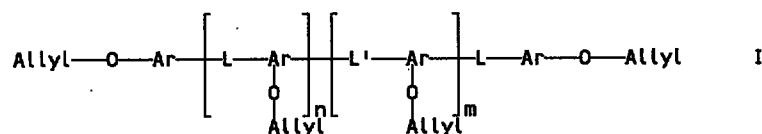


PHENOLIC ALLYL ETHER CROSS-LINKING AGENTS

This invention relates to novel phenolic allyl ethers and polymaleimide resins cross-linked with those ethers.

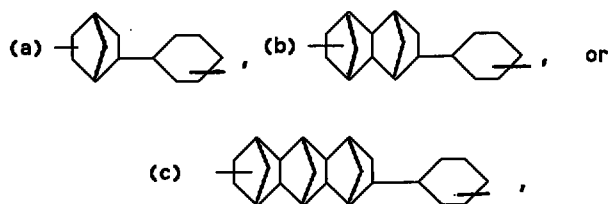
Phenolic allyl ether or allyl phenol compounds, for example, o,o'-diallylbisphenol-A, have been reported to be useful as toughing agents for polymaleimides. Polymaleimides are useful in structural and electronic applications where high-performance is required. However, polymaleimides are brittle and require toughing agents, and in addition have high melting points and are difficult to process. Therefore it is desirable to have phenolic allyl ethers which are useful not only as toughing agents, but also promote easier processing of polymaleimides.

In one embodiment, the present invention provides novel phenolic allyl ethers of the formula I:-



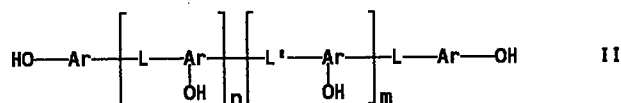
in which Ar is C₆-20 aromatic moiety, L is a divalent cyclohexanenorbornane linking moiety, L' is a divalent cycloaliphatic moiety, Allyl is the group CH₂=CH-CH₂-, and each of m and n is a number from 0 to 20.

Preferred phenolic allyl ethers of formula I are those wherein Ar is a phenyl group; and/or n is 0 to 10, especially 0 to 3, and L is a cyclohexanenorbornane of the formula



group a) being especially preferred; and/or m is zero. A particularly preferred compound is the reaction product of allyl halide with the product of the addition reaction of a phenol and a cyclohexenenorbornene compound such as 5-(3-cyclohexen-1-yl)-bicyclo[2.2.1]hept-2-ene.

The phenolic allyl ether of this invention can be prepared by reacting an allyl halide, such as allyl bromide, with a precursor polyphenol of the formula II



wherein Ar, L and each of m and n are as defined in formula I. This reaction can be carried out in the presence of a base at a temperature within the range of from 80°C, to 150°C, preferably 100°C-150°C and especially about 130°C. The base can be any conventional base such as, for example, carbonates and hydroxides of alkali and alkaline earth metals (e.g. sodium carbonate, potassium carbonate, calcium carbonate, sodium hydroxide and potassium hydroxide).

The precursor polyphenols can be prepared by the addition reaction of a phenol with a cyclohexenenorbornene compound such as 5-(3-cyclohexen-1-yl) bicyclo[2.2.1]hept-2-ene (herein referred to as the "cyclohexenenorbornene" compound). Suitable

phenols include mono- and polynuclear phenols having at least one unsubstituted position ortho- or para- to a phenolic hydroxyl group, such as phenol, cresol, 3,4- and 3,5-dimethylphenol, resorcinol, biphenol, 1-naphthol and bisphenol A or F. Phenol is preferred.

Other suitable cyclohexenenorbornene compounds include



referred to herein as "diadduct" and "triadduct," respectively, and isomers thereof.

The cyclohexenenorbornene compound is an addition product of 4-vinylcyclohexene and cyclopentadiene, which can be prepared by contacting 4-vinylcyclohexene and dicyclopentadiene, preferably in the presence of a polymerization inhibitor such as t-butyl catechol, at a temperature of at least 150°C, preferably 180 to 260°C, for a time within the range of 2 hours to 8 hours. Under these conditions, the dicyclopentadiene is cracked to cyclopentadiene, and the vinylcyclohexene and cyclopentadiene undergo an addition reaction to produce a mixture of mono-, di- and poly-adducts as well as cyclopentadiene oligomers (e.g., trimer, tetramer, pentamer, etc.). For recovery of one or more desired compounds, the reaction product mixture containing predominately 5-(3-cyclohexen-1-yl)bicyclo[2.2.1]hept-2-ene is allowed to cool to about 50 - 70°C and is stirred under reduced pressure to strip off unreacted vinylcyclohexene. The reaction product may then be purified by fractional vacuum distillation for removal of unwanted by-products including, optionally, di- and polyadducts, and the purified product passed through an adsorbent bed for removal of

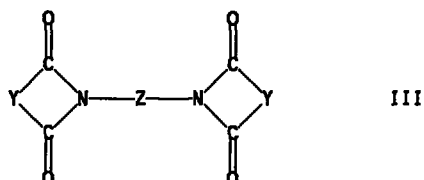
t-butyl catechol. Preparation of a vinylcyclohexene/cyclopentadiene adduct is described in U.S. Patent Nos. 5,260,498, and 5,284,929.

The starting phenol can also include a derivative L' of a cyclo-aliphatic diene such as dicyclopentadiene, cyclopentadiene, norbornadiene dimer, norbornadiene, methylcyclopentadiene dimer, limonene, 1,3- and 1,5-cyclooctadiene, α - and γ -terpinene, 5-vinylnorbornene, 5-(3-propenyl)-2-norbornene and cyclopentadiene oligomers, for example.

The phenolic precursors of formula II can be prepared by contacting, under addition reaction conditions, one or more of the above-described vinylcyclohexene/cyclopentadiene adduct(s) with a molar excess, preferably 10 to 30 moles, of the selected phenol per mole of the adduct(s). The reaction is most efficiently carried out in the presence of a Lewis acid such as BF₃, coordination complexes thereof such as boron trifluoride etherate, AlCl₃, FeCl₃, SnCl₄, ZnCl₂, silica and silica-alumina complexes and at an elevated temperature within the range of 70 to 200°C, preferably 100 to 180°C. The reaction is continued until the desired degree of reaction has been completed, usually for a time within the range of 30 minutes to 10 hours, preferably 1 hour to 3 hours. Preparation of such polyphenols is described in Examples 2 and 4 of U. S. Patent No. 5,284,929.

The invention phenolic allyl ethers can be combined with polymaleimides and the mixture cured by exposure to elevated temperature, e.g. within the range of 150 to 250°C for a time which can vary widely depending on the cure schedule and thickness of the part, generally greater than 0.25 hour, and the cured products are useful as the resinous components of electrical laminating and encapsulation formulations.

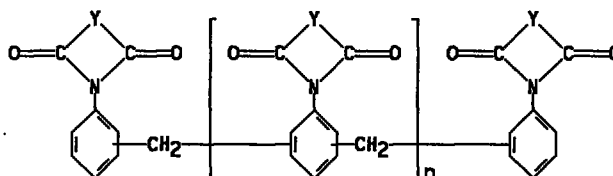
The preferred polymaleimides may be bis- and higher-maleimide resins such as tris- and tetra-maleimide resins, but preferably are N,N-unsaturated bismaleimides which can be represented by the formula III



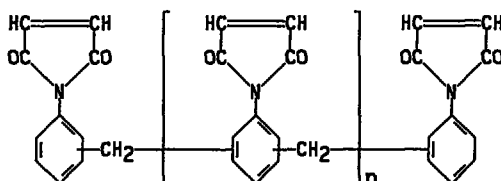
in which Y is a substituted or unsubstituted divalent radical having at least 2 carbon atoms and a carbon-carbon double bond, and Z is a divalent radical containing from about 2 to about 40 carbon atoms. Z can be aliphatic, cycloaliphatic, aromatic or heterocyclic. Z can include heteroatoms and can be substituted or unsubstituted. Examples of bismaleimides which can be employed are N,N-bismaleimides of ethylene diamine, hexamethylene diamine, trimethylhexamethylene diamine, phenylene diamine, trimethylhexamethylene diamine, methylene dianiline, toluene diamine, 4,4-diphenylmethane diamine, 3,3-diphenylsulfone diamine, 4,4-diphenylether diamine, 4,4-dicyclohexanemethane diamine, metaxylylene diamine, and 4,4-diphenylcyclohexane diamine. Various N,N-bismaleimides are disclosed in U.S. Pat. Nos. 3,562,223, 4,100,140, 4,211,860, 4,211,860 and 4,816,531, for example, and can be prepared by methods known in the art. The N,N-unsaturated bismaleimides are preferably derived from at least one aromatic diamine. The preferred bismaleimide is bismaleimide of methylenedianiline. The bismaleimide can contain various additives as processing aids. Suitable N,N-unsaturated bismaleimides are available commercially

from Shell Chemical Co. as Compimide® resins, for example.

Other suitable polymaleimide resins include compounds which can be represented by the formula



in which Y is a substituted or unsubstituted divalent radical having at least 2 carbon atoms, preferably 2 to 6 carbon atoms, and a carbon-carbon double bond and n is a number having an average value of 0 or greater, preferably an average value from about 0 to about 4. Such polymaleimides are disclosed in U. S. Pat. No. 4,298,720, for example. Specific examples of such compounds include polymethylenephenylenemaleimides having the formula



in which n is a number having an average value of 0 or greater, preferably an average value from about 0 to about 4. These polymaleimides can be obtained by reacting an aniline-formaldehyde condensation product with maleic anhydride as described in the above patent.

The amount of the phenolic allyl ether combined with the polymaleimide can vary depending on the process conditions, such as the reactivity of the polymaleimides to the allyl ether groups and reaction

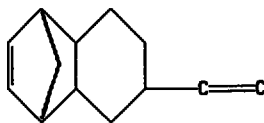
temperatures. Generally phenolic allyl ethers will be present in an amount effective to promote ease of processing or to give a tougher cured composition. The weight ratio of polymaleimides to phenolic allyl ether is preferably within the range from 10:90 to 90:10, most preferably from 40:60 to 60:40. Optimum properties in the cured resin can be achieved by a staged heating process employing higher temperature in each successive stage, as illustrated in section D of the Example below.

The invention is illustrated in the following Example.

Example

A) Preparation of 5-(3-cyclohexen-1-yl)bicyclo[2.2.1]hept-2-ene.

Dicyclopentadiene and 4-vinylcyclohexene in equimolar mixture were heated in an autoclave at 240°C for 4-4.5 hours. The reaction product was diluted with cyclohexane and passed through a packed bed of alumina to remove the t-butyl-catechol inhibitor introduced with the reactants. The resulting product mixture was distilled in a wiped film evaporator at 3 mm Hg pressure at 90°C to produce a light fraction containing unreacted vinylcyclohexene and dicyclopentadiene and the mono-adducts of 4-vinylcyclohexene and cyclopentadiene. A 150g sample of this distillate was vacuum distilled using a 10-tray Oldershaw column to give four fractions. The fourth fraction, 65g, was shown by gas chromatographic analysis to consist of 0.15% dicyclopentadiene, 88.3% endo-5-(3-cyclohexen-1-yl)-2-norbornene, 6.1% exo-5-(3-cyclohexen-1-yl)-2-norbornene and two additional components present in the amount of 1.9% and 2.4% which are believed to be isomeric adducts of the formula

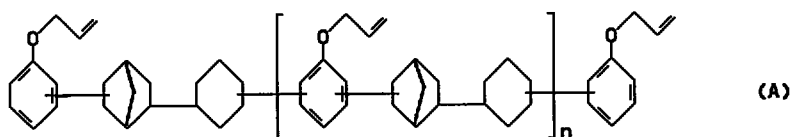


several additional components totalling about 0.4%, 0.4% tricyclopentadiene and about 0.4% unidentified components. Analysis of the fraction by nuclear magnetic resonance indicated about 87 mole percent of the endo adduct, about 9 mole percent of the exo adduct and about 5% of the isomeric adducts.

B) Preparation of Monoadduct Polyphenol

To a reactor equipped with a stirrer, condensor and additional funnel were added 188.2g (2.0 mole) of phenol and 1.0g of $\text{BF}_3\text{Et}_2\text{O}$. The mixture was heated to 70°C and 13.67g of 5-(3-cyclohexen-1-yl)bicyclo[2.2.1]hept-2-ene was added over a 20-minute period. The temperature was raised to 150°C over a 1 1/2-hour period and was held for about 2 1/2 hours. Unreacted phenol was distilled off. The recovered polyphenol had a terminal hydroxyl group concentration of 0.495 equivalent/100g and a melting point of $70-80^\circ\text{C}$.

C) Preparation of allyl ether



A mixture of 50g of a polyphenol which has been prepared from phenol and 5-(3-cyclohexen-1-yl)bicyclo[2,2,1]hept-2-ene according to the procedure in Example 2 above (a terminal hydroxyl group concentration of 0.495 equivalent/100g and a melting

point of 70-80°C), 18.66g of potassium carbonate and 200ml of toluene was placed in a 1 liter round bottomed flask equipped with a mechanical stirrer and a condensor, and warmed to 120-130°C while stirring. Water was removed by azeotropic distillation until completion, then the temperature was lowered to 80-90°C. Allyl bromide (32.66g) in 50ml of toluene was added over 60 minutes to the reaction mixture. Then the reaction temperature was raised to 125°C and held there for 12 hours. After cooling, the reaction mixture was filtered and filtrates were concentrated to give a liquid composition (Recovered 57.1g). Confirmation of the above structural formula A for the product where n is 0.5 is made by nuclear magnetic resonance spectra.

D) Use of allyl ether as bismaleimide cross-linking agent.

1.39g of allyl ether A was cross-linked with 1.36g of bismaleimide/ methylene dianiline resin ("MDA"; melting point 150°C) by heating at 200°C for 4 hours and 240°C for 2 hours to give a cured material having $T_g > 300^\circ\text{C}$ and 10% wt. loss temp in Thermal Gravimetric Analysis (Air) at 450°C.



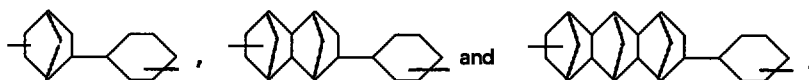
C L A I M S

1. A phenolic allyl ether of the formula I

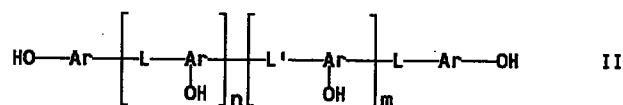


in which Ar is a C₆-20 aromatic moiety, L is a divalent cyclohexanenorbornane linking moiety, L' is a divalent cyclo-aliphatic linking moiety, allyl is the group CH₂=CH-CH₂- and each of m and n is a number from 0 to 20.

2. A phenolic allyl ether as claimed in claim 1, in which each Ar is phenyl.
3. A phenolic allyl ether as claimed in claim 1 or 2, in which L is selected from at least one of



4. A phenolic ether as claimed in claim 1,2 or 3 wherein n is from 0 to 10.
5. A phenolic ether as claimed in claim 4 wherein n is from 0 to 3 and m is zero.
6. A process for the preparation of a phenolic allyl ether as defined in claim 1 which comprises reacting an allyl halide with a precursor polyphenol of formula II



7. Process as claimed in claim 6 wherein the reaction is carried out by heating to 80°C-150°C in the presence of a base.
8. A composition comprising a polymaleimide and a phenolic allyl ether as claimed in any one of the preceding claims.
9. A composition as claimed in claim 8 wherein the polymaleimide is the bismaleimide of methylene dianiline.
10. A cured product obtained by heating a composition as claimed in claim 8 or 9.