patentansprüche für folgende Vertragsstaaten : AT, ES

1. Verfahren zur Herstellung eines polyfunktionellen Vinylbenzylethers der Formel:

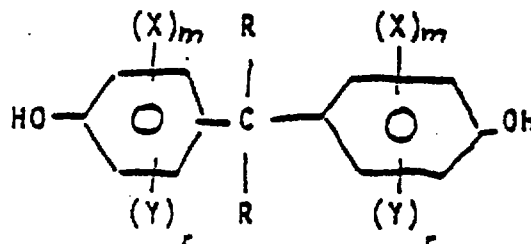


in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe durch eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogensgruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder Sauerstoff enthaltender Gruppe besetzt sind, durch Inberührungbringen unter geeigneten Reaktionsbedingungen einer mehrwertigen, halogenierten, phenolischen Verbindung der Formel:



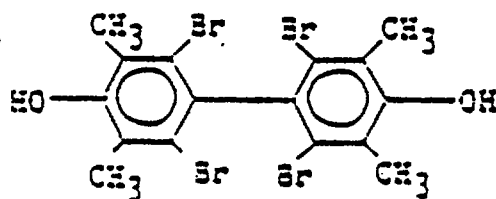
in der Ar, X, R, n und o die für Formel I angegebene Bedeutung haben, p ist die verbleibende Zahl von Stellen am aromatischen Kern, die nicht mit Halogen oder Hydroxylgruppen besetzt sind, mit der Bedingung, daß die mehrwertigen, halogenierten, phenolischen Verbindungen der Formel





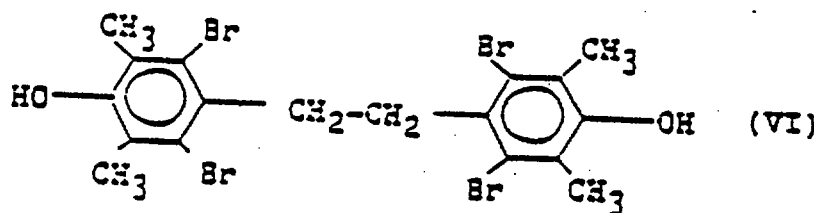
in der R und X die für Formel I angegebene Bedeutung haben, Y eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist und m eine ganze Zahl von 1 oder 2 ist und r eine ganze Zahl von 0 oder 1 ist und die Summe von m+r nicht größer als 2 ist, ausgeschlossen sind, wobei die Menge an Vinylbenzylchlorid ausreichend ist, um ein Reaktionsprodukt zu ergeben, das mindestens 2 Vinylbenzylethergruppen pro mehrwertiger, phenolischer Verbindung aufweist.

2. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß die verwendete mehrwertige, halogenierte, phenolische Verbindung ein polyhalogeniertes Biphenol ist.
3. Verfahren nach Anspruch 2,
dadurch gekennzeichnet,
daß das verwendete polyhalogenierte Biphenol 3,3',5,5'-Tetramethyl-2,2',6,6'-tetrabrom-4,4'-dihydroxybiphenyl ist, das der Formel entspricht



(V)

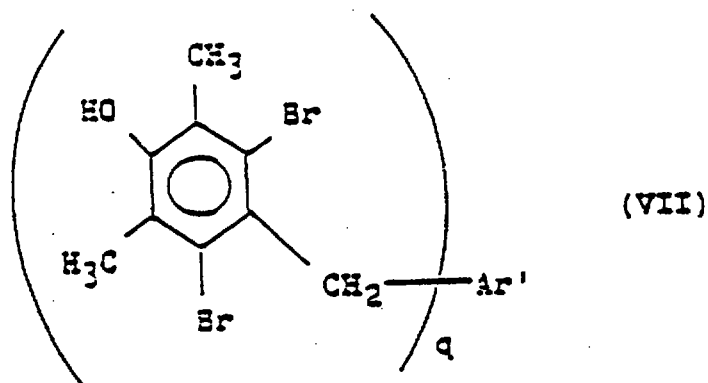
oder 1,2-bis-(2,6-Dibrom-3,5-dimethyl-4-hydroxyphenyl)-ethan ist, das der folgenden Formel entspricht



(VI)

4. Verfahren nach Anspruch 1,
dadurch gekennzeichnet,
daß die verwendete mehrwertige, halogenierte, phenolische Verbindung ein alkyliertes, halogeniertes Mesitol der folgenden Formel ist





15 in der Ar' ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte aromatische Ringe oder die aromatischen Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, wobei Ar' die gleiche oder unterschiedliche Bedeutung wie Ar der Formel I haben kann und q eine ganze Zahl von

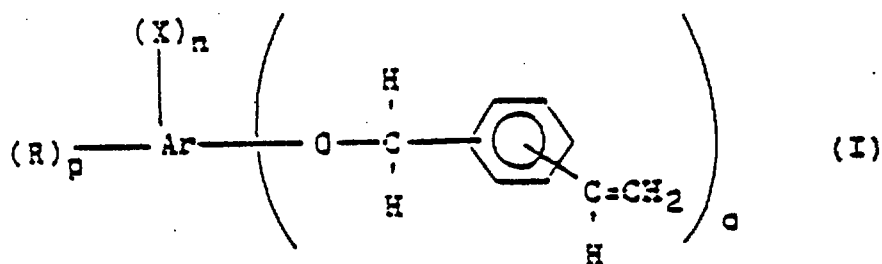
20 mindestens 2 ist.

5. Verfahren nach jedem der Ansprüche 1-4,
dadurch gekennzeichnet,
daß es in Gegenwart eines Lösemittels ausgeführt wird.

6. Verfahren nach jedem der Ansprüche 1-4,
dadurch gekennzeichnet,
daß es in Gegenwart einer geeigneten Base ausgeführt wird.

7. Verfahren nach jedem der Ansprüche 1-4,
dadurch gekennzeichnet,
daß es bei Temperaturen im Bereich von 20 °C-150 °C ausgeführt wird.

8. Verfahren zur Herstellung einer Copolymerzusammensetzung durch Erwärmen in Gegenwart eines geeigneten Trimerisationskatalysators einer aromatischen Polycyanatesterverbindung mit einem polyfunktionellen Vinylbenzylether der Formel



50 in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogengruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder einer Sauerstoff enthaltenden Gruppe besetzt sind.

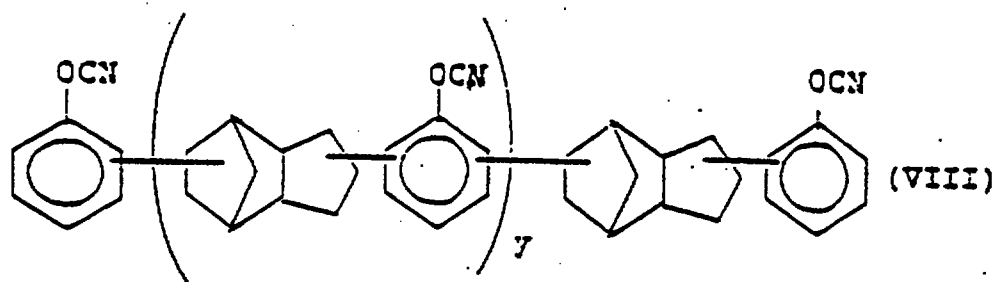
9. Verfahren nach Anspruch 8,
dadurch gekennzeichnet,
daß die verwendete aromatische Polycyanatesterverbindung ein Polycyanatester ist mit Dicyclopenta-



dienbrücke, der der Formel entspricht

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in der y größer als oder gleich Null ist und der Katalysator Kobalnaphthenat oder Kobaltacetylacetonat ist.

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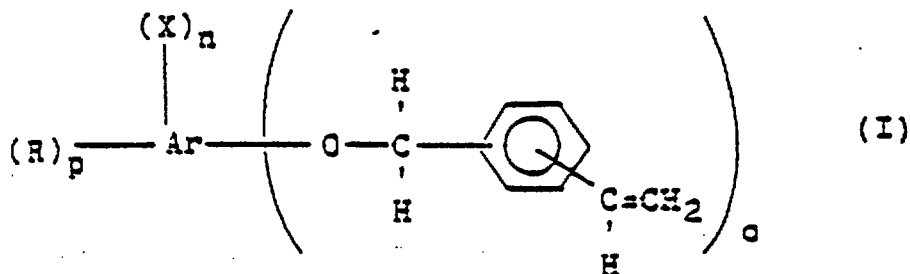
10. Verfahren nach Anspruch 9,
dadurch gekennzeichnet,
daß y in der Formel VIII 0,2 ist.

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11. Verfahren nach Ansprüchen 9 oder 10,
dadurch gekennzeichnet,
daß die Copolymerzusammensetzung eine Dielektrizitätskonstante von kleiner 3 bei 10 kHz und eine V-O Leistung bei UL-94 Prüfung aufweist.

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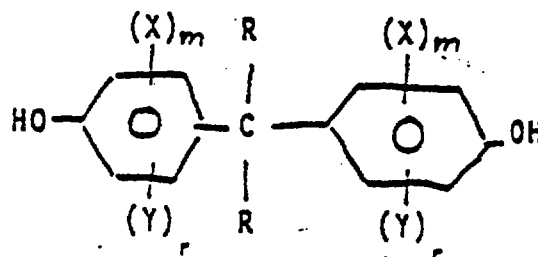
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in der Ar ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe durch eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, X eine Halogengruppe ist, R Wasserstoff oder eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist, n eine ganze Zahl von mindestens 1 ist, o eine ganze Zahl von mindestens 2 ist und p die verbleibende Zahl von Stellen am aromatischen Kern ist, die nicht mit Halogen oder Sauerstoff enthaltender Gruppe besetzt sind, mit der Bedingung, daß, wenn das ethylenisch polymerisierbare Comonomer Styrol oder ein Acrylat ist, die polyfunktionellen Vinylbenzylether der Formel I, die das Reaktionsprodukt von Vinylbenzylchlorid und einer mehrwertigen, halogenierten, phenolischen Verbindung der Formel sind

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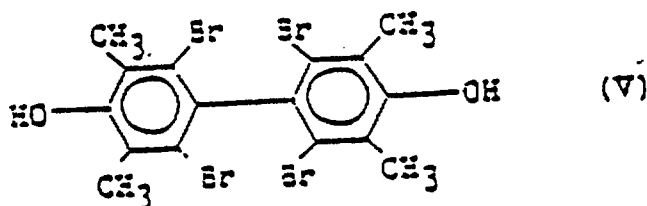
in der R und X die für Formel I angegebene Bedeutung haben, Y eine Alkylgruppe mit 1-6 Kohlenstoffatomen ist und m eine ganze Zahl von 1 oder 2 ist und r eine ganze Zahl von 0 oder 1 ist und die Summe von $m + r$ nicht größer als 2 ist, ausgeschlossen sind.

13. Verfahren nach Anspruch 12,
dadurch gekennzeichnet,

daß die zur Herstellung des polyfunktionellen Vinylbenzylesters verwendete mehrwertige, halogenierte, phenolische Verbindung ein polyhalogeniertes Biphenol ist.

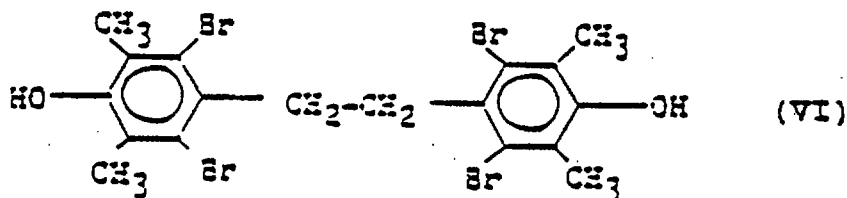
14. Verfahren nach Anspruch 13,
dadurch gekennzeichnet,

daß das verwendete polyhalogenierte Biphenol 3,3',5,5'-Tetramethyl-2,2',6,6'-tetrabrom-4,4'-dihydroxybiphenol ist, das der Formel entspricht



15. Verfahren nach Anspruch 13,
dadurch gekennzeichnet,

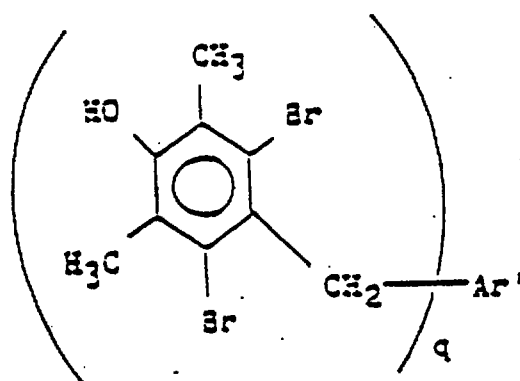
daß das polyhalogenierte Biphenol 1,2-bis(2,6-Dibrom-3,5-dimethyl-4-hydroxyphenyl)ethan ist, das der Formel entspricht



16. Verfahren nach Anspruch 12,
dadurch gekennzeichnet,

daß die zur Herstellung des polyfunktionellen Vinylbenzylethers verwendete mehrwertige, halogenierte, phenolische Verbindung ein alkyliertes, halogeniertes Mesityl ist, das der Formel entspricht





(VII)

in der Ar' ein aromatischer Kern mit 6-24 Kohlenstoffatomen ist, enthaltend einen einzigen aromatischen Ring oder mehrere kondensierte, aromatische Ringe oder die Ringe über eine direkte Bindung oder eine Kohlenwasserstoffbrückengruppe miteinander verbunden sind, wobei Ar' gleich oder unterschiedlich zu Ar von Formel I sein kann und q eine ganze Zahl von mindestens 2 ist.

