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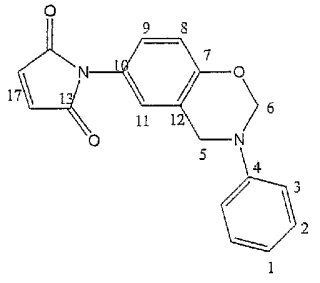
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(54) Title: FUNCTIONALIZED BENZOXAZINES, POLYMERS AND COPOLYMERS THEREOF



(57) Abstract: The present invention relates to monofunctional benzoxazines having non-benzoxazine functional groups thereon. Polymers of benzoxazine can be formed from the monomers through functional group polymerization as well as benzoxazine polymerization utilizing the same or different mechanisms. The functionalized benzoxazine materials are high performance polymers having glass transition temperature about 200° C and which exhibit other desirable properties such as increase of char yield without a significant increase in viscosity of the monomer. Furthermore, the functionalized benzoxazine monomers can be copolymerized with other monomers such as epoxy. The benzoxazine copolymers exhibit toughness, processability, and excellent thermal properties.

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FUNCTIONALIZED BENZOXAZINES, POLYMERS AND COPOLYMERS THEREOF

FIELD OF THE INVENTION

The present invention relates to monofunctional benzoxazines having non-benzoxazine functional groups thereon. Polymers of benzoxazine can be formed from the monomers through functional group polymerization as well as benzoxazine polymerization utilizing different mechanisms. The functionalized benzoxazine materials are high performance polymers having glass transition temperatures above 200°C and exhibit other desirable properties such as increase of char yield without a significant increase in viscosity of the monomer. Benzoxazine polymers having a crosslinked network structure are formed from the monomers. In further embodiments, the functionalized benzoxazine monomers are copolymerized with other reactive monomers, oligomers, or polymers such as epoxy resins, vinyl containing monomers, or other benzoxazines. In yet another embodiment, interpenetrating polymer networks are formed between the monobenzoxazines of the present invention and another monomer or polymers that does not form a copolymer with the benzoxazine monomer used. The thermoset benzoxazine copolymers exhibit toughness, processability, and excellent thermal properties.

BACKGROUND OF THE INVENTION

In recent years, various polymers have been developed to withstand severe thermal and/or chemical environments for aerospace, electronic and structural applications. Such polymers include high performance thermosets such as bismaleimides, bisnadimides and advanced epoxy resins. Although such resins may exhibit improved thermal and thermo-oxidative resistance,

chemical resistance, and high mechanical strength, the known resins face numerous processability issues due to their high viscosity, high melting points, and low solubility in organic solvents. Various approaches to improved processability have been attempted, with incorporating softer molecular segments into the polymer chain, using two-step curing systems, or by creating copolymers or blends, for example.

Polybenzoxazine and polymers derived from the ring opening polymerization of benzoxazine compounds compete with the above-noted thermoset or thermoplastic resins in various applications as they have been shown to have desirable thermal and mechanical properties. Polybenzoxazines exhibit advantages over conventional thermoset resins as the benzoxazines can be readily molded and polymerized without releasing substantial amounts of polymerization reaction by-products, i.e., volatiles.

SUMMARY OF THE INVENTION

Functionalized monofunctional benzoxazines and the synthesis thereof are disclosed. The various functionalities which can be incorporated into the benzoxazines are derived in part from functional group containing phenols and/or amines and include, but are not limited to, maleimide groups, norbornene groups, vinyl groups, allyl groups, alkyne groups, and thiol groups.

The functionalized monofunctional benzoxazines are formed into polymers through functional group polymerization and/or benzoxazine polymerization utilizing multiple polymerization mechanisms. Thus, three different reactive mechanisms are possible. The functionalized monofunctional benzoxazines are polymerized through a) reaction of the benzoxazine functionality, b)

reaction of the functional group on the benzoxazine monomer derived from the phenol, or c) reaction of the functional group on the benzoxazine monomer derived from the amine, or a combination thereof. The functional group polymerizations may be carried out by a different polymerization mechanism than the benzoxazine functionality polymerization, i.e., ring opening polymerization. The polymerization mechanisms have been monitored by Fourier transform infrared spectroscopy (FT-IR) and differential scanning scanning calorimetry (DSC), wherein the extent and type of polymerization, which impact the final network structure of the polymer have been characterized. The functionalized monofunctional benzoxazine polymers exhibit improved thermal properties such as char yields above 55% and glass transition temperatures above 250°C.

In addition to the above-noted polymerization, the functionalized benzoxazines in one embodiment are copolymerized with other monomers, polymers, or resins, such as epoxy, vinyl containing monomers, and other benzoxazines. It has been unexpectedly found that toughness and processability can be improved without compromising thermal properties. In fact, glass transition temperatures can even be improved when compared with some functionalized benzoxazine polymers. Highly crosslinked polymers are formed in one embodiment. In yet a further embodiment, interpenetrating polymer networks are formed utilizing the functionalized monobenzoxazines of the present invention.

The compounds, polymers and copolymers of the present invention can be utilized whenever thermal resistance or flame resistance is needed such as in molded applications; adhesive applications; electronic packaging materials such as circuit boards

and chip housings; and fuel cell parts. Importantly, the present invention embodiments can be used as a thermosetting resin replacement, such as for epoxy.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood and other features and advantages will become apparent by reading the detailed description of the invention, taken together with the drawings, wherein:

FIGS. 1A-B illustrate the structures of maleimide functionalized benzoxazine and norbornene functionalized benzoxazine and ^{13}CNMR assignments.

FIG. 2 illustrates the ^{1}HNMR spectra of (a) maleimide functionalized benzoxazine and (b) norbornene functionalized benzoxazine in $(CD_3)_2CO$.

FIG. 3 illustrates the ^{13}CNMR spectra of (a) maleimide functionalized benzoxazine and (b) norbornene functionalized benzoxazine in $CDCl_3$.

FIG. 4 illustrates the TGA thermogram of maleimide functionalized benzoxazine polymer cured at 150°C for 2 hours, 170°C for 2 hours, and 190°C for 1 hour.

FIG. 5 illustrates the TGA thermogram of norbornene functionalized polymer cured at 150°C for 1 hour, 180°C for two hours and 220°C for 1 hour.

FIG. 6 illustrates the shear viscosity of maleimide functionalized benzoxazine at various temperatures.

FIG. 7 illustrates the differential scanning calorimetry (DSC) thermograms of norbornene functionalized benzoxazine polymerization.

FIG. 8 illustrates the differential scanning calorimetry (DSC) thermogram of maleimide functionalized benzoxazine polymerization and (a) its polymerization with different initiators; (b) 2,2'-azobisisobutyronitrile (AIBN), (c) benzoyl peroxide (BPO) and (d) dicumyl peroxide (DICUP).

FIG. 9 illustrates the Fourier transform infrared spectroscopy (FTIR) spectra of (a) maleimide functionalized benzoxazine monomer (b) partially cured monomer at 140°C, (c) 180°C and (d) 220°C.

FIG. 10 illustrates the FTIR spectra of (a) norbornene functionalized benzoxazine monomer and (b) partially cured monomer at 170°C.

FIG. 11 illustrates the FTIR spectra of (a) maleimide functionalized benzoxazine monomer with 5 mol% 2,2'-azobisisobutyronitrile (AIBN) (a) partially cured monomer at 140°C (b), 180°C (c), and 220°C (d).

FIG. 12 illustrates the FTIR spectra of maleimide functionalized benzoxazine at (a) 160°C and (b) 240°C and 1:1 mole ratio of maleimide functionalized benzoxazine and diglycidyl ether of bisphenol-A at (c) 160°C and (d) 240°C between 1550 cm^{-1} and 1800 cm^{-1}.

FIG. 13 illustrates the FTIR spectra of maleimide functionalized benzoxazine at (a) 160°C and (b) 240°C and 1:1 mole ratio of maleimide functionalized benzoxazine and diglycidyl ether of bisphenol-A at (c) 160°C and (d) 240°C between 750 cm^{-1} and 1250 cm^{-1}.

FIG. 14 illustrates the DSC thermograms of (a) maleimide functionalized benzoxazine; and maleimide functionalized benzoxazine/diglycidyl ether of bisphenol-A copolymers with

different percentages of diglycidyl ether of bisphenol-A (b) 10%, (c) 20%, (d) 30%, (e) 40% and (f) 50%.

FIG. 15 illustrates the dynamic mechanical spectra of 30% epoxy copolymer, cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 30 minutes. G' (solid line), G'' (dotted line), and tan delta (dashed line).

FIG. 16 illustrates the dynamic mechanical spectra of 30% epoxy copolymer, cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 12 hours. G' (solid line), G'' (dotted line), and tan delta (dashed line).

FIG. 17 illustrates the dynamic mechanical spectra of 10% epoxy copolymer, cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 30 minutes. G' (solid line), G'' (dotted line), and tan delta (dashed line).

FIG. 18 illustrates the dynamic mechanical spectra of 10% epoxy copolymer, cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 12 hours. G' (solid line), G'' (dotted line), and tan delta (dashed line).

FIG. 19 illustrates the storage modulus versus different compositions of maleimide functionalized benzoxazine/diglycidyl ether of bisphenol-A copolymer.

FIG. 20 illustrates the glass transition temperature versus composition of diglycidyl ether of bisphenol-A, (●) cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 12 hours, (♦) cured at 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours, and 210°C for 30 minutes.

FIG. 21 illustrates the tan δ curve from dynamic mechanical analysis with (a) 10%, (b) 20%, (c) 30%, (d) 40%, and (e) 50% diglycidyl ether of bisphenol-A.

FIG. 22 illustrates density versus composition of diglycidyl ether of bisphenol-A.

FIG. 23 illustrates the variations of flexural modulus of different compositions of maleimide functionalized benzoxazine/diglycidyl ether of bisphenol-A copolymers.

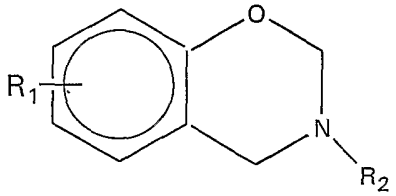
FIG. 24 illustrates the variations of flexural strain at breakage of different compositions of maleimide functionalized benzoxazine/diglycidyl ether of bisphenol-A copolymers.

FIG. 25 illustrates the variations of flexural stress at breakage of different compositions of maleimide functionalized benzoxazine/diglycidyl ether of bisphenol-A copolymers.

DETAILED DESCRIPTION OF THE INVENTION

Functionalized Monobenzoxazine Monomers

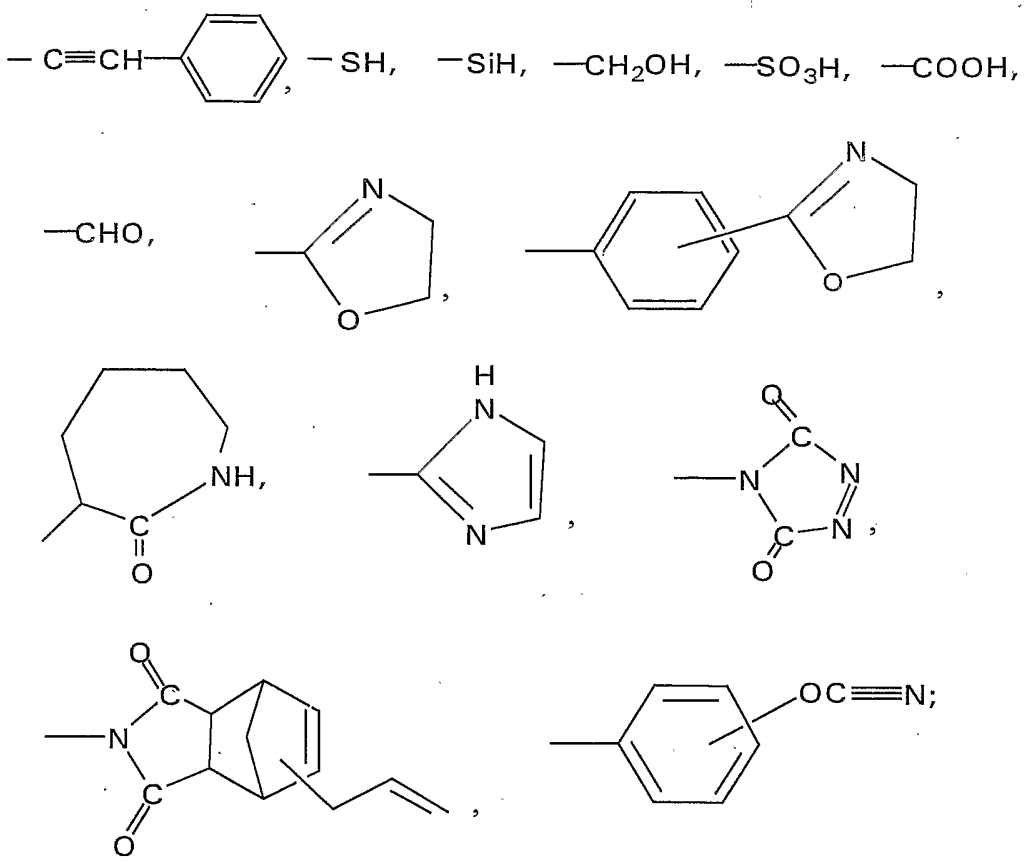
The functionalized monobenzoxazine monomers of the present invention are disclosed by the general formula:



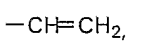
Formula I

wherein R_1 is hydrogen, an alkyl having 1 to about 18 carbon atoms with about 1 to about 12 carbon atoms being preferred, an aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

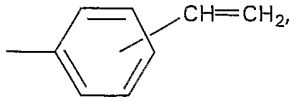
$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$ where n =1 - 6, $-C\equiv CH$, $-CH_2-C\equiv CH$,

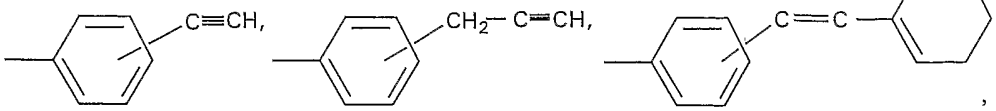


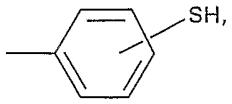
wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms with about 1 to about 12 carbon atoms being preferred, an aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,

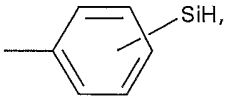


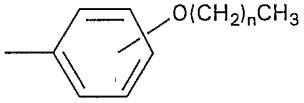
where n =1 - 6,



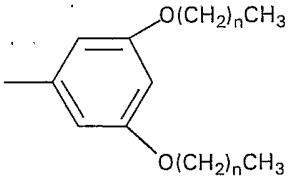




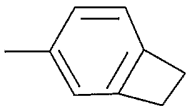


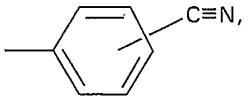


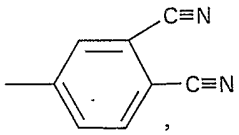
where n =0 -3,

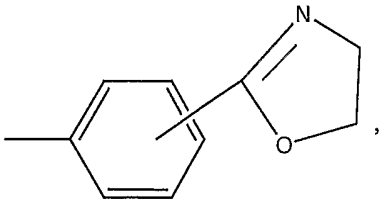


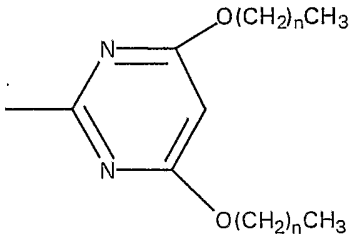
where n =0 - 2,



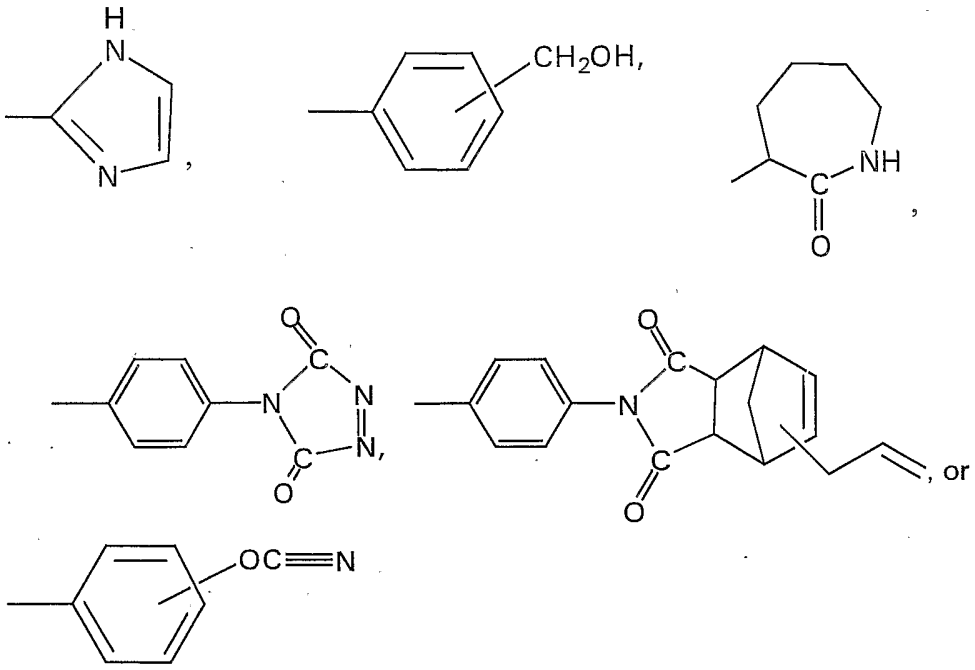






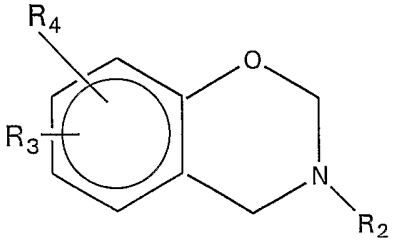


where n =0 - 2,



with the proviso that at least one of R_1 or R_2 includes a reactive functional group. The term reactive functional group is known in the art and refers to a functional group or substituent which is capable of undergoing or participating in a polymerization or other coupling reaction, such as free radical polymerization. The reactive functional group is dormant and does not react during the benzoxazine monomer formation. R_1 can be in an ortho, meta or para position. As will be discussed hereinbelow, the R_1 substituent and associated benzene ring are generally derived from a phenol, preferably a functionalized phenol.

The functionalized monobenzoxazine monomers of the present invention are also disclosed by the general formula:



Formula II

wherein R_3 and R_4, independently, is R_1 as defined herein, or —C≡N,

or wherein R_3 and R_4 together form a cyclic structure with the benzene ring and have from 2 to about 12 carbon atoms collectively, with 2 to about 6 carbon atoms preferred, not including the benzene ring carbon atoms; and

wherein R_2 is defined hereinabove;

with the proviso that at least one of R_2, R_3, or R_4 is a reactive functional group as defined herein.

The functionalized monobenzoxazine monomers of the present invention are generally synthesized from the reaction of three reactants: a) phenols, optionally containing a reactive functional group; b) aldehydes or aldehyde derivatives and c) primary amines, which optionally contain a reactive functional group; using a solvent or solventless system with the proviso that at least one of the phenol or amine components contains a reactive functional group.

The procedure of using solvents to form benzoxazine is common to the literature of benzoxazine monomers and is known to one of ordinary skill in the art. An article by Ning and Ishida in the Journal of Polymer Science, Chemistry Edition, vol. 32, page 1121 (1994) sets forth a procedure using a solvent which can be used to prepare benzoxazine monomers. U. S. Patent No. 5,543,516, hereby incorporated by reference, sets forth a generally solventless method of forming benzoxazine monomers.

The phenols of the present invention either do not contain a reactive functional group or are mono-, di-, or poly-functional phenols having a reactive functional group(s) which are located in an ortho, meta and/or para position. Various preferred

functionalized phenols include but are not limited to, 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione, and p-hydroxyphenylnadimide. The phenols are commercially available or can be synthesized as known to those of ordinary skill in the art.

The aldehydes and aldehyde derivatives used to form the benzoxazine monomers can be any aldehyde such as formaldehyde, or aldehyde derivatives such as but not limited to, paraformaldehyde and polyoxymethylene, with formaldehyde and paraformaldehyde being preferred. The aldehydes have the general formula RCHO, where R is hydrogen; an aliphatic having 1 to about 6 carbon atoms; or a cyclic group having from about 1 to about 12 carbon atoms, with 1 to about 6 carbon atoms being preferred. Preferably R is hydrogen. Mixtures of aldehydes and/or aldehyde derivatives can be utilized.

The amines used to form the benzoxazine monomers are preferably monoamines and can be aromatic, aliphatic, alkyl substituted aromatic, or aromatic substituted alkyl amines. The amines can optionally contain reactive functional groups defined by R_2. The amine can also be a polyamine so long as the benzoxazine monomer formed remains monobenzoxazine. The amines used to form the benzoxazine generally have from about 1 to about 40 carbon atoms, unless they include an aromatic ring in which case the amine would have from 6 to about 40 carbon atoms. Preferred amines include aniline.

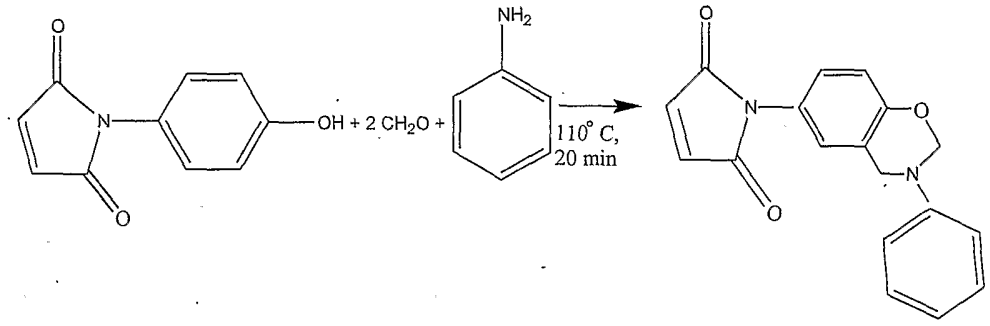
The reaction time for forming the monofunctional benzoxazine monomers can vary widely and depend on reactant concentration, reactivity of the reactants, and temperature. Reaction time can vary from a few minutes for a solventless reaction, or be from about a few minutes to about 100 hours and

preferably from about 1 to about 50 hours when utilizing solvents. Solid components may be premixed as solids and subsequently melted; or first melted and then mixed. The temperature of reaction is determined by routine experimentation as known to those of ordinary skill in the art, noting the formation of benzoxazine and less desired products and optimizing temperature and time for a desirable product. Reaction temperatures generally range from about 0°C to about 160°C, desirably from about room temperature to about 155°C, and preferably from about 50°C to about 150°C.

The functionalized monobenzoxazine synthesis reaction may be conducted at atmospheric pressure or at pressures up to about 100 psi. In some instances, a reaction carried out under pressure may be preferred in order to produce fewer by-products. The relative amounts of reactants required will depend upon their chemical nature, e.g., the number of reactive groups taking part in the reaction. The stoichiometry is well within the skills of those conversant with the art and the relative required amounts of reactants are readily selected depending on the functionality of the reacting compounds. The reacted mixture contains the desired functionalized monobenzoxazine monomer, and possibly impurities. If desired, the mixture may be purified to obtain a more concentrated form of the product, for example by well known crystallization or solvent washing techniques. The functionalized monobenzoxazines can be partially or fully shaped by melt processing in conventional polymer and/or composite processing equipment.

The following examples are meant to illustrate, but not to limit, the formation of functionalized monobenzoxazine monomers.

A functionalized monobenzoxazine, more specifically a maleimide functionalized benzoxazine monomer, 1-(3-phenyl-2H, 4H, benzo[3,4-e] 1,3-oxazaperhydroin-6-yl)azoline-2,3-dione (MIB) was formed according to the present invention. The reaction synthesis is generally depicted below.



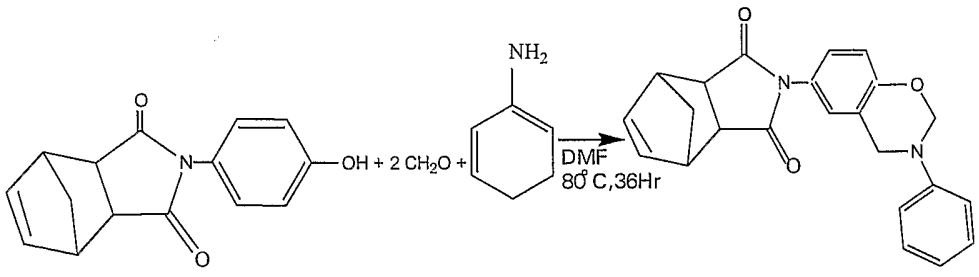
Formula III

In a first step, the maleimide functionalized phenol 1-(4-hydroxy-phenyl)-pyrrole-2,5-dione (HPMI) was synthesized as known in the art. In a 100ml round bottom flask were added 30g (360mmol) maleic anhydride and 30.6g (280mmol) p-aminophenol and 80ml DMF at 0°C. A mixture of 15g (106mmol) P_2O_5 in 50ml DMF and 8g of concentrated H_2SO_4 was added over 30 minutes to a round bottom flask while the flask was being stirred by a magnetic stirrer. The reaction mixture was then stirred at 70°C for 3 hours in an oil bath. The mixture was then poured into 500ml of de-ionized ice water and yellow precipitation was observed. The precipitate was dried under a vacuum chamber for approximately 12 hours and was purified by recrystallization in isopropanol. The product was in the form of yellow needle-like crystals (30.1g yielded 57%). The melting point was 176°C. ^1H NMR (200MHz, DMSO-d^6, 298K) δ: 6.80 (d, 1H), 7.06 (d,2H) 7.13 (d, 2H), and 9.70 (s, 1H).

In a next step, the maleimide functionalized monobenzoxazine monomer was formed from the maleimide functionalized phenol, an aldehyde, and an amine. More specifically, a mixture of HPMI, p-formaldehyde, and aniline with a mole ratio of 1:2:1 was added to a flask and stirred at 110°C for 20 minutes. The product was then dissolved in dichloromethane, filtered, and washed with de-ionized water. The solvent was evaporated using a rotary evaporator and product was vacuum dried. The product was a yellow powder (yield 80%), and the melting point was 147°C. ^{1}H NMR (200MHz, $(CD_3)_2CO$, 298K) δ: 4.73 (s, 2H), 5.49 (s, 2H), and 6.80- 7.28 (Ar, 10H).

Anal. Calcd. For $C_{18}H_{14}N_2O_3$: C, 70.58%; H, 4.61%; N, 9.15. Found: C, 70.60%; H, 4.81%; N, 9.00.

A further functionalized monobenzoxazine monomer, more specifically a norbornene functionalized benzoxazine monomer, 4-aza-4-(3-phenyl(2H,4H-benzo[2,4-3]1,3–oxazaperhydroin-6yl))tri-cycle[5.2.1.0<2,6>]dec-8-ene-3,5 dione (NOB) was formed according to the present invention. The reaction synthesis is generally depicted below.



Formula IV

In a first step, the norbornene functionalized phenol p-hydroxyphenylnadimide (HPNI) was formed as known in the art. In a 50 ml round bottom flask, 1.0g (6.09mmol) norbornene and 0.7g

(6.09mmol) p-aminophenol were dissolved in 20ml of glacial acetic acid and stirred with a magnetic stirrer for 12 hours. The mixture was then poured into 500ml of deionized ice water and was allowed to precipitate and left to dry in a vacuum oven for about 10-12 hours. The final product was white crystals and the yield was 85%. The melting point was 242°C. ^{1}H NMR (200MHz, $(CD_3)_2CO$, 298K) δ: 1.66 (s, 2H), 3.35 (s, 2H), 3.46(s, 2H), 6.21 (s, 2H), 6.82-6.96 (Ar, 4H), and 8.56 (s, OH).

In a next step, a mixture of HPNI, p-formaldehyde, and aniline with a mole ratio of 1:2:1 and DMF were added to a flask and stirred at 90°C for 36 hours. The product was then precipitated into water and collected. The precipitate was dried, dissolved in chloroform, and washed with 1N NaOH solution and de-ionized water. The solvent was evaporated using a rotary evaporator and the product was vacuum dried. The product was a white powder (yield 82%) with a melting point of 200°C. ^{1}H NMR (200MHz, $(CD_3)_2CO$, 298K) δ: 1.66 (s, 2H), 3.35 (s, 2H) 3.45 (s, 2H), 4.69 (s, 2H), 5.47 (s, 2H), 6.21 (s, 2H) and 6.74-7.26 (Ar, 8H).

Anal. Calcd. For $C_{23}H_{20}N_2O_3$: C, 74.18%; H, 5.41%; N, 7.52. Found: C, 74.04%; H, 5.46%; N, 7.47.

Benzoxazine Polymers

In a further embodiment of the present invention, benzoxazine polymers or copolymers having a crosslinked network structure are formed from the functionalized benzoxazine monomers. It is to be understood that the same or different benzoxazine monomers can be polymerized, thus forming benzoxazine homo or copolymers. Advantageously, multiple methods of polymerization can be utilized to form the benzoxazine

polymers. That is, in addition to polymerization through the oxazine ring of the benzoxazine, the monomers can also be polymerized utilizing the same or a different mechanism through the additional functionality, such as the maleimide or norbornene functionalities, present on the monomer which is derived from the functionalized phenol and/or functionalized amine. The phenols produced upon benzoxazine ring opening can be further utilized for an additional polymerization mechanism. Thus, three different reactive mechanisms are possible. The functionalized monofunctional benzoxazines are polymerized through a) reaction of the benzoxazine functionality, b) reaction of the functional group on the benzoxazine monomer derived from the phenol, or c) reaction of a functional group on the benzoxazine monomer derived from the amine, or a combination thereof. The functional group polymerizations are carried out by a different polymerization mechanism than the benzoxazine functionality polymerization, i.e., ring opening polymerization.

Multiple polymerization mechanisms of the functionalized benzoxazine monomer with different free radical initiators have been monitored by Fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC). The extended type of polymerization, which affect the final network structure of the benzoxazine polymer can be characterized and optimized by one of ordinary skill in the art utilizing the teachings of the present invention.

As known in the art, the ring opening polymerization of benzoxazine compounds can be performed through thermally activated polymerization. The temperature to induce thermally activated polymerization ranges generally from about 50°C to about

300°C, and preferably from about 100°C to about 250°C. Polymerization is typically performed in bulk, but can be done from solution or otherwise. Catalysts, such as carboxylic acids, have been used to slightly lower the polymerization temperature or accelerate the polymerization rate at the same temperature.

The benzoxazine polymerization can also be initiated by the class of cationic initiators know as Lewis acids in addition to the other known cationic initiators. These include metal halides such as $AlCl_3$, $AlBr_3$, BF_3, $SnCl_4$, $SbCl_4$, $ZnCl_2$, $TiCl_5$, WCl_6, VCl_4, PCl_3, PF_5, $SbCl_5$, $(C_6H_5)_3C^+(SbCl_6)^-$, and PCl_5 ; organometallic derivatives such as $RAlCl_2$, R_2AlCl, and R_3Al where R is a hydrocarbon and preferably an alkyl of 1 to 8 carbon atoms; metallophorphyrin compounds such as aluminum phthalocyanine chloride; methyl tosylate, methyl triflate, and triflic acid; and oxyhalides such as $POCl_3$, CrO_2Cl, $SOCl_2$, and $VOCl_3$. Other initiators include $HClO_4$ and H_2SO_4. The Lewis acid initiators are often used with a proton or cation donor such as water, alcohol, and organic acids, desirably of about 0.001 to about 50 mol% initiator based on the monomer, more desirably from about 0.01 to about 10 mol% initiator is used for the cationic initiated polymerziations. Cationic polymerization initiators have been found to result in polymerization of benzoxazine monomers at temperatures as low as cryogenic temperatures. Preferred temperatures are from about minus 100°C to about 200°C, with about minus 70°C to about 150°C most preferred. The cationic initiators can be used either in the benzoxazine melt or in the presence of solvent, allowing the solvent content to be from 0 percent to about 99 percent. Many different solvents can be used in cationic polymerizations and selection is known by those skilled in the art.

The reactive functional groups of the benzoxazine monomer can be polymerized utilizing free radical inititators, or other catalysts, depending on the functional group and the corresponding polymerization mechanism used. The polymerization of the reactive functional groups are well known to those of ordinary skill in the art and to the literature. Any free radical initiators can be utilized. Examples of free radical initiators include, but are not limited to, those known in the art such as peroxides including benzoyl peroxide and dicumyl peroxide; azo compounds including 2,2'-azobisisobutyronitrile (AIBN); disulfides; and tetrazenes.

A suitable method for preparation of the benzoxazine polymers is generally as follows. A predetermined amount of monomer and initiator or other catalyst are mixed together in a suitable vessel. The polymer is formed in the vessel or placed in another suitable apparatus such as a mold. Occasionally, it may be necessary to place the mixture under a vacuum at a predetermined temperature for a predetermined period of time such as about 1 to about 2 hours in order to remove residual solvent and/or air from the mixture. The material is cured at a predetermined temperature as noted hereinabove. In one embodiment, it is desirable to utilize a step-cure procedure, wherein the mixture is subjected to increasing temperatures over an extended period of time. For example, the mixture in one embodiment is cured at about 150°C for about 1 hour, 170°C for about 2 hours, 190°C for about 2 hours and then at about 210°C for about 1 hour. After the monomer has been polymerized, the polymers are generally cooled to room temperature over an extended period of time. Of course, the curing temperature is varied depending on the initiator utilized and to create a balance

between the functional group polymerization and benzoxazine polymerization.

In order to better illustrate the polymerization of the functionalized benzoxazine monomers, the following experiments were performed. The maleimide functionalized benzoxazine and norbornene functionalized benzoxazine monomers prepared as stated above were polymerized both individually and with free radical initators. The free radical initiators were utilized in an amount of 5 mol% and were dry mixed into the monomer at room temperature before polymerization.

In order to measure the mechanical properties, rectangular polymer bars made from a specific monomer with different monomer and initiator compositions were prepared. For each sample, the monomer, or monomer and initiator were weighed and mixed and subsequently placed in a mold. The mold consisted of two glass plates with a 3.2 mm thick silicone rubber placed along the edges therebetween. The parts were treated with a silicone based mold release. The mold was filled with the mixture and placed into a vacuum oven at 110°C for 1 to 2 hours in order to remove residual solvent and air trapped in the silicone rubber. The assembly was then placed into an air vented oven where it was subjected to a step cure procedure. Step cure procedure consisted of curing at 150°C for one hour, 170°C for two hours, 190°C for two hours and then 210°C for one hour. The samples were then slowly cooled to room temperature.

Fourier transform infrared spectra (FTIR) were obtained using a Bomen Michelson MB100 FTIR spectrometer which was equipped with a liquid nitrogen cooled, mercury cadmium-telluride (MCT) detector with a specific detectivity, D*, of $1x10^{10}$

$cmHz^{0.5}W^{-1}$. Co-addition of 128 scans was recorded at a resolution of 4 cm^{-1} after a 20 minute purge with dry nitrogen. FTIR spectra of the monomers were taken using KBr powder technique while the thin film was cast on a KBr plate for partially cured samples.

Both ^{1}H NMR and ^{13}C NMR were recorded using a Varian XL 200 nuclear magnetic resonance (NMR) spectrometer at a proton frequency of 200 MHz and the corresponding carbon frequency. Deuterated chloroform, acetone, and dimethyl sulfoxide were used as NMR solvents with 0.05% tetramethylsilane as the internal standard. Co-addition of 128 transients yielded a good signal-to-noise ratio spectrum for ^{1}H NMR while 2,000 transients were used for ^{13}C NMR spectrum. Relaxation time (D1) of 10 seconds was used to obtain integration results for the proton spectrum.

The thermal stability and curing behavior were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), respectively. TA Instruments High Resolution 2950 thermogravimetric analyzer was used with nitrogen as a purging gas for all testing. A heating rate of 20°C/min with a flow rate of 90ml/min was used for all tests. TA Instruments DSC model 2920 was used with heating rate of 10°C/min and a nitrogen flow rate of 65 ml/min for all tests. All samples were crimped in hermetic aluminum pans with lids.

Dynamic mechanical analyses (DMA) of the samples were performed to determine the glass transition temperature, Tg, storage modulus, G', and loss modulus, G'. Tests were performed using a Rheometrics dynamic mechanical spectrometer (RMS-800) equipped with a 2kg-cm force rebalance transducer. A maximum strain of 0.1% was applied sinusoidally to samples with dimensions of approximately 50 x 13 x 3.2 mm in a rectangular torsion fixture

at each temperature at a frequency of 1Hz. This strain was verified to be within linear viscoelastic limits by first obtaining the strain sweep data. The samples were heated at approximately 2°C/min and measurements were taken at intervals of 2°C until the temperature reached to about 50°C above the material's Tg. Thermal soak time of 30 seconds was used to stabilize the sample temperature.

The structure of the monofunctional benzoxazine polymers, MIB and NOB were verified by ^{1}H NMR and ^{13}C NMR spectroscopy (Figures 2-3). In ^{1}H NMR, resonances appearing at 4.73 ppm and 5.47 ppm are assigned to the methylene protons in the oxazine ring of MIB. Column chromatography was used to separate the impurities, which were identified as unreacted phenols, amines, and benzoxazine oligomers. No resonance was recorded at 5.0-5.3 ppm, which corresponds to the methylene protons in the triazine intermediate. The prominent resonance at 6.98 ppm in the aromatic frequency corresponds to the protons attached to the vinylene group. NOB has proton resonances at 4.69 ppm and 5.47 ppm which correspond to the methylene protons in the oxazine ring. The protons attached to the vinylene group of NOB appear at 6.21 ppm. Furthermore, the structures of both MIB and NOB monomers are confirmed by using ^{13}C NMR and the corresponding chemical shifts are shown in Table 1.

Table 1

	MIB (ppm)	NOB (ppm)
C1	125.47	122.76
C2	130.33	130.32
C3	122.22	119.43
C4	154.05	149.13
C5	49.19	53.18
C6	80.50	80.48
C7	160.42	155.41
C8	121.29	118.66
C9	127.85	127.28
C10	133.86	132.36
C11	125.76	125.36
C12	128.92	125.96
C13	177.23	176.90
C14	-	46.63
C15	-	46.41
C16	-	51.42
C17	138.99	122.76

Along with the excellent agreement between the calculated and observed data of the elemental analysis, it shows that the targeted compounds were obtained in high purity.

Thermal properties of both MIB and NOB which were polymerized according to the cure schedule described in the previous section were examined by TGA (Figures 4-5). The polymers from MIB and NOB exhibit thermal stability up to 375°C and 365°C, respectively. The char yields at 800°C for MIB and NOB under nitrogen were 56% and 58%, respectively, when heated at 20°C/min. In Table 2, the thermal properties of MIB and NOB are summarized and compared to other known prior art benzoxazines.

Table 2

Monomer	Abbreviation	Char Yield	5% Wt Loss	10% Wt Loss	Reference
	MIB	56%	375 °C	392°C	Present invention
	NOB	58%	365 °C	383°C	Present invention
	Ph-a	35%	326 °C	353 °C	Prior art
	BA-a	30%	339 °C	348 °C	Prior art

It is observed that there is a significant improvement of at least 20% higher char yield than regular monofunctional benzoxazines. Previous studies have shown that degradation occurs in the sequence of evaporation of the amine, and then breakage of phenolic linkage which occurs simultaneously with degradation of the Mannich base. In case of MIB, due to the incorporation of the imide group, which has a planar five membered ring structure, and the partial conjugation with the benzene ring, the rotation of the imide residues are hindered. This phenomenon resulted in the increased stiffness and thermal stability of the material. It is also important to note that the incorporation of the imide group increased the viscosity compared to monofunctional benzoxazines but did not increase above typical difunctional benzoxazines, which allows processibility. While MIB had steady-state shear viscosity of 2.0 Pa•s at 100°C as shown in FIG. 6, bisphenol-A based benzoxazines had similar viscosity of 3.0 Pa•s at the same temperature.

The polymerization reactions were studied by DSC as shown in Figures 7-8. MIB and NOB show benzoxazine polymerization exotherms at 213°C and 261°C, respectively. Since MIB has a maleimide group, it can be further polymerized by free radical mechanism by either thermal activation or with an initiator. Different free radical initiators were dry mixed into the monomer with a concentration of 5 mol% to determine the extent and temperature at which vinyl polymerization occurs.

Three initiators, 2,2'-azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), and dicumyl peroxide (DICUP), were chosen to show that the polymerization can be initiated at different

temperatures. When MIB is polymerized in the presence of AIBN and BPO, it has distinct polymerization peaks for vinyl polymerization from the benzoxazine polymerization. In addition, the heat of reaction of the benzoxazine polymerization is much greater than the maleimide polymerization. However, when DICUP was added to the system, the benzoxazine polymerization peak around 210°C is significantly lower in intensity than the maleimide polymerization peak. This may explain why the T_g of the MIB with DICUP is approximately 20°C lower than the T_g observed in the other systems.

The FTIR spectra of the MIB and NOB monomers and polymers are shown in Figures 9-10. IR band assignments were made for MIB and NOB based on the assignments of monofunctional benzoxazines previously reported by Dunkers and Ishida, Dunkers, J.; Ishida, H. *Spectrochimica Acta* 6 (1995) 1061. The benzoxazine ring modes were determined by comparing the spectra of the monomer and polymer of the MIB polymerized at 170°C, since we do not expect thermal polymerization of the maleimide group at this temperature. Absorption bands at 1500 cm^{-1} and 935 cm^{-1} are due to tri-substituted benzene ring. The band at 1236 cm^{-1} was assigned to the C-O-C antisymmetric stretch, while the band at 1032cm^{-1} was assigned to the C-O-C symmetric stretch. As polymerization proceeds, the appearance of the C-O stretch of the phenolic group can be seen by the appearance of the band at 1272cm^{-1}. The tetra-substituted benzene mode at 1494cm^{-1} was also observed, suggesting benzoxazine polymerization via ring opening.

The prominent band at 1713cm^{-1} is attributed to imide I, and other imide bands can be found at 1397cm^{-1}, imide II, and 695cm^{-1},

imide IV. The band at 828 cm^{-1} was assigned to the imide CH wag of the vinylene group and the 1600 cm^{-1} was assigned to the C=C stretch. At temperatures of 180°C and above, the bands attributed to the CH wag and C=C stretch of the vinylene group starts to disappear. The band at 1146 cm^{-1}, assigned to the C-N-C bending mode, imide III, of the maleimide ring, shifted to 1180cm^{-1} which corresponds to the C-N-C bending mode of the succinimide ring increased with maleimide polymerization.

In FIG. 11 FTIR spectra obtained during the polymerization of MIB monomer with 5 mol% AIBN are shown. By monitoring the bands at 1600 cm^{-1} and 825 cm^{-1} which correspond to the vinylene group, we determine the reaction temperatures at which the free radical and thermal polymerization of the maleimide group and thermally activated polymerization of the benzoxazine ring occur. According to the spectra, at 140°C there is a significant decrease of the band at 825 cm^{-1}, before the tri-substituted benzene mode at 935 cm^{-1} disappears. This indicates that, with the addition of a free-radical initiator, the maleimide polymerization takes place before the benzoxazine polymerization as previously concluded from the DSC results. On the other hand, without the free-radical initiator, the benzoxazine polymerization takes place before the maleimide thermal polymerization.

The order and extent of each polymerization mechanisms have a considerable effect on the resulting glass transition temperatures. The T_g of the pure MIB polymer was 252°C, but when AIBN was added to the system, the T_g increased to 260°C. It is interesting to observe that when DICUP was added, in which case the largest heat of reaction was observed for vinyl polymerization before benzoxazine polymerization, the T_g was

decreased to 232°C. It can be concluded that a vinyl polymerization before benzoxazine polymerization improves the network structure and thermal properties of the final polymer compared to polymerization without any free radical initiator. However, a more extensive vinyl polymerization experienced when adding DICUP will hinder benzoxazine polymerization due to the large formation of a rigid backbone structure.

Although maleimide functionalized benzoxazine and norbornene functionalized benzoxazines and polymers created therefrom have been extensively documented, various other functionalized monobenzoxazine monomers are polymerized in the same general manner as described hereinabove by one of ordinary skill in the art without undue experimentation.

The incorporation of functional groups, especially maleimide and norbornene functionality into monofunctional benzoxazine resulted in increase of char yield and glass transition temperature without significantly increasing the viscosity of the monomer. Char yields above about 40%, about 50% and about 55% to about 80% or about 85% and glass transition temperatures (T_g) above about 225°C, about 240°C and about 250°C to about 300°C or about 350°C can be obtained for polymers from functionalized benzoxazine monomers. The relatively low viscosity benzoxazine materials are easily processed even though they contain a traditionally high viscosity group such as a norbornene or imide. Furthermore, different polymerization processes have been characterized by using various free radical initiators for vinyl polymerization at different temperatures.

Benzoxazine Copolymers or Interpenetrating Networks (IPN)

In yet a further embodiment of the present invention, the functionalized monobenzoxazine monomers are copolymerized with at least a co-component comprising another monomer, oligomer, or polymer. Any comonomer etc. which has functionality that can react with the functionality present on the functionalized monobenzoxazine monomer is utilized. Examples of the co-components include epoxy resins, vinyl containing monomers, bismaleimide resins, acetylene terminated resins, bisnadimide resins, arylethynyl resins, cyanate ester resins, benzocyclobutene resins, phenolic resins, polyurethanes, polyimide resins, other benzoxazines, or the like. For example, if a vinyl functional group is used for a R_1-R_4 functional group, co-components such as unsaturated polyester, vinylester, norbornene-terminated polyimide resin and vinyl containing monomers, such as styrene, methyl methacrylate, ethyl methacrylate, methyl acrylate, maleic anhydride can be used. Other compounds that react with the vinyl group, such as –SiH and $-NH_2$, can also be used. Polymers with reactive side groups, such as amines as co-components can also be used.

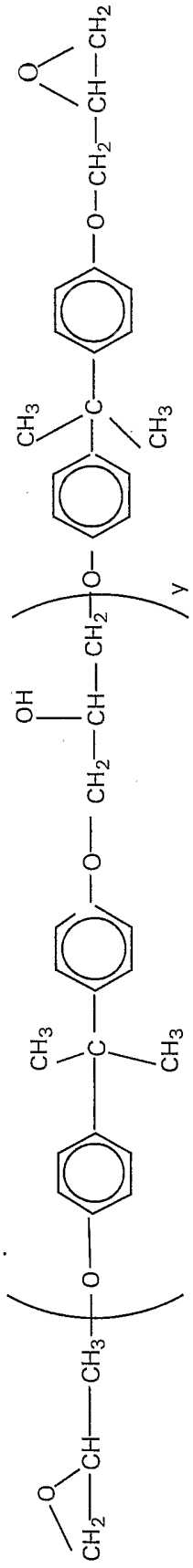
The selection of the partner molecule is vast and is known to those skilled in art. For example, the functionalized monobenzoxazine monomer includes at least one functional group (A) present on the phenol derived portion of the benzoxazine monomer, or a functional group (B) present on the amine derived portion of the benzoxazine monomer, or a combination thereof, and (C) the benzoxazine ring which is thermally polymerizable. The (A) functional group as known in the art is reacted with a partner molecule (A'), (A''), or (A''') etc. Likewise, (B) and (C) have partner molecules known to one of ordinary skill in the art (B'), (B'') etc.

and (C'), (C'') etc, respectively which can be reacted therewith. Accordingly, numerous different benzoxazine copolymers are anticipated by the present invention. It has been discovered that functionalized monobenzoxazine copolymers are prepared having excellent toughness and processability without compromising thermal properties. Highly crosslinked copolymers are produced.

In yet another embodiment of the present invention the functionalized monobenzoxazine monomers are utilized to form interpenetrating polymer networks. The benzoxazine monomers are polymerized or copolymerized to form a crosslinked network in the presence of different monomers, a polymer, or resin which are nonreactive or do not form covalent bonds with the benzoxazine network. The resulting interpenetrating network has interwoven or intertwined chains among the crosslinked benzoxazine polymer or copolymer. Methods for forming interpenetrating networks are well known to those of ordinary skill in the art.

In one embodiment, when an epoxy is utilized, the system has at least three reactive groups or moieties which can undergo polymerization, 1) the epoxy ring, 2) the benzoxazine ring, and 3) the at least one functional group present on the phenolic portion of the benzoxazine monomer and/or the amine portion of the benzoxazine monomer. The copolymerization results in a crosslinked polymer with good thermal and mechanical properties. Advantageously, the copolymer systems do not require any catalysts for epoxy polymerization since the phenol group of the benzoxazine can act as an initiator as well as a catalyst. Any of the above-noted functionalized monobenzoxazine monomers or combinations thereof can be utilized in the copolymerization reaction.

The epoxy or epoxy resin as used herein refers to any chemical compound that has the characteristic oxirane ring. A commonly used epoxy resin is based upon bisphenol A and epichlorohydrin reacted to form the diglycidyl ether of bisphenol A. The formula for this compound is given on the next page.



Formula V

where y is from 0 to about 10, about 20, or about 30. When y is 0 or 1 the compound is a liquid at 25°C. This is an example of an aromatic epoxy. Higher molecular weight epoxy compounds are generally tougher than lower molecular weight compounds.

Aliphatic epoxies may be useful instead of aromatic epoxies or in addition to aromatic epoxies when particular properties are desired. Aliphatic epoxies can be formed from the reaction of alcohols, glycols, and polyols with epichlorohydrin. Aliphatic epoxies can also be formed from polyolefinic compounds such as animal and vegetable oils, polyesters, polyether, butadiene derivatives etc. by processes such as peracetic acid oxidation of a double bond in the starting material.

Cycloaliphatic epoxies can be prepared by the oxidation (e.g. by peracetic acid) of cycloaliphatic olefins.

Novolac epoxies can be used and are prepared by reacting a phenol or a substituted phenol with formaldehyde to create methylol groups and then reacting that product with epichlorohydrin. Epoxies formed from novolacs are well known and commercially available.

Brominated epoxies are useful for specific applications, especially where flame retardency is desired. Brominated epoxies generally are defined as those epoxies with from about 15-50 weight percent bromine and generally one or more epoxy groups per molecule. An example of a brominated epoxy is tetrabromobisphenol A reacted with epichlorohydrin.

Depending on the amount of epoxy reactant in the blend and the presence of phenolic molecules, a hardener for the epoxy reactant may or may not be necessary. Typical hardeners for epoxies include aliphatic amines, polyamides,

phenol/urea/melamine, formaldehyde and Lewis acid catalysts. In addition crosslinking agents such as an anhydride may be added.

The general method for forming the benzoxazine epoxy copolymers comprise physically mixing predetermined amounts of the functionalized monobenzoxazine monomer and epoxy, and curing the resulting mixture, which typically comprises heating the mixture at a predetermined temperature or temperatures for a predetermined amount of time. As with the above-noted benzoxazine polymerizations, the copolymers can also be prepared utilizing open molds, machine molding, compression molding and the like as familiar to those of ordinary skill in the art. Preferably a step cure procedure is utilized to prepare the copolymers wherein the functionalized benzoxazine and epoxy mixture is cured at increasing temperatures for predetermined periods of time. In an especially preferred embodiment, step cure procedure comprises the steps of heating at about 150°C for about 1 hour, about 170°C for about 2 hours, about 190°C for about 2 hours, and then at about 210°C for about 30 minutes to about 12 hours. The copolymer can then be cooled to room temperature, depending on the polymerization mechanism.

In order to illustrate this particular embodiment of the present invention, a series of copolymers with different ratios of functionalized benzoxazine monomer and epoxy were prepared. In this particular example, maleimide functionalized benzoxazine was utilized as the functionalized benzoxazine monomer and Epon 825 epoxy resin, which is a diglycidyl ether of bisphenol-A (DGEBA), was utilized as obtained from Miller-Stephenson Chemical Company.

Table 3

Summary of DSC Results and Tan Delta Peaks from DMA

MIB %	DGEBA %	Exotherm Peak Temperatures	ΔHrxn (J/mol of MIB)	Tan delta Peak Temperature	Peak Height
50	50	246°C	0.68	177°C	0.21
60	40	244°C	0.98	259°C	0.18
70	30	230°C, 257°C	1.19	268°C	0.22
80	20	214°C, 247°C	1.25	286°C	0.25
90	10	214°C, 247°C	1.26	282°C	0.31
100	0	213°C, 244°C	0.87		

Various weight ratios of functionalized benzoxazine monomer to epoxy were separately prepared as shown in Table 3.

In the experiment, the functionalized benzoxazine monomer and epoxy were weighed, added to a vessel, mixed at 100°C, and placed into a mold. The mold has been described hereinabove. The mold was placed into a vacuum of at 110°C for about 1 to about 3 hours to remove residual solvent and trapped air in the silicone rubber. The mixture was then placed into an air vented oven where it was subjected to a step cure procedure. During the step cure procedure, the mixture was heated to 150°C for 1 hour, 170°C for 2 hours, 190°C for 2 hours and then 210°C for 30 minutes to 12 hours. The samples were then slowly cooled to room temperature over several hours.

Fourier transform infrared spectra were obtained as described herein. Nuclear magnetic resonance (NMR) spectra were recorded as described herein. Dynamic mechanical analysis (DMA) of the samples were performed as described herein.

The curing behavior was investigated by differential scanning calorimetry (DSC) (TA Instruments DSC model 2920) with a heating

rate of 10°C/min with a nitrogen flow rate of 65ml/min for all tests. All samples were crimped in hermetic aluminum pans with lids.

Three point bending tests were conducted to determine the flexural properties in accordance with ASTM D790m. Instron Universal Testing Machine (model 1125) fitted with a 25kN load cell, an automated control system, and the Merlin analysis software were used. Three specimens with dimensions of 70 x 10 x 3 mm were tested for each composition. Samples with a support span of 48mm were held in ASTM specified boundary conditions until breakage occurred at a crosshead speed of 1mm min^{-1}. Flexural strain was calculated based upon crosshead displacement.

The copolymer system tested had three possible polymerization reactions, benzoxazine polymerization, epoxy polymerization, and functional group (in this case vinyl) polymerization. In order to determine that all reactions take place, Fourier transform infrared spectra (FT-IR) were taken at different temperatures for a monomer sample with 1:1 ratio of MIB and DGEBA. The epoxy polymerization is monitored by the disappearance of the epoxide ring modes at 915 cm^{-1} and 861 cm^{-1}. Epoxy polymerization takes place concurrently with the benzoxazine polymerization, since the phenolic groups of the benzoxazine act as an epoxy polymerization initiator and catalyst. The epoxide ring bands disappeared almost completely after 20 minutes at about 160°C.

Benzoxazine polymerization is monitored by the disappearance of the absorption bands at 1500 cm^{-1} and 935 cm^{-1} which corresponds to the tri-substituted benzene ring mode. Also, the antisymmetric C-N-C stretching mode of the oxazine ring observed at 1117 cm^{-1} decrease as a function of temperature during

the benzoxazine polymerization. At the same time, the bands at 1240 cm^{-1} and 1032 cm^{-1}, which correspond to the C-O-C antisymmetric and symmetric stretching modes, respectively, of the benzoxazine ring decrease. The maleimide polymerization is monitored by the bands at 1600 cm^{-1} and 825 cm^{-1} that correspond to the C=C stretching vibration and CH wag of the vinylene group, respectively. The C=C stretching band overlaps with the mono-substituted benzene ring mode at 1585cm^{-1} which does not disappear during polymerization. The bands which correspond to the vinylene group disappear at temperatures above 240°C, which shows that maleimide polymerization occurs at higher temperatures than benzoxazine polymerization. The evidence of vinyl polymerization is obtained by the shift of the band at 1180 cm^{-1} due to the symmetric C-N-C bending mode of the succimide group.

The comparison of the polymerization of pure MIB and MIB/DGEBA which were cured at the same polymerization conditions as described in the experimental section are shown in Figures 11-25. The spectra indicate that for the MIB/DGEBA copolymer, clear evidence of benzoxazine polymerization is observed at 240°C, although there is less maleimide polymerization compared to the spectrum of MIB polymer. The dilution of monomer results in decreased proximity of the maleimide bonds and less vinyl polymerization takes place, especially at high concentrations of epoxy.

The polymerization behavior was also studied by differential scanning calorimetry (DSC) as summarized in Table 3. The MIB monomer had two exotherm peaks at 214°C and 243°C. The first exotherm peak corresponds to the benzoxazine polymerization and the overlapping exotherm at the higher temperature corresponds to

the maleimide polymerization. As the epoxy concentration is increased, the exotherm peaks shift to a higher temperature. This is due to the dilution of benzoxazine monomers which also result in the decrease of epoxy polymerization initiators. At high concentrations of MIB, the homopolymerization exothermic peak is more prominent at 213°C, but with addition of epoxy, the copolymerization peak at around 240°C heightens in intensity. Eventually, at 30% or more epoxy content, only the copolymerization exotherm, overlapping with the maleimide polymerization is observed, due to the dilution of MIB. The heat of reaction, which is proportional to the extent of reaction, was highest at approximately 10-20% DGEBA. It appears that, at this stoichiometry, the polymerization is optimum because of the lowered viscosity by the presence of epoxy which improves the mobility of the monomers and because of the minimized dilution of MIB monomer.

Dynamic mechanical analysis (DMA) was performed for different compositions of MIB/DGEBA. DMA can provide important thermal and mechanical properties such as storage modulus, G', and loss modulus, G". The storage modulus at room temperature, which provides the material stiffness under shear stress, was compared at different compositions. As epoxy content was increased, the modulus decreased, since epoxy segments are more flexible than the MIB segments. An amine initiated epoxy polymer has a modulus of about 1.0 GPa while the polybenzoxazine homopolymer from MIB has a higher modulus of about 2.0 GPa. According to the rule of mixtures, we expected the modulus of the copolymer to be between these two values.

In addition, DMA was taken for two samples with different cure profiles for different compositions. The 30% DGEBA sample was greatly affected by the cure profile and exhibited an incomplete cure after 30 minutes at 210°C (Figures 15-16). This phenomenon was indicated by the increase in G' above 250°C in the DMA scan. On the other hand, the 10% DGEBA sample with different curing profiles hardly showed any change in modulus and transition temperature (Figures 17-18). At higher concentrations, due to the dilution of the benzoxazine, the completion of polymerization takes significantly longer, while at low concentration of epoxy, a shorter curing time is sufficient.

For bisphenol-A based benzoxazine/ DGEBA copolymers, only copolymers with 25% or lower DGEBA content were successfully cured. However, in our system, even samples with high concentration of 70% DGEBA had mechanical integrity, which shows that maleimide based benzoxazine is more compatible with epoxy than bisphenol-A based benzoxazine.

It should be noted that T_g was determined by the peak position of the G" spectrum. However, due to the insensitivity of tan δ to the geometrical variation of samples, tan δ was used to compare transition behavior of the samples with various compositions. The T_gs of copolymers were determined for polymers of the same composition with two different curing profiles. The first sample was cured according to the cure profile described in the previous section while another sample was post-cured for additional 11 hours at 210°C. The T_g of typical benzoxazines was lowered during an extended post-curing, due to the rearrangement of the molecular structure at this temperature. However, maleimides usually undergo long post-curing stages for further crosslinking

reaction that results in the improvement of thermal stability. For T_g of MIB/DGEBA copolymer, an increase of 15°C to 30°C was observed for the post-cured material. This was more evident at higher concentrations of epoxy because the benzoxazine and maleimide polymerization were slowed by the dilution effect of epoxy and further postcuring allowed a more complete polymerization. Furthermore, while the T_g of MIB homopolymer was between 253°C and 268°C, we observed a maximum T_g of 278°C at a mole ratio of 10 mol% DGEBA. This corresponds well to our DSC results where the most complete reaction at 10 mol% DGEBA was observed. A similar trend was observed for bisphenol-A based benzoxazine where a maximum T_g of 156°C was observed at 15 mol% DGEBA.

The glass transition temperatures of the copolymers with free radical initiator were investigated at different DGEBA concentrations as summarized in Table 4.

Table 4

Summary of Glass Transition Temperatures from DMA Results

Polymerization Conditions	T_g of MIB	T_g of 20% DGEBA	T_g of 40% DGEBA
Shorter Cure 210°C (30min)	252 °C	242 °C	215 °C
Longer Cure 210°C (12hr)	268 °C	262 °C	232 °C
Shorter Cure with BPO	246 °C	222°C	159 °C

When benzoyl peroxide was added to the homopolymer, a 15°C decrease in T_g was observed, while larger shifts in T_g were observed for higher concentrations of DGEBA. For example, a 70°C decrease

of T_g was observed for 40% DGEBA. The formation of the rigid backbone at lower temperatures by the maleimide polymerization decreases the mobility of the molecular segments to hinder benzoxazine and epoxy polymerization. The combination of the lowered mobility and the dilution effect of epoxy results in a larger decrease of T_g at the higher concentration DGEBA copolymers.

Further analysis of the DMA results showed that the height of tan δ peak decreased and the transition peak shifted as epoxy concentration was increased, as shown in Table 3. The formation of more crosslinks by the epoxy between the linear benzoxazine chains, resulted in the lower mobility of segmental chain and a decrease in tan δ peak height. In addition, while the shift in the tan δ peak was no larger than 30°C for concentrations between 10% and 40% DGEBA, between 40% and 50%, there was a shift of 100°C due to a possible phase inversion. At 50% DGEBA, the volume fraction of the epoxy became larger than that of MIB, resulting in the drastic shift of the peak.

The flexural properties were determined by three point bending test and the results are shown in Figures 24-26. Flexural strength of polymers is affected by glass transition, network structure and regularity, free volume, chemical structure, and other factors. In this system, since there was a change in glass transition temperature and we are also changed the network structure by adding more physical crosslinks, it was expected that the flexural properties would change. The flexural strain at breakage was 1.5 % at 10 % DGEBA and increased to 3.2% with 50% DGEBA. In addition, the stress at break increased about 50 MPa with the addition of 50% epoxy. Previous studies have also shown that increasing the epoxy content in copolymers results in an increase of

flexural strain and a decrease in modulus since the segmental mobility of the epoxy chain is greater than the benzoxazine chain. The modulus was between 4.2 MPa and 5.0 MPa, and the greatest modulus was found at the highest concentration of benzoxazine monomer for MIB/DGEBA copolymer as expected.

The thermal and mechanical properties of maleimide-functionalized benzoxazine and diglycidyl ether bisphenol-A were investigated for different compositions of epoxy. We observed that the two monomers copolymerized without any addition of initiator or catalyst. The three polymerization reactions which include an epoxy ring, a benzoxazine ring, and a vinyl polymerization were confirmed to have taken place using DSC and FT-IR. For copolymers with high content of epoxy, we observed less complete polymerization of the maleimide group, while epoxy and benzoxazine polymerizations were less affected. The resulting polymer achieved a high glass transition temperature of 278°C at 10 mol% DGEBA and was higher than the homopolymer that has a T_g of 253°C. Also, the curing time and temperature affected the glass transition temperature about 10°C to 30°C due to the further crosslinking of the maleimide bond. While flexural strain at breakage increased with the increase in epoxy content, the flexural modulus was approximately 5.0 GPa for 10 mol% DGEBA and decreased to 4.2 GPa with 50 mol% DGEBA. In conclusion, functionalized benzoxazines have been successfully copolymerized with epoxy resin to tailor for desired flexural properties without decreasing the thermal properties.

Accordingly, copolymers having sought after properties are prepared from blends of functionalized benzoxazine monomer and epoxy. The functionalized benzoxazine monomers of the invention

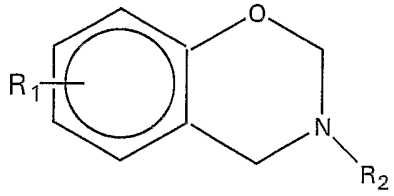
are utilized in copolymer compositions in an amount from about 40 to about 99 weight percent, desirably from about 50 or about 60 to about 98 weight percent, and preferably from about 80 or about 85 to about 97 weight percent based on the total weight of the functionalized benzoxazine monomer and non-benzoxazine monomer or polymer, such as epoxy, in the composition. Glass transition temperature depends on the type of epoxy used, however, the Tg will generally not be more than 350°C. By utilizing the blend approach, the property tailoring is fine tuned.

The functionalized benzoxazine polymers and copolymers of the present invention are useful for a variety of applications including adhesive, molded, and electronic applications. Articles or parts prepared according to the present invention exhibit good thermal stability and/or flame resistance. Example end uses include molded circuit boards, electronic packaging materials, fuel cell parts, flame resistant laminates, and molded articles in general. The polymers and copolymers can be a source of precursor to high temperature resistant chars. The common uses for high temperature resistant chars include air craft brake discs, and heat shields or heat shielding materials. The compounds of the present invention can be used as alternatives or replacements for epoxies or vinyl ester resins.

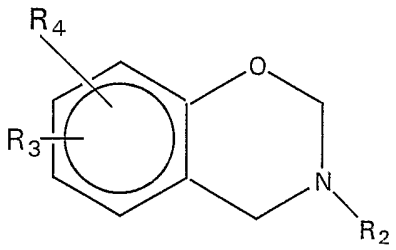
In accordance with the patent statutes, the best mode and preferred embodiment have been set forth, the scope of the invention is not limited thereto, but rather by the scope of the attached claims.

WHAT IS CLAIMED IS:

1. A functionalized monobenzoxazine monomer having the structure comprising:



Formula I, or

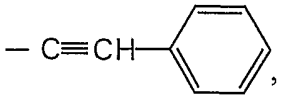


Formula II

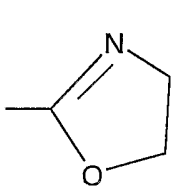
wherein R_1, R_3, and R_4, independently is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

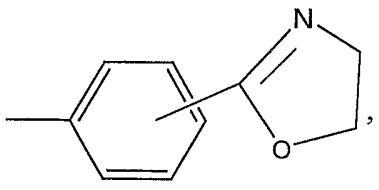
$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$

where n =1 - 6, $-C\equiv CH$, $-CH_2-C\equiv CH$,

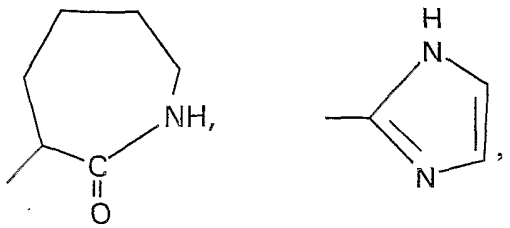


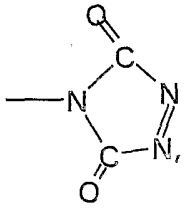
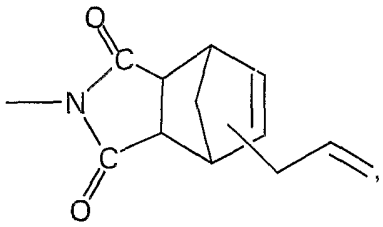
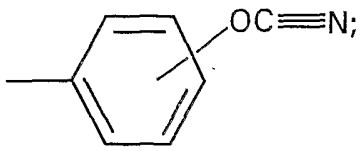
, $-SH$, $-SiH$, $-CH_2OH$, $-SO_3H$,

$-COOH$, $-CHO$, 

, 

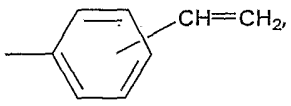
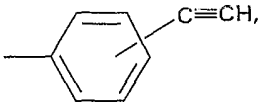
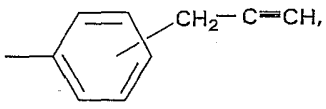
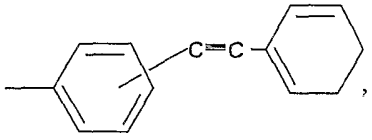
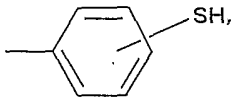
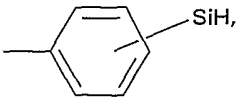
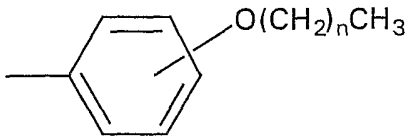
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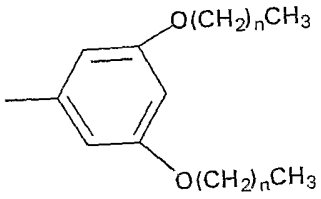


or


wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,

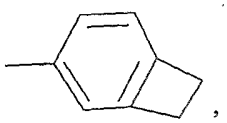
$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$, where n =1 - 6,

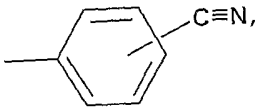








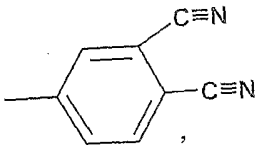
where n =0 -3,

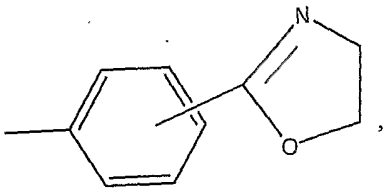


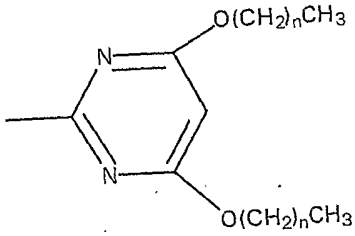
where n =0 - 2,



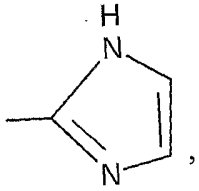


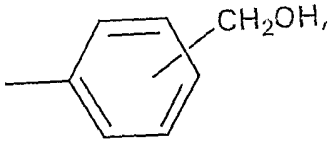


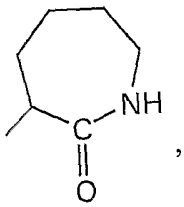


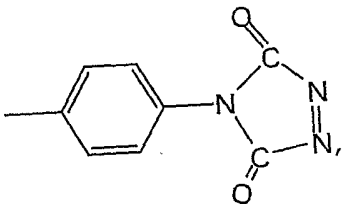


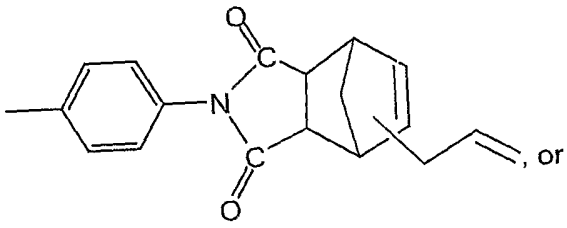
where n =0 - 2,

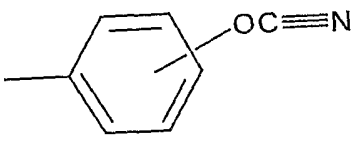












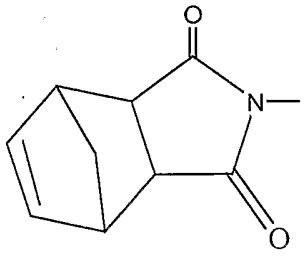
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with the proviso that in Formula I at least R_1 or R_2 is a reactive functional group and in Formula II at least R_2, R_3 or R_4 is a reactive functional group.

2. A monomer according to claim 1, wherein said monomer is Formula I and at least said R_1 is said reactive functional group.

3. A monomer according to claim 2, wherein said R_1 is maleimide or norbornene functionalized maleimide.

4. A monomer according to claim 3, wherein R_1 is said norbornene functionalized maleimide and has the formula:



5. A monomer according to claim 3, wherein said R_2 is hydrogen, said alkyl having 1 to about 18 carbon atoms, said aromatic having from about 6 to about 18 carbon atoms, or said alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms.

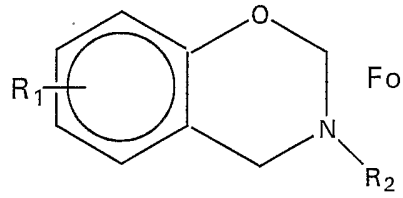
6. A monomer according to claim 5, wherein said R_2 is an aromatic having from about 6 to about 18 carbon atoms.

7. A monomer according to claim 6, wherein said R_2 is an aromatic having 6 carbon atoms.

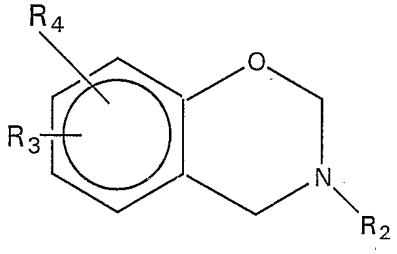
8. A method for forming a functionalized monobenzoxazine monomer, comprising the step of:

reacting a phenol optionally having a reactive functional group; an aldehyde or aldehyde derivative; and an amine optionally having a reactive functional group to form said monomer having a reactive functional group thereon, wherein at least one of said phenol or said amine has said reactive functional group.

9. A method according to claim 8, wherein said functionalized monobenzoxazine monomer has the formula:



Formula I, or

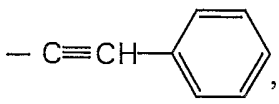


Formula II

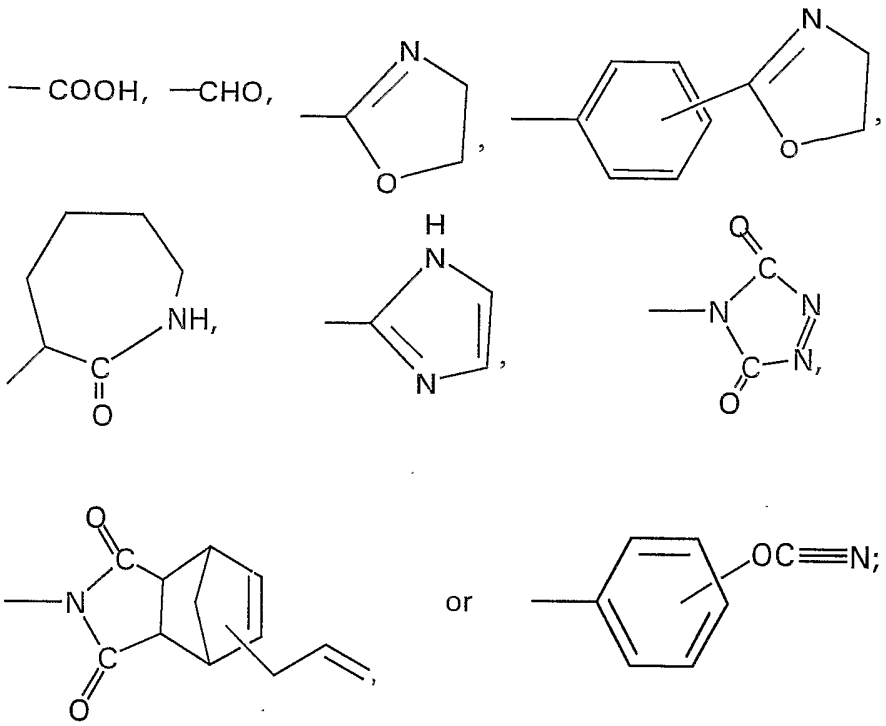
wherein R_1, R_3, and R_4, independently is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$

where n =1 - 6, $-C\equiv CH$, $-CH_2-C\equiv CH$,

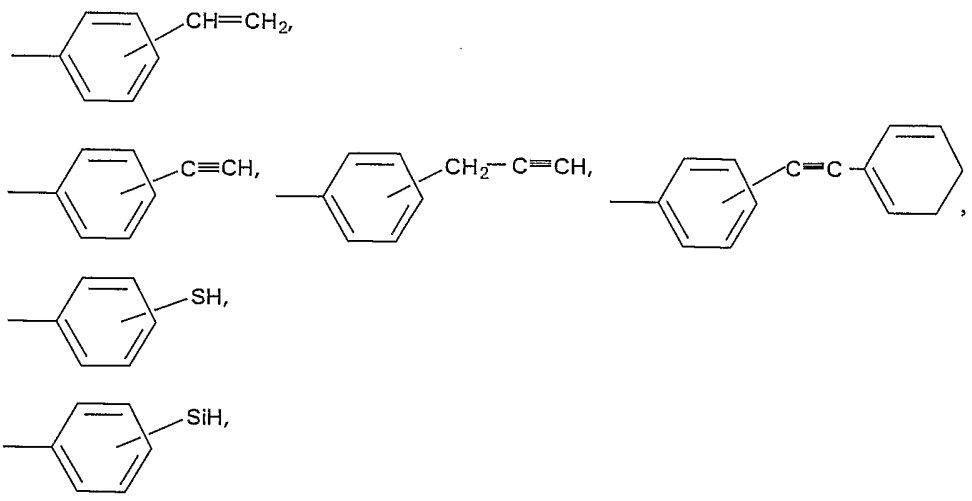


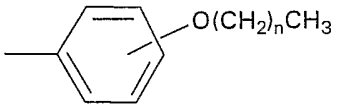
, $-SH$, $-SiH$, $-CH_2OH$, $-SO_3H$,



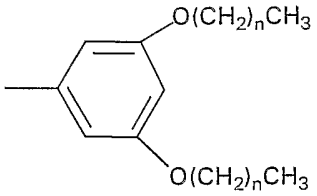
wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,

$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$, where n =1 - 6,

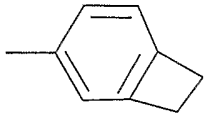


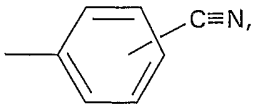


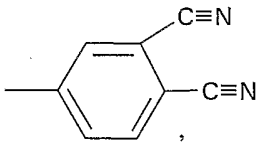
where n =0 -3,

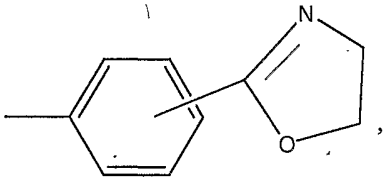


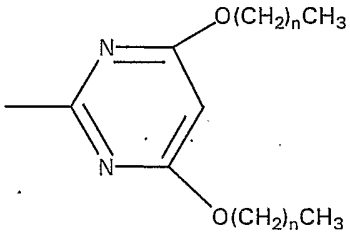
where n =0 - 2,



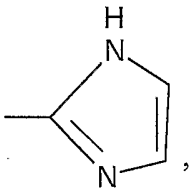


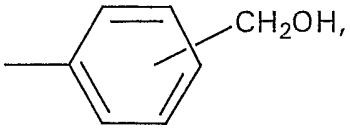


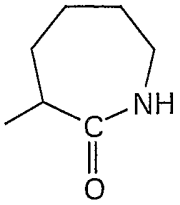


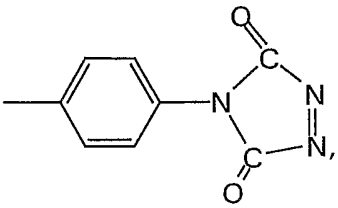


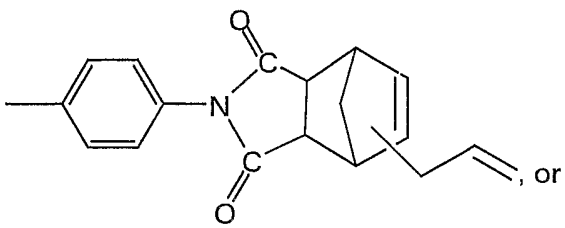
where n =0 - 2,

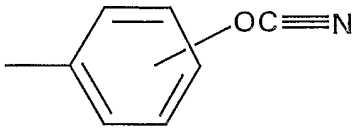












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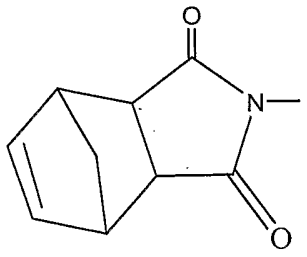
with the proviso that in Formula I at least R_1 or R_2 is a reactive functional group and in Formula II at least R_2, R_3 or R_4 is a reactive functional group.

10. A method according to claim 9, wherein said reaction is conducted with or without a solvent, and wherein said reaction temperature ranges from about 0°C to about 160°C.

11. A method according to claim 10, wherein said monomer formed by the reaction is Formula I and at least said R_1 is said reactive functional group.

12. A method according to claim 11, wherein said R_1 is maleimide or a norbornene functionalized maleimide.

13. A method according to claim 12, wherein R_1 is said norbornene functionalized maleimide and has the formula:



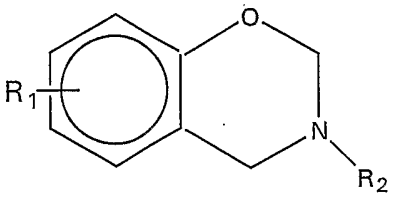
14. A method according to claim 12, wherein said R_2 is hydrogen, said alkyl having 1 to about 18 carbon atoms, said aromatic having from about 6 to about 18 carbon atoms, or said alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms.

15. A method according to claim 14, wherein said R_2 is an aromatic having from about 6 to about 18 carbon atoms.

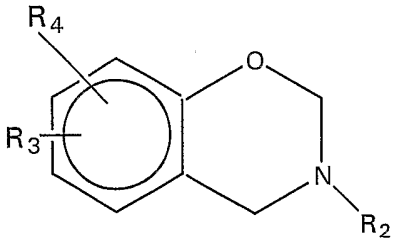
16. A method according to claim 15, wherein said R_2 is an aromatic having 6 carbon atoms.

17. A benzoxazine polymer, comprising:

repeat units derived from a functionalized monobenzoxazine monomer having the following formula:



Formula I, or

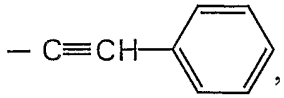


Formula II

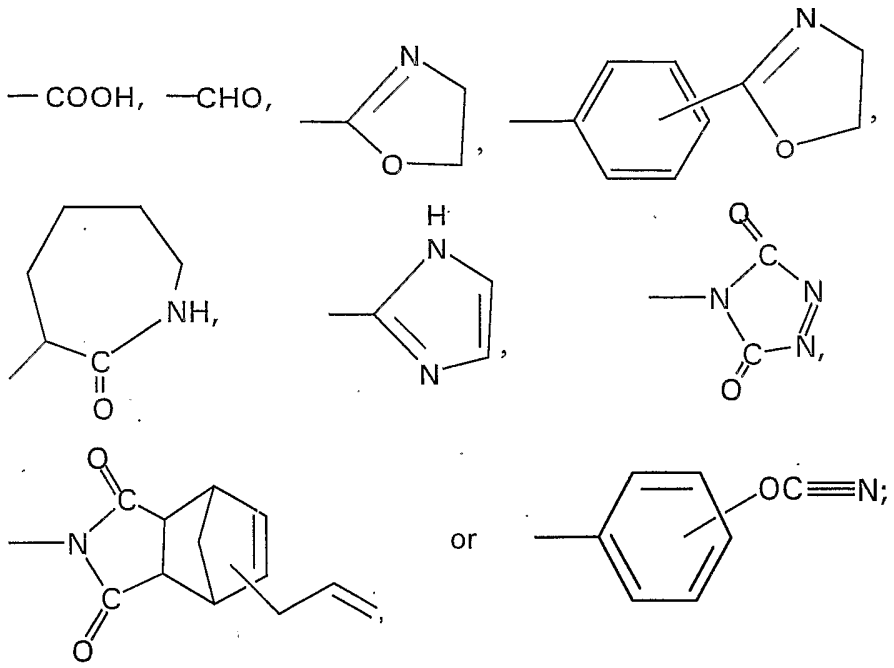
wherein R_1, R_3, and R_4, independently is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$

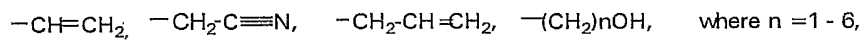
where n =1 - 6, $-C\equiv CH$, $-CH_2-C\equiv CH$,

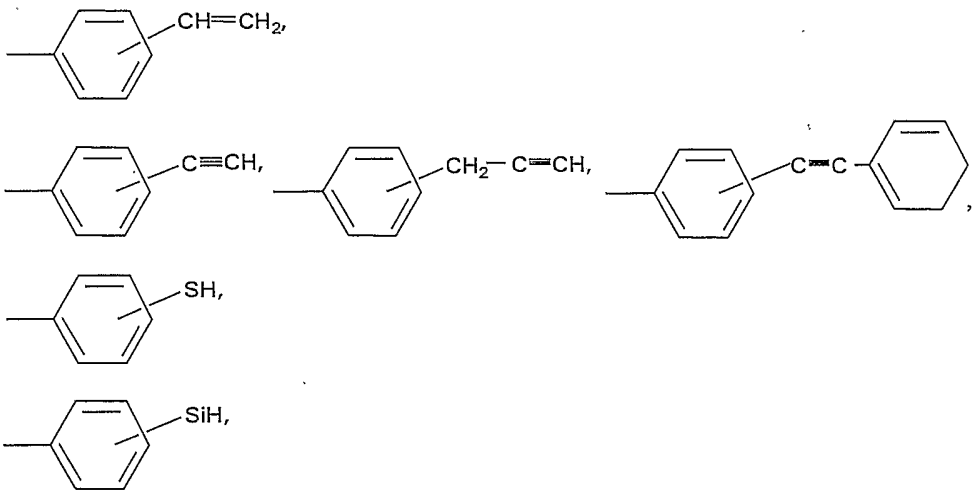


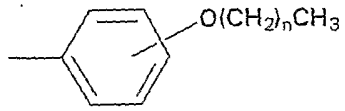
$-SH$, $-SiH$, $-CH_2OH$, $-SO_3H$,



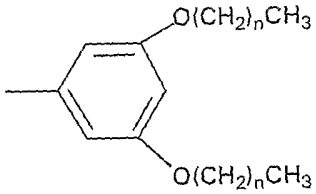
wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,



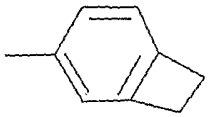




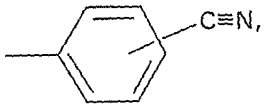
where n =0 -3,

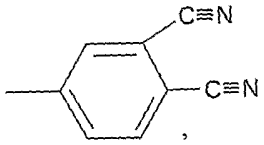


where n =0 - 2,

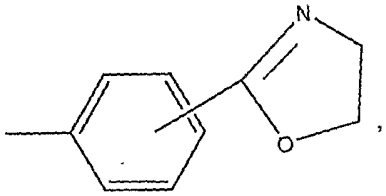


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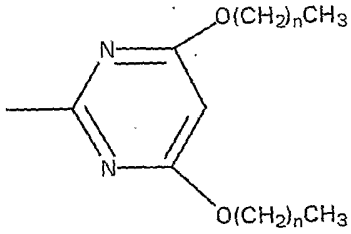




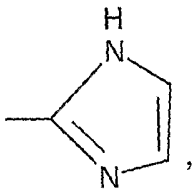
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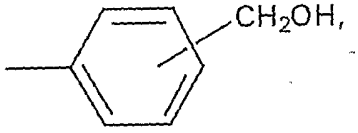
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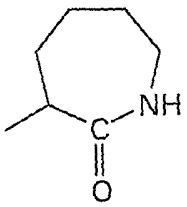


where n =0 - 2,

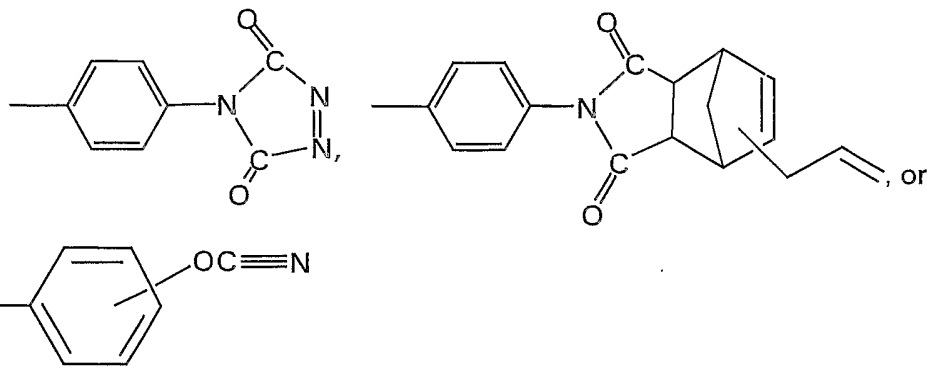


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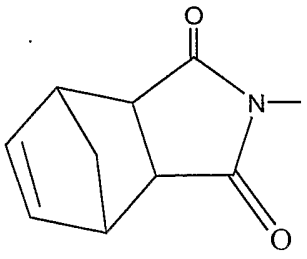


with the proviso that in Formula I at least R_1 or R_2 is a reactive functional group and in Formula II at least R_2, R_3 or R_4 is a reactive functional group.

18. A benzoxazine polymer according to claim 17, wherein said repeat unit is derived from Formula I and at least said R_1 is said reactive functional group.

19. A benzoxazine polymer according to claim 18, wherein said R_1 is maleimide or a norbornene functionalized maleimide.

20. A benzoxazine polymer according to claim 19, wherein R_1 is said norbornene functionalized maleimide and has the formula:



21. A benzoxazine polymer according to claim 19, wherein said R_2 is hydrogen, said alkyl having 1 to about 18 carbon atoms, said aromatic having from about 6 to about 18 carbon atoms, or said

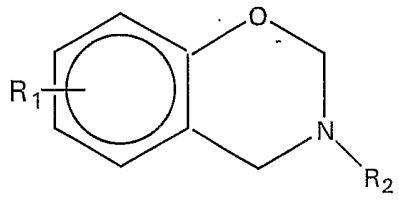
alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms.

22. A benzoxazine polymer according to claim 21, wherein said R_2 is an aromatic having from about 6 to about 18 carbon atoms.

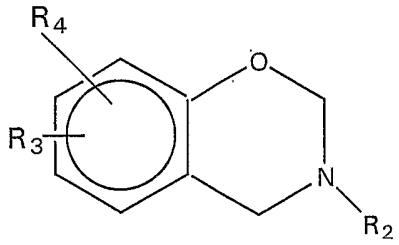
23. A benzoxazine polymer according to claim 22, wherein said R_2 is an aromatic having 6 carbon atoms.

24. A method for forming a benzoxazine polymer, comprising the steps of:

forming said polymer via a polymerization reaction from at least one functionalized monobenzoxazine monomer having the formula:

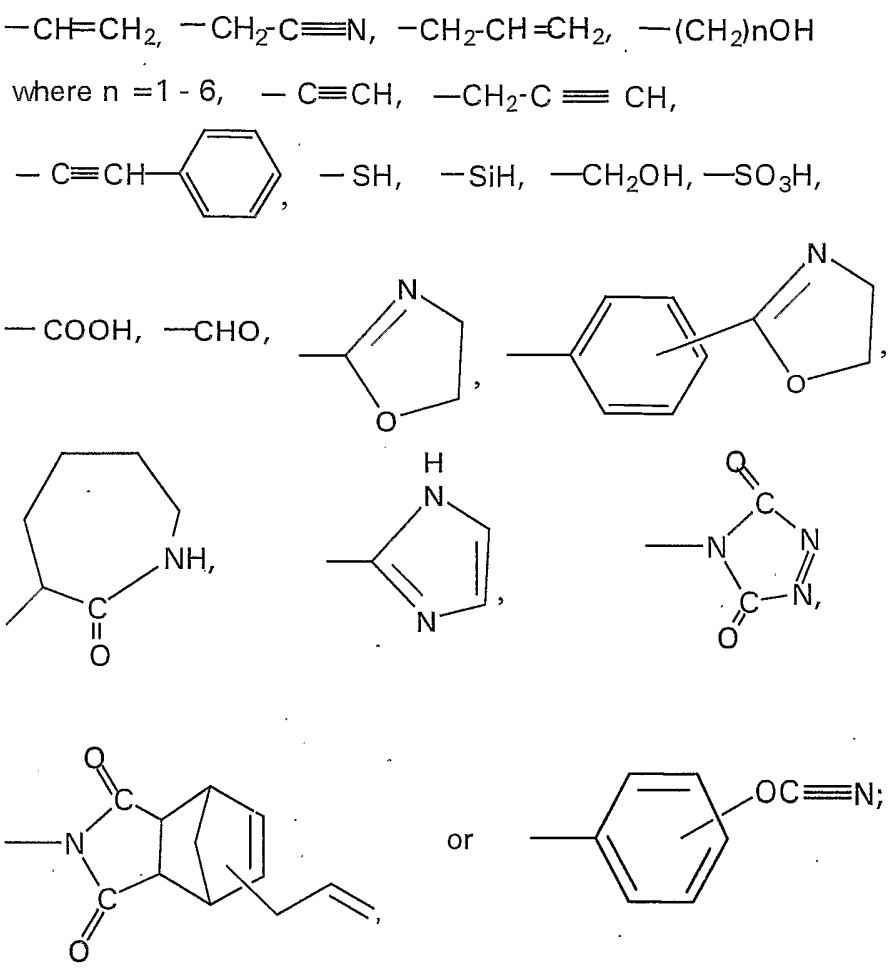


Formula I, or



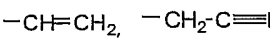
Formula II

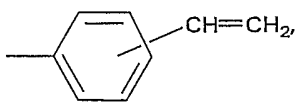
wherein R_1, R_3, and R_4, independently is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

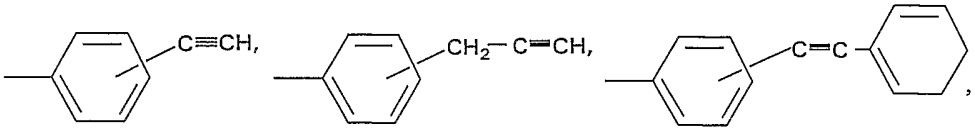


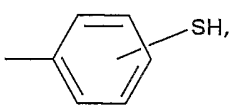
or

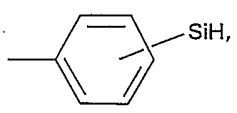
wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,

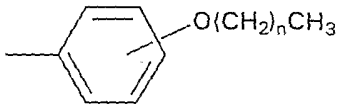




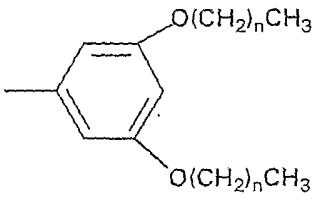






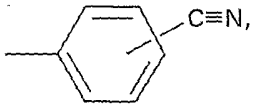


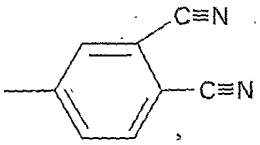
where n =0-3,

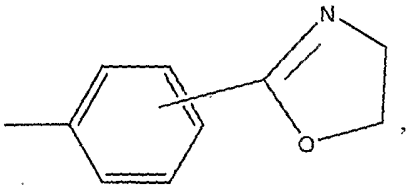


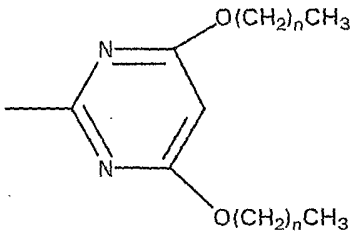
where n =0 - 2,



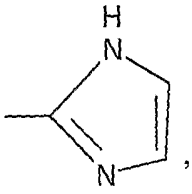


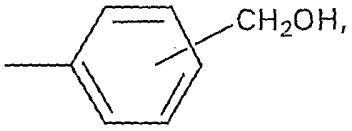


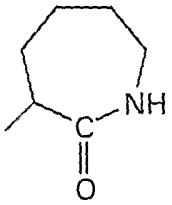


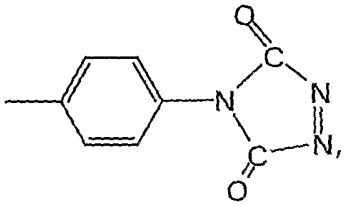


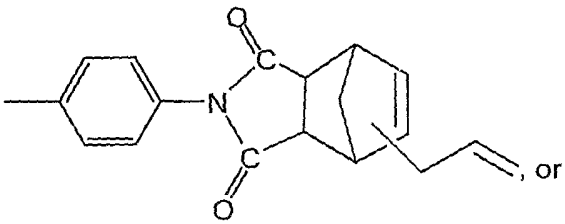
where n =0 - 2,

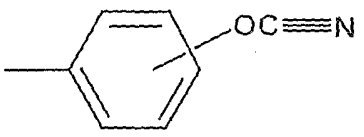












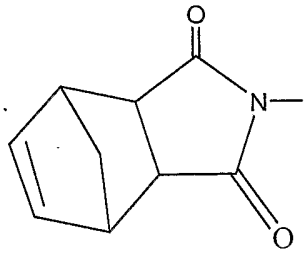
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with the proviso that in Formula I at least R_1 or R_2 is a reactive functional group and in Formula II at least R_2, R_3 or R_4 is a reactive functional group.

25. A method according to claim 24, wherein said monomer is Formula I and at least said R_1 is said reactive functional group.

26. A method according to claim 25, wherein said R_1 is maleimide or norbornene functionalized maleimide.

27. A method according to claim 26, wherein R_1 is said norbornene functionalized maleimide and has the formula:



28. A method according to claim 26, wherein said R_2 is hydrogen, said alkyl having 1 to about 18 carbon atoms, said aromatic having from about 6 to about 18 carbon atoms, or said alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms.

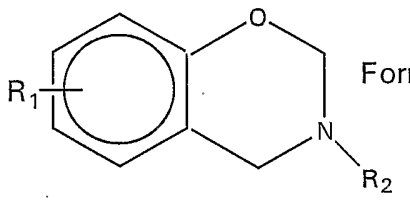
29. A method according to claim 28, wherein said R_2 is an aromatic having from about 6 to about 18 carbon atoms.

30. A method according to claim 29, wherein said R_2 is an aromatic having 6 carbon atoms.

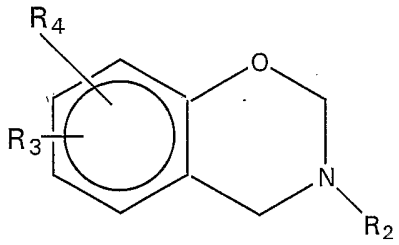
31. A method according to claim 24, wherein said polymer is formed in the presence of a free radical initiator, a cationic initiator, or a combination thereof.

32. A benzoxazine copolymer, comprising:

repeat units derived from a functionalized monobenzoxazine monomer which is copolymerized with a co-component comprising at least a monomer, an oligomer or polymer, and said functionalized monobenzoxazine having the following formula:



Formula I, or

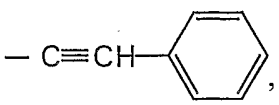


Formula II

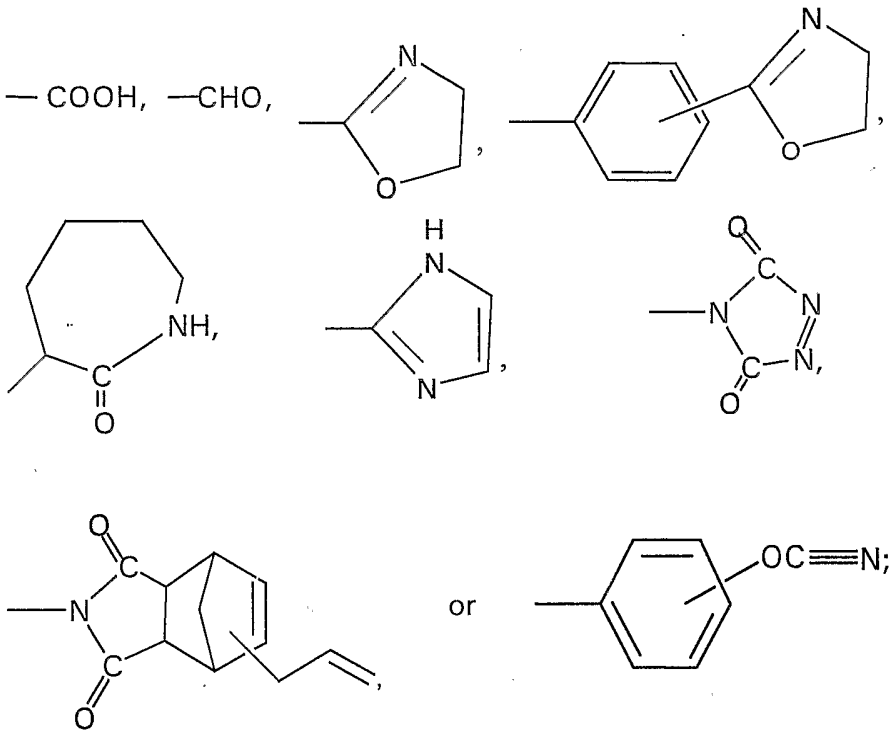
wherein R_1, R_3, and R_4, independently is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms, a maleimide, a norbornene functionalized maleimide,

$-CH=CH_2$, $-CH_2-C\equiv N$, $-CH_2-CH=CH_2$, $-(CH_2)nOH$

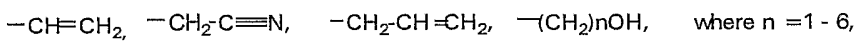
where n =1 - 6, $-C\equiv CH$, $-CH_2-C\equiv CH$,

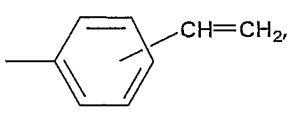


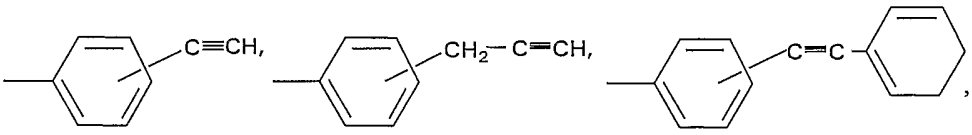
, $-SH$, $-SiH$, $-CH_2OH$, $-SO_3H$,

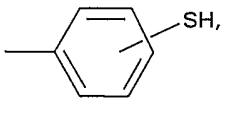


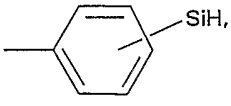
wherein R_2 is hydrogen, an alkyl having 1 to about 18 carbon atoms, aromatic having from about 6 to about 18 carbon atoms, an alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms,

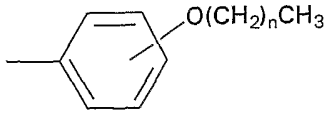




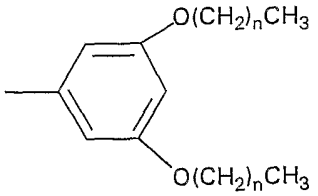




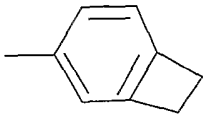


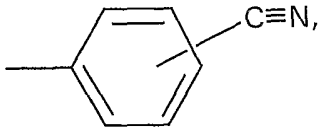


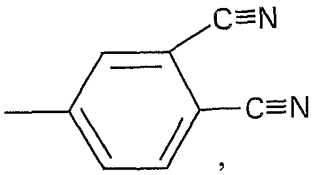
where n =0 -3,

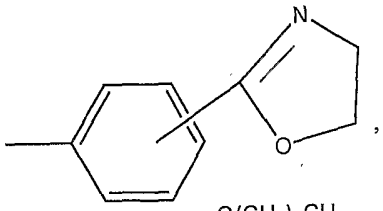


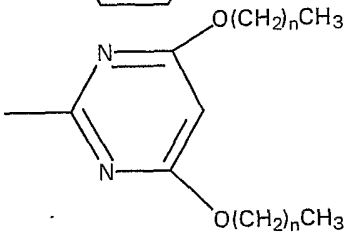
where n =0 - 2,



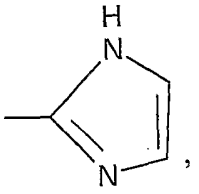


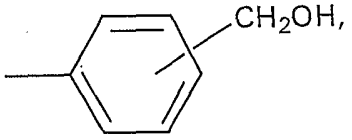


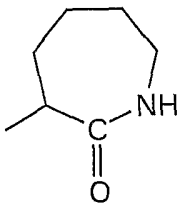




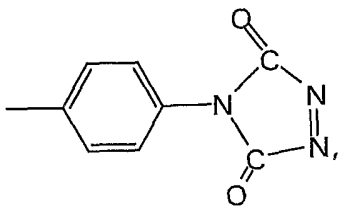
where n =0 - 2,

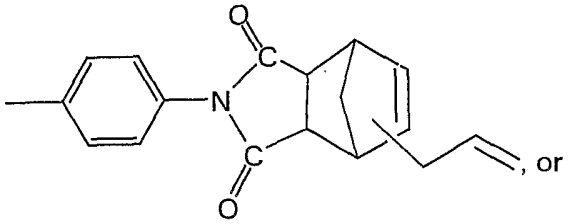




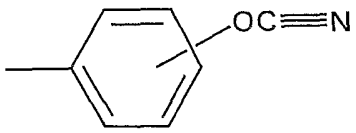


5





, or



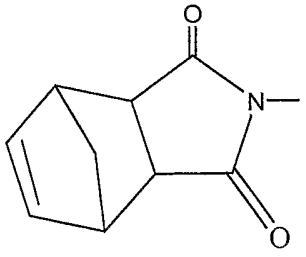
with the proviso that in Formula I at least R_1 or R_2 is a reactive functional group and in Formula II at least R_2, R_3 or R_4 is a reactive functional group.

33. A copolymer according to claim 32, wherein said co-component is an epoxy resin, a vinyl containing monomer, a bismaleimide resin, an acetylene terminated resin, a bisnadimide resin, an arylethynyl resin, a cyanate ester resin, a benzocyclobutene resin, a phenolic resin, a polyurethane, a polyimide resin, a polymer with reactive side groups, or at least one other benzoxazine monomer, or a combination thereof.

34. A copolymer according to claim 32, wherein said monomer is Formula I and at least said R_1 is said reactive functional group.

35. A copolymer according to claim 34, wherein said R_1 is maleimide or norbornene functionalized maleimide.

36. A copolymer according to claim 35, wherein R_1 is said norbornene functionalized maleimide and has the formula:



37. A copolymer according to claim 36, wherein said R_2 is hydrogen, said alkyl having 1 to about 18 carbon atoms, said aromatic having from about 6 to about 18 carbon atoms, or said alkyl substituted aromatic or aromatic substituted alkyl of about 7 to about 40 carbon atoms.

38. A copolymer according to claim 37, wherein said R_2 is an aromatic having from about 6 to about 18 carbon atoms.

39. A copolymer according to claim 38, wherein said R_2 is an aromatic having 6 carbon atoms.

40. A copolymer according to claim 39, wherein said co-component is an epoxy resin.

41. A copolymer according to claim 39, wherein said co-component is an epoxy resin, a vinyl containing monomer, a bismaleimide resin, an acetylene terminated resin, a bisnadimide resin, an arylethynyl resin, a cyanate ester resin, a benzocyclobutene resin, a phenolic resin, a polyurethane, a polyimide resin, a polymer with reactive side groups or at least one other benzoxazine monomer, or a combination thereof.

42. An interpenetrating network comprising a benzoxazine polymer according to claim 17 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

43. An interpenetrating network comprising a benzoxazine polymer according to claim 18 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

44. An interpenetrating network comprising a benzoxazine polymer according to claim 19 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

45. An interpenetrating network comprising a benzoxazine polymer according to claim 20 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

46. An interpenetrating network comprising a benzoxazine polymer according to claim 22 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

47. An interpenetrating network comprising a benzoxazine copolymer according to claim 32 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

48. An interpenetrating network comprising a benzoxazine copolymer according to claim 33 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

49. An interpenetrating network comprising a benzoxazine copolymer according to claim 34 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

50. An interpenetrating network comprising a benzoxazine copolymer according to claim 35 and a polymer or resin which does not form covalent bonds with said benzoxazine polymer.

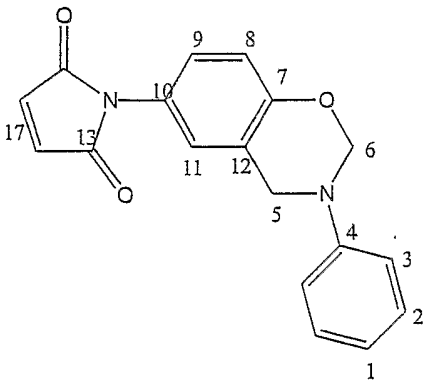


FIG. 1A

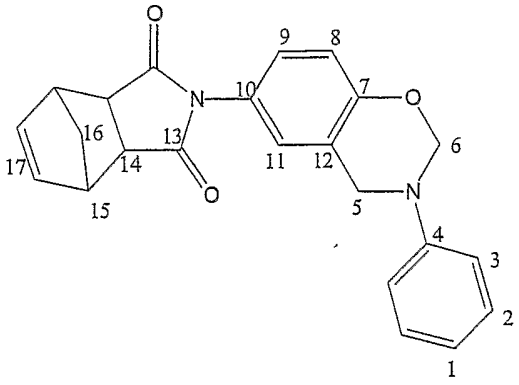


FIG. 1B

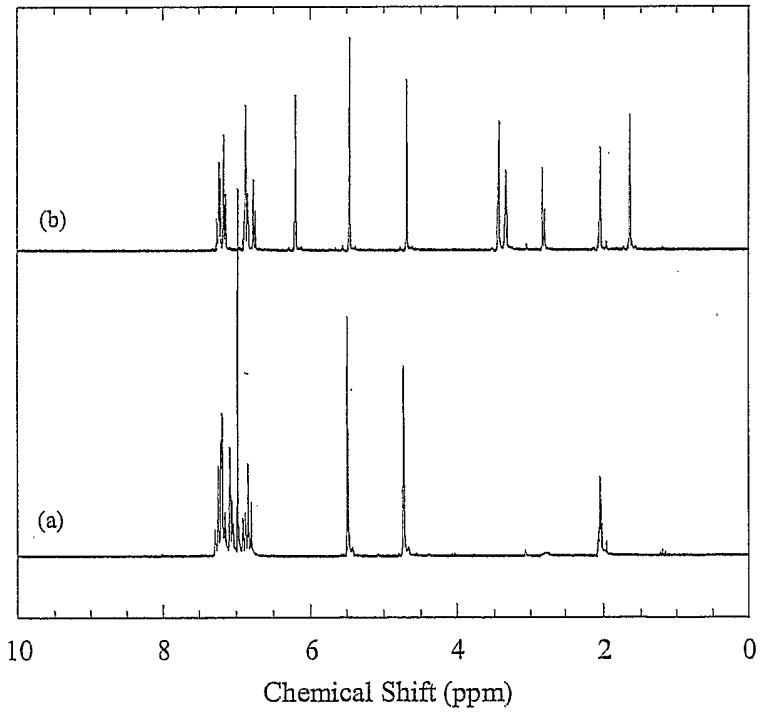


FIG. 2

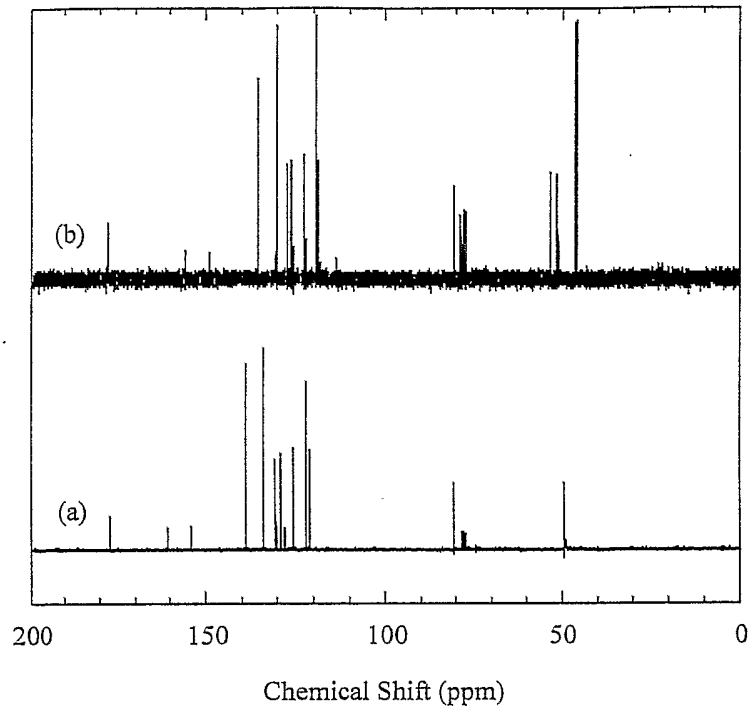

(b)
(a)
200
150
100
50
0
Chemical Shift (ppm)

FIG. 3

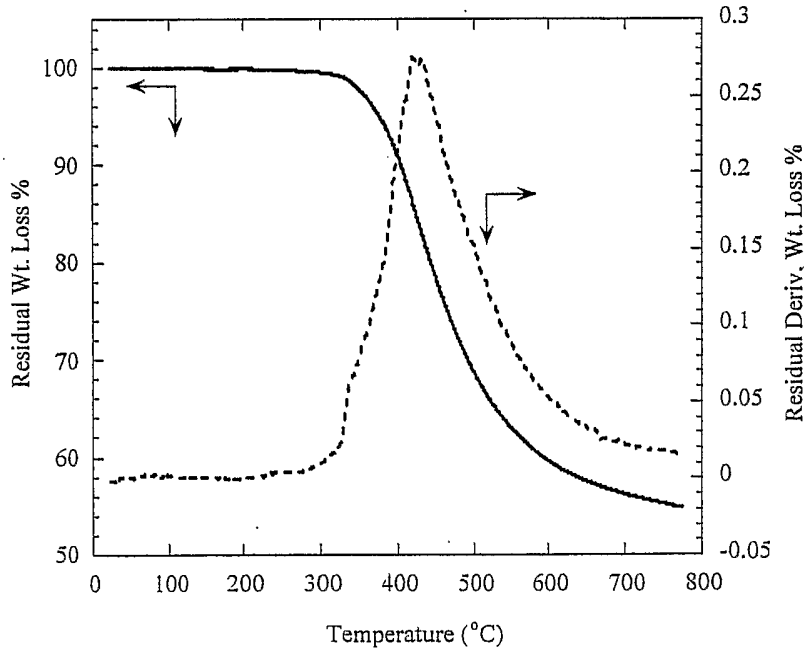

Residual Wt. Loss %
Residual Deriv. Wt. Loss %
100
90
80
70
60
50
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0
100
200
300
400
500
600
700
800
Temperature (°C)

FIG. 4

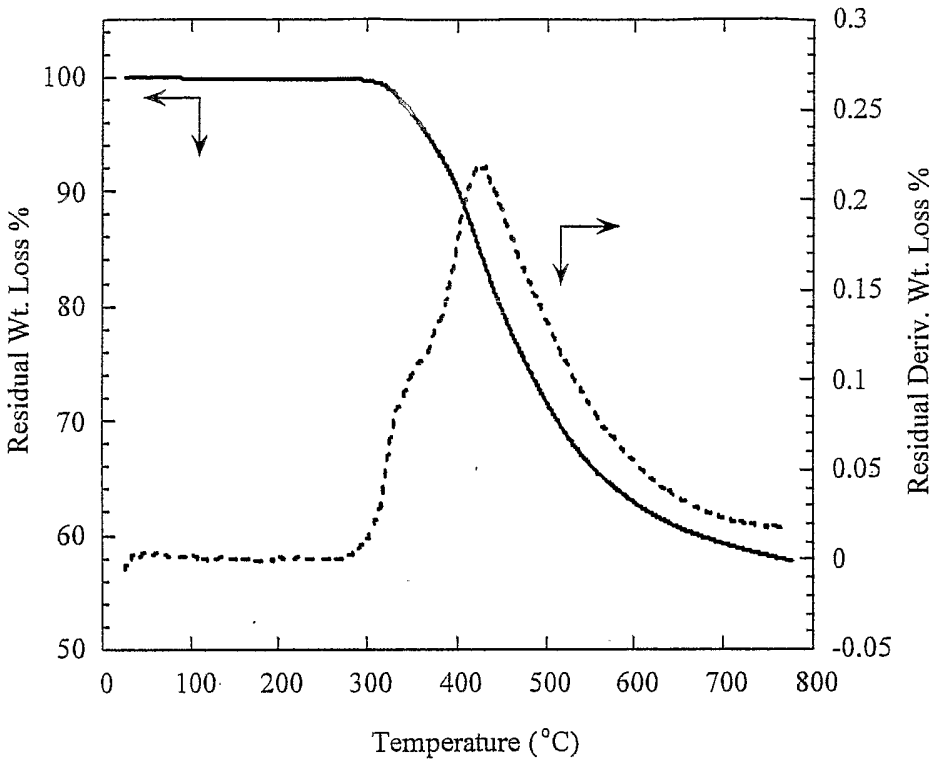

Residual Wt. Loss %
Residual Deriv. Wt. Loss %
Temperature (°C)
100
90
80
70
60
50
0.3
0.25
0.2
0.15
0.1
0.05
0
-0.05
0
100
200
300
400
500
600
700
800

FIG. 5

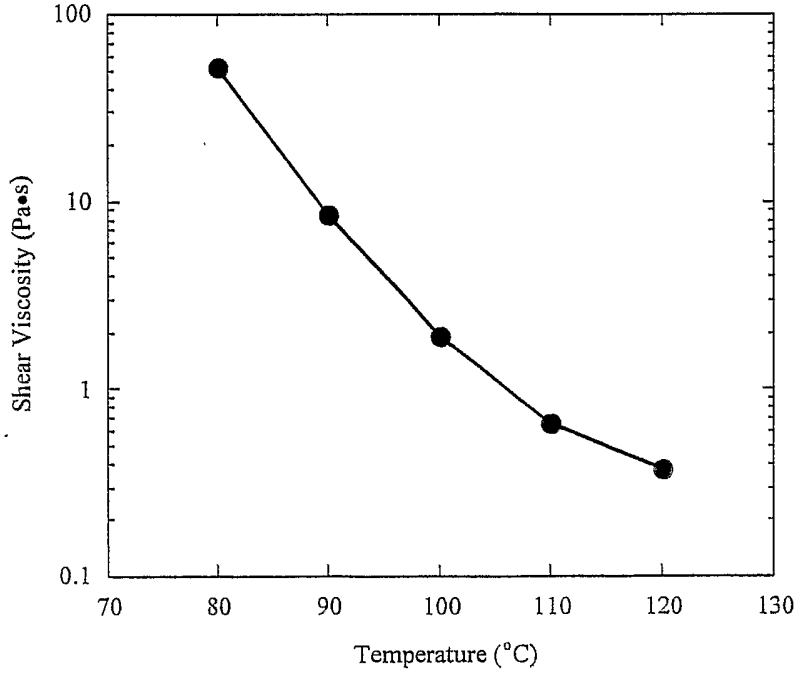

Shear Viscosity (Pa•s)
Temperature (°C)
100
10
1
0.1
70
80
90
100
110
120
130

FIG. 6

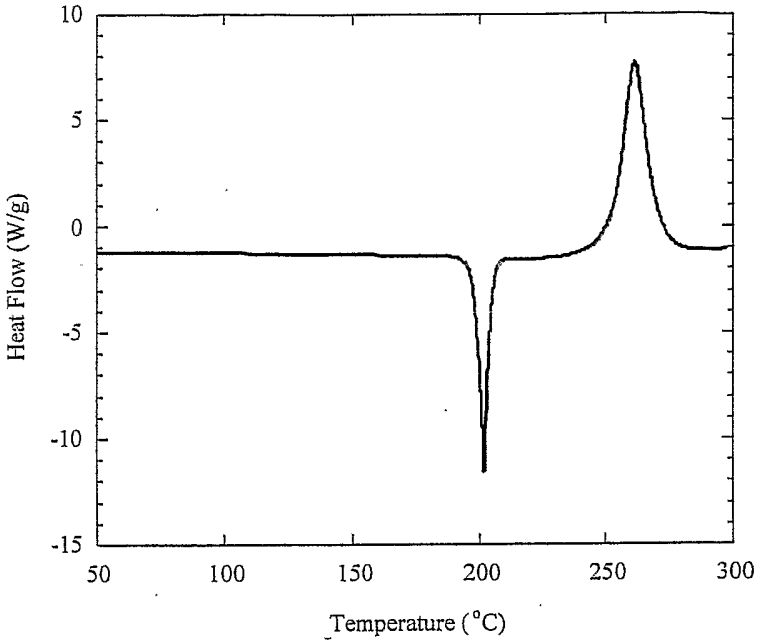

10
5
0
-5
-10
-15
Heat Flow (W/g)
50
100
150
200
250
300
Temperature (°C)

FIG. 7

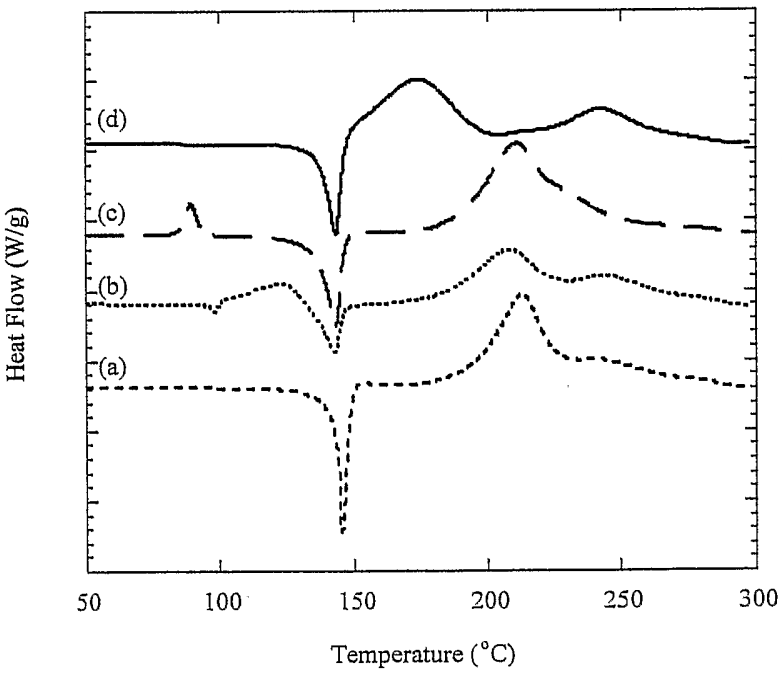

(d)
(c)
(b)
(a)
Heat Flow (W/g)
50
100
150
200
250
300
Temperature (°C)

FIG. 8

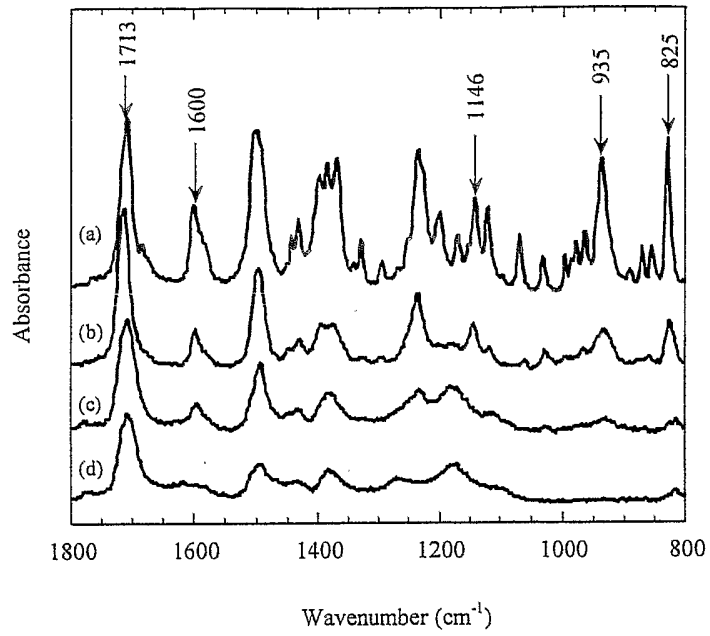

1713
1600
1146
935
825
(a)
(b)
(c)
(d)
Absorbance
1800
1600
1400
1200
1000
800
Wavenumber (cm-1)

FIG. 9

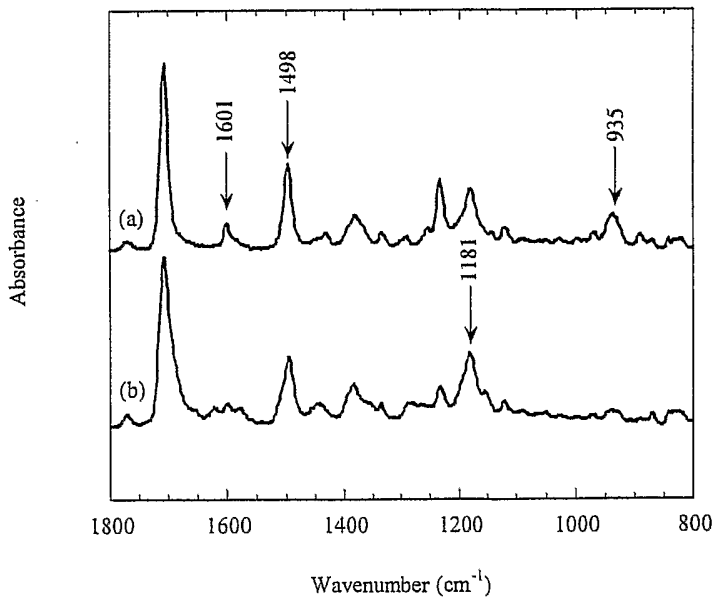

1601
1498
935
1181
(a)
(b)
Absorbance
1800
1600
1400
1200
1000
800
Wavenumber (cm-1)

FIG. 10

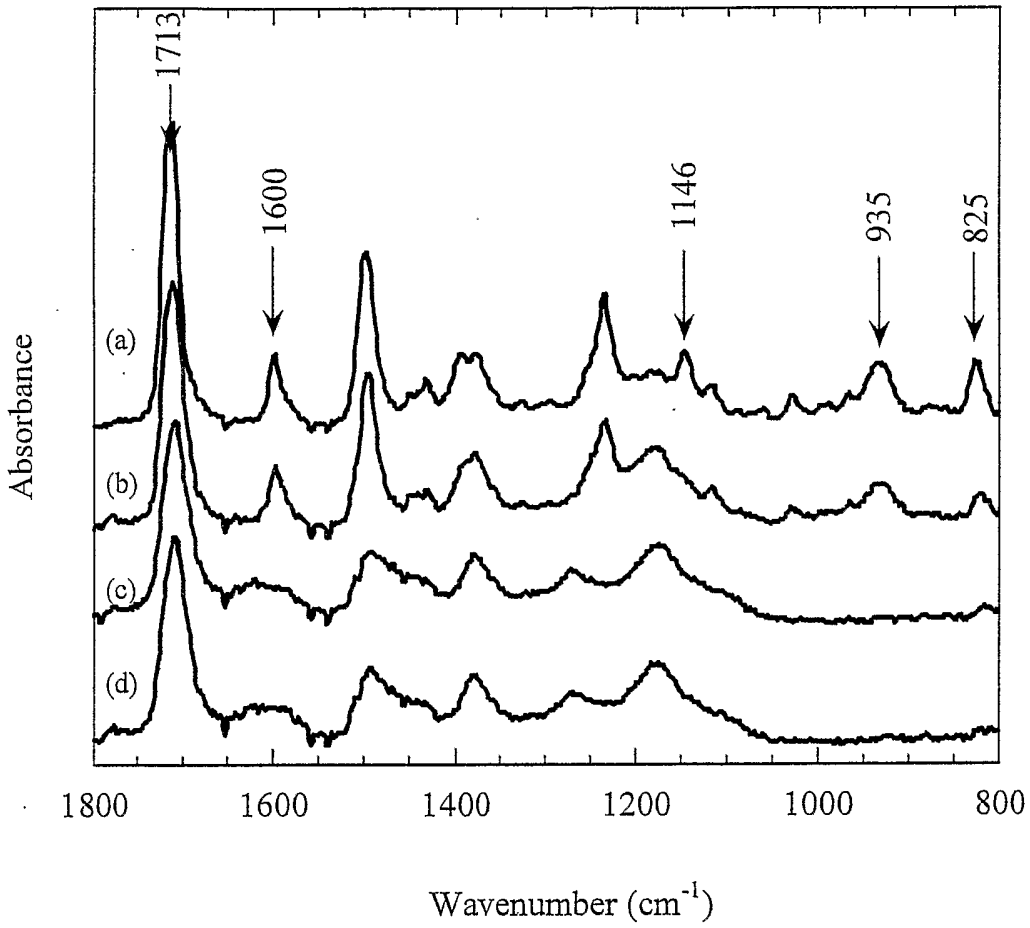

1713
1600
1146
935
825
(a)
(b)
(c)
(d)
Absorbance
1800
1600
1400
1200
1000
800
Wavenumber (cm-1)

FIG. 11

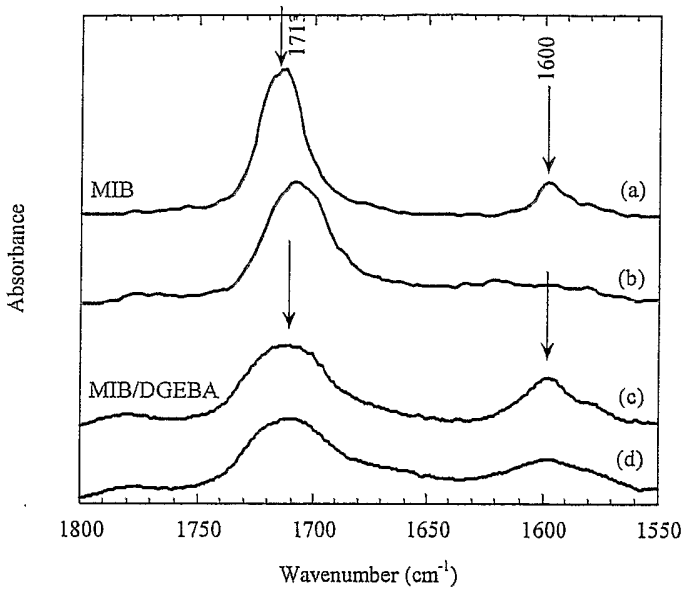

1715
1600
MIB
(a)
(b)
MIB/DGEBA
(c)
(d)
Absorbance
1800
1750
1700
1650
1600
1550
Wavenumber (cm-1)

FIG. 12

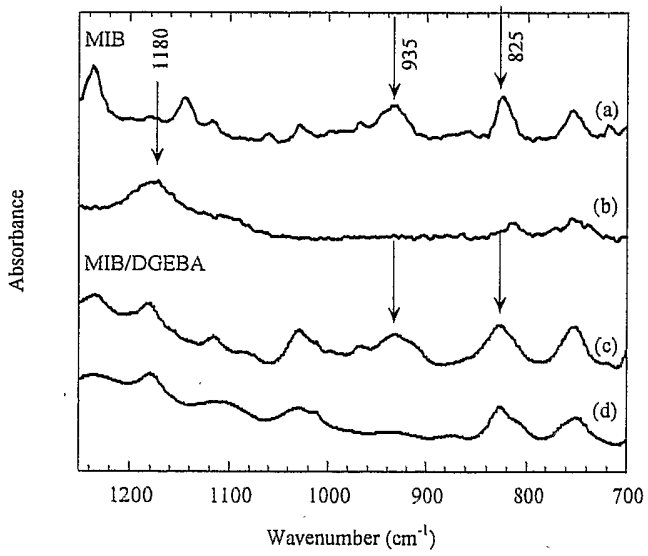

MIB
1180
935
825
(a)
(b)
MIB/DGEBA
(c)
(d)
Absorbance
1200
1100
1000
900
800
700
Wavenumber (cm-1)

FIG. 13

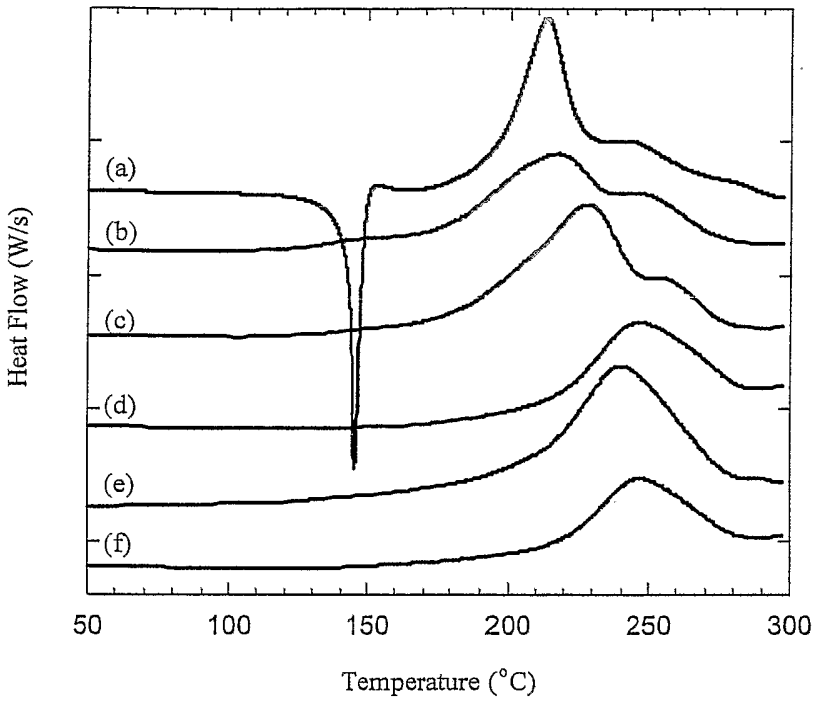

Heat Flow (W/s)
(a)
(b)
(c)
(d)
(e)
(f)
50
100
150
200
250
300
Temperature (°C)

FIG. 14

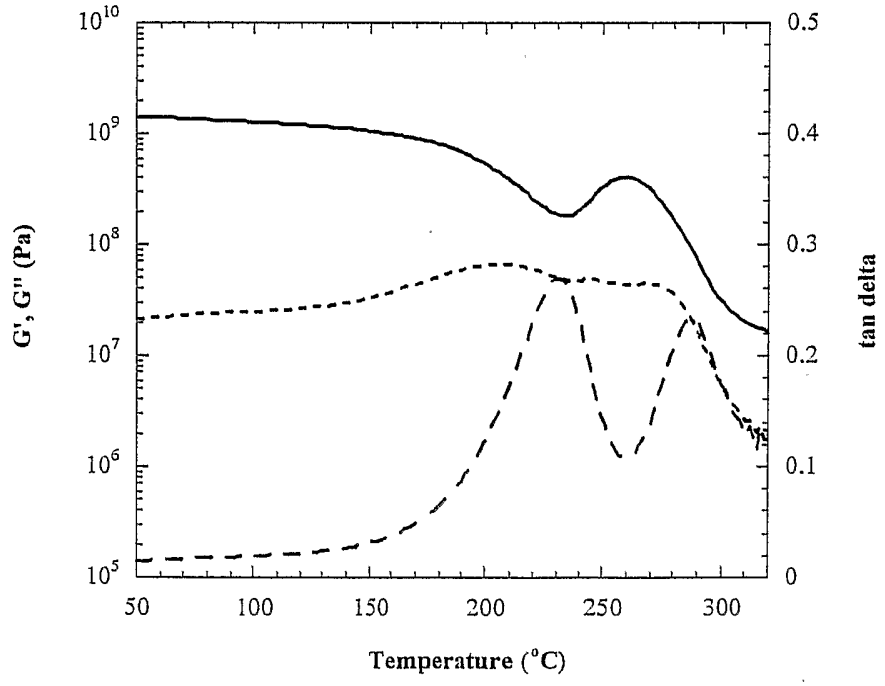

G', G'' (Pa)
10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
0.5
0.4
0.3
0.2
0.1
0
tan delta
50
100
150
200
250
300
Temperature (°C)

FIG. 15

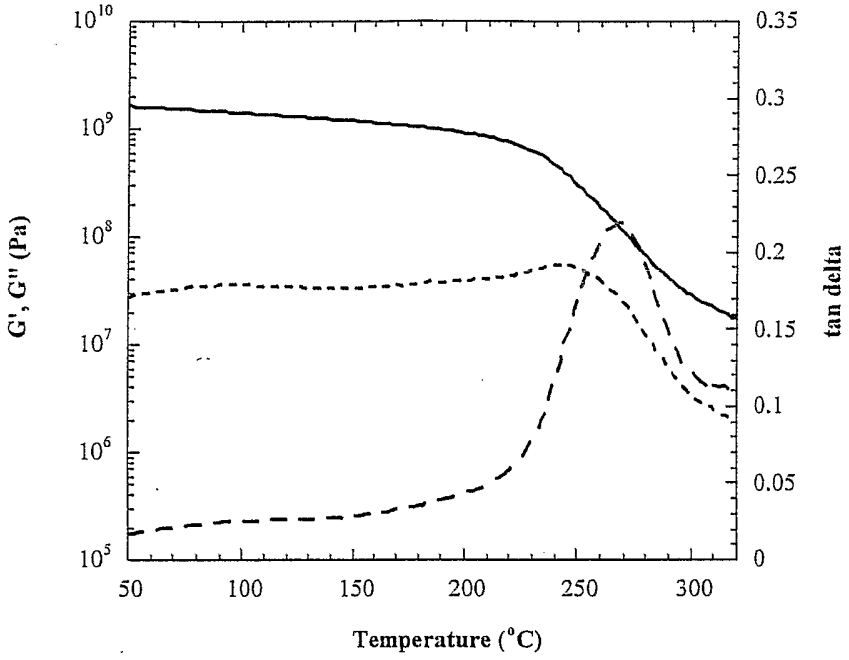

10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
G', G'' (Pa)
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
tan delta
50
100
150
200
250
300
Temperature (°C)

FIG. 16

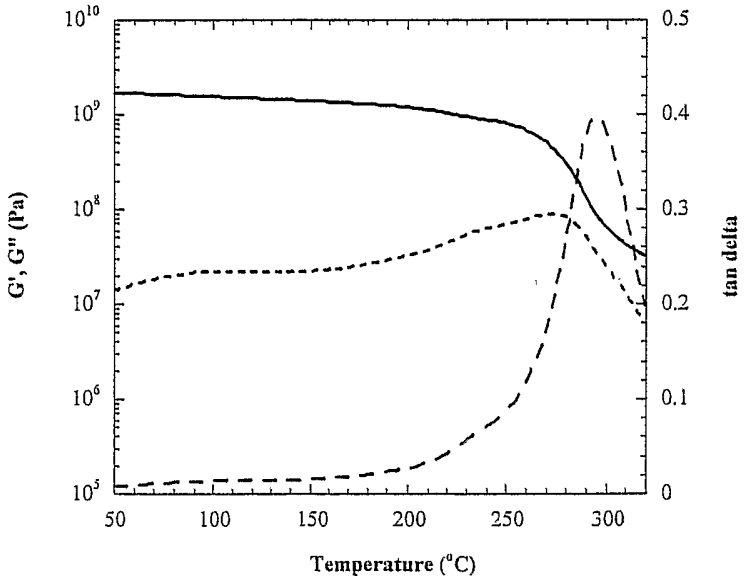

10^{10}
10^{9}
10^{8}
10^{7}
10^{6}
10^{5}
G', G'' (Pa)
0.5
0.4
0.3
0.2
0.1
0
tan delta
50
100
150
200
250
300
Temperature (°C)

FIG. 17

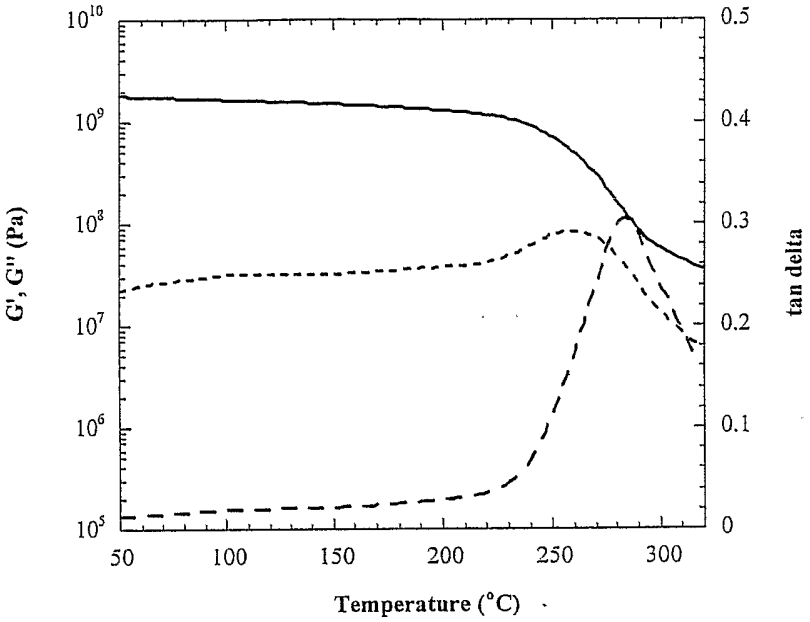

G', G'' (Pa)
tan delta
Temperature (°C)

FIG. 18

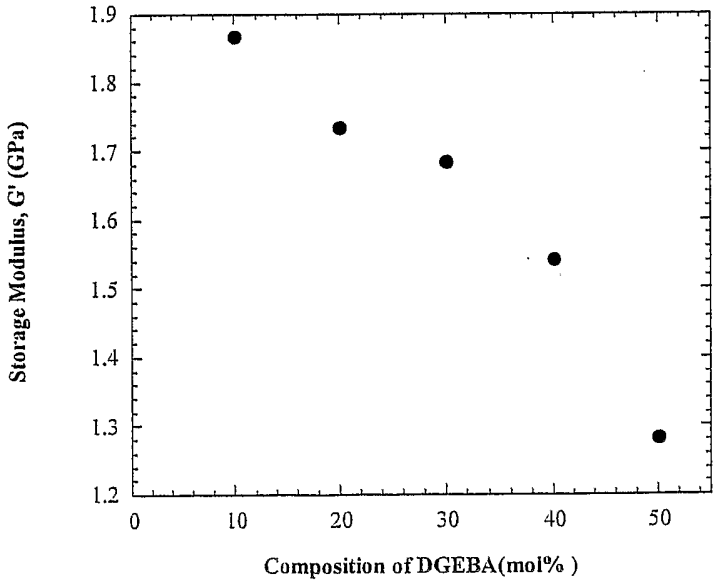

Storage Modulus, G' (GPa)
Composition of DGEBA(mol%)

FIG. 19

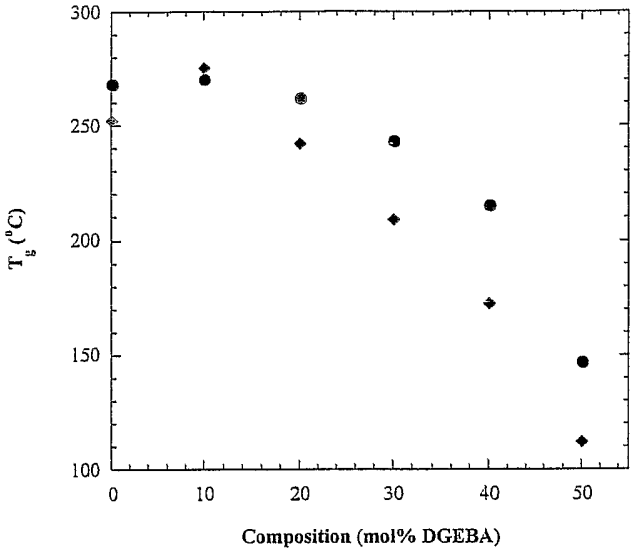

300
250
200
150
100
T_g (°C)
0
10
20
30
40
50
Composition (mol% DGEBA)

FIG. 20

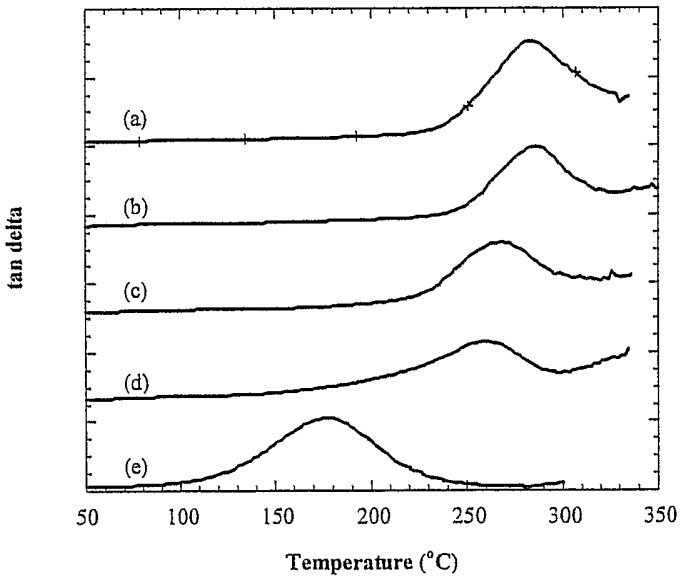

(a)
(b)
(c)
(d)
(e)
tan delta
50
100
150
200
250
300
350
Temperature (°C)

FIG.21

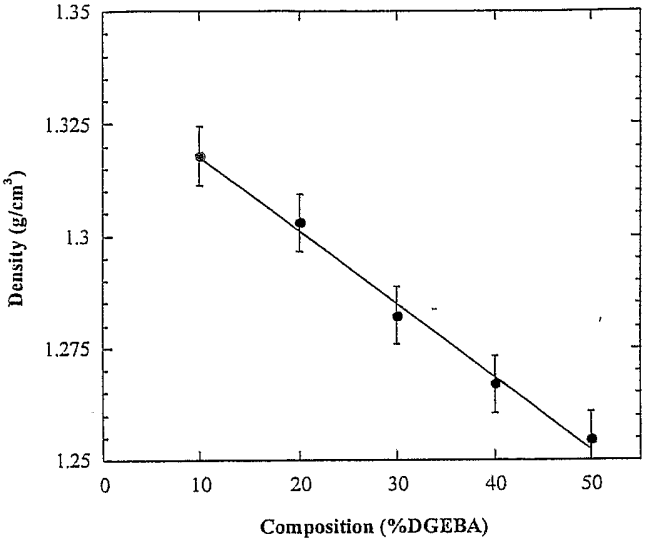

1.35
1.325
1.3
1.275
1.25
Density (g/cm3)
0
10
20
30
40
50
Composition (%DGEBA)

FIG. 22

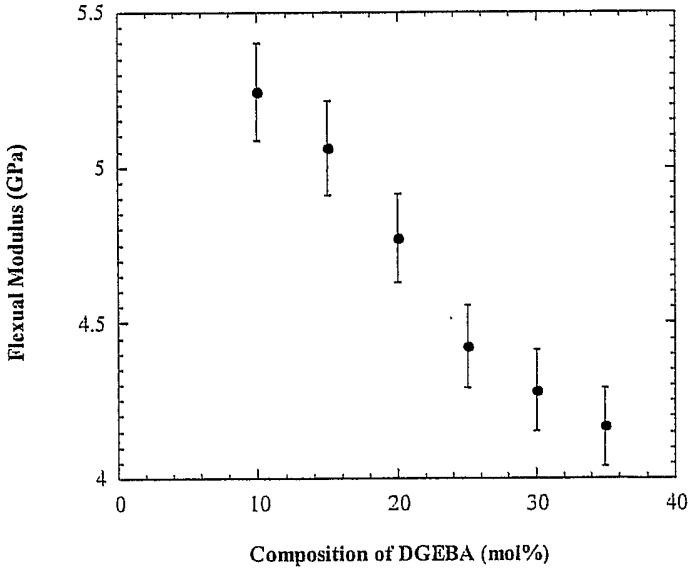

5.5
5
4.5
4
Flexual Modulus (GPa)
0
10
20
30
40
Composition of DGEBA (mol%)

FIG. 23

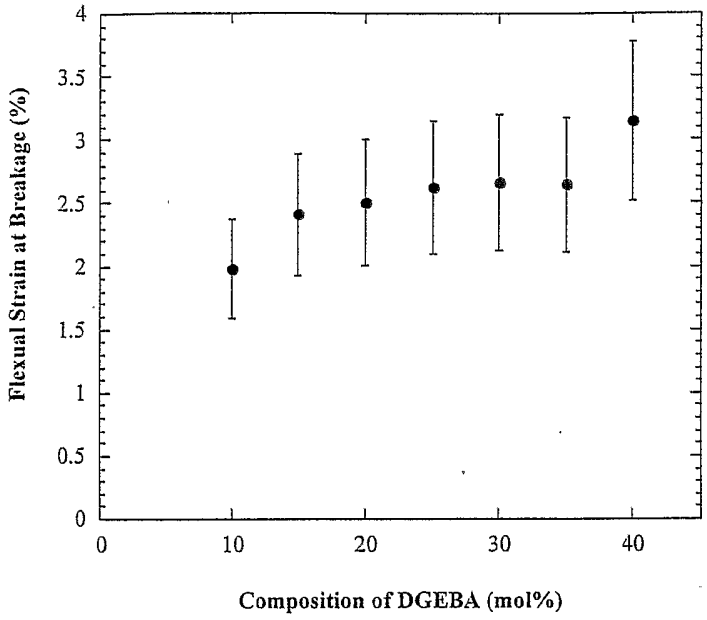

Flexual Strain at Breakage (%)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
Composition of DGEBA (mol%)

FIG. 24

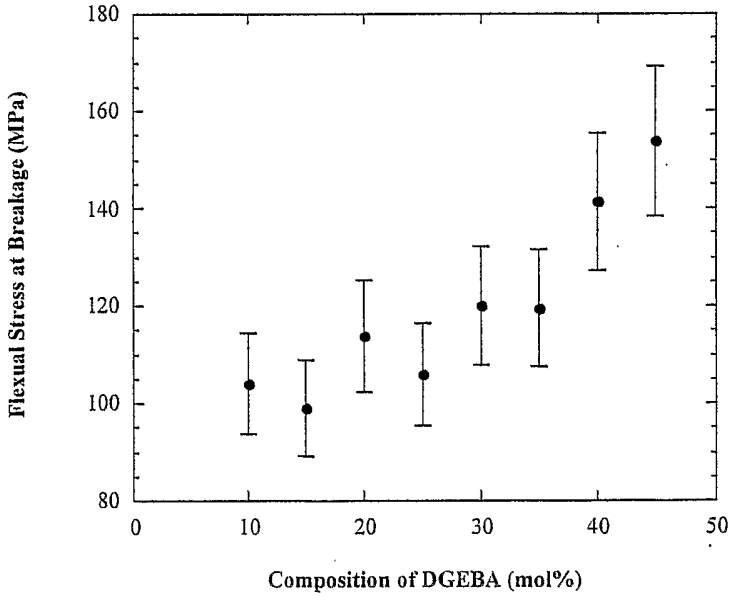

Flexual Stress at Breakage (MPa)
180
160
140
120
100
80
0
10
20
30
40
50
Composition of DGEBA (mol%)

FIG. 25