

Description

FIELD OF THE INVENTION

5 This invention relates to energy-polymerizable compositions comprising cyanate monomers and as curing agent an organometallic compound and a method therefor. In another aspect, cured articles comprising the composition of the invention are disclosed. The compositions are useful in applications requiring high performance, such as high temperature performance; in composites, particularly structural composites; structural adhesives; tooling for structural composites; electronic applications such as printed
10 wiring boards and semiconductor encapsulants; graphic arts; injection molding and prepregs; and high performance binders.

BACKGROUND OF THE INVENTION

15 Industry is constantly searching for lighter, stronger, and more resistant materials to replace those in present use. Cyanate ester resins are known for their thermal stability, chemical inertness, solvent resistance, and dielectric properties. Thus, more and more uses are being found in a variety of fields which demand high performance materials, such as structural composites, printed wiring boards, semiconductor encapsulants, structural adhesives, graphic arts, injection molding and prepregs, and high performance binders.

Cyanate ester resins are formed from polyfunctional cyanate monomers (see U. S. Patent No. 4,094,852). Generally, because it is desirable to achieve lower curing temperatures and faster curing times, a catalyst is employed. Catalysts which are effective include acids, bases, salts, nitrogen and phosphorus compounds, for example, Lewis acids such as $AlCl_3$, BF_3 , $FeCl_3$, $TiCl_4$, $ZnCl_2$, $SnCl_4$; Bronsted acids such
25 as HCl , H_3PO_4 ; aromatic hydroxy compounds such as phenol, p-nitrophenol, pyrocatechol, dihydroxynaphthalene; various other compounds such as sodium hydroxide, sodium methoxide, sodium phenoxide, trimethylamine, triethylamine, tributylamine, diazabicyclo[2.2.2]octane, quinoline, isoquinoline, tetrahydroquinoline, tetraethylammonium chloride, pyridine-N-oxide, tributylphosphine, zinc octoate, tin octoate, zinc naphthenate, and mixtures thereof.

30 Oehmke (U. S. Patent No. 3,694,410) teaches that chelates of metal ions of the nonionic type or ionic type, with 1 to 6 or more chelate rings, can catalyze the formation of polytriazines from aromatic polyfunctional cyanates. Similarly, Woo and Deller (U. S. Patent No. 4,528,366) have shown that cobalt salts of C_6-20 carboxylic acids are useful catalysts for polytriazine formation, preferably cobalt octoate and cobalt naphthenate. Shimp (U. S. Patent Nos. 4,604,452 and 4,608,434) has shown that alcoholic solutions of metal
35 carboxylates are effective catalyst compositions for polytriazine formation. Organometallic cobalt compounds have been used to catalyze the trimerization of acetylenes (U. S. Patent No. 4,183,864) and the co-trimerization of acetylenes and nitriles (U. S. Patent No. 4,328,343). The photocatalyzed cyclotrimerization of aryl isocyanates using metal carbonyl complexes has also been taught (E. Martelli, C. Pellizzi, and G. Predieri, J. Molec. Catalysis 22, 89-91 (1983)).

40 Energy polymerizable compositions comprising ionic salts of organometallic complex cations and cationically sensitive materials and the curing thereof has been taught [see European Patent Nos. 109,851, 1984; 094,914, 1983 and Derwent Abstract; and 094,915, 1983 and Derwent Abstract (English language equivalent So. Afr. 837966)]. EP 094,915 and EP 109,851 disclose curing in one and two stages. Energy polymerizable compositions comprising ionic salts of organometallic complex cations and polyurethane
45 precursors or isocyanates has also been taught (U.S. Patent No. 4,740,577 which also discloses curing in one and two stages; European Patent Nos. 265,373, 1988, Derwent Abstract; and 250,364, 1987, Derwent Abstract).

In certain applications, advantages in terms of improved potlife, physical properties of the cured material, and flexibility with respect to process parameters, particularly temperature, can be achieved with
50 the use of photocatalysts. Gaku, Kimbura, and Yokoi (U. S. Patent No. 4,554,346) disclosed (photo)curable resins from cyanate ester compounds. The inventors acknowledged that "the degree of radical-polymerizability or photo-polymerizability of the cyanate ester itself is small," resulting in poorly cured materials. Instead, Gaku, et al., used mixtures of polyfunctional cyanate esters with at least one compound having hydroxy group(s) and radical-polymerizable unsaturated double bonds, the compounds used in quantities
55 such that the ratio of cyanato groups to the hydroxy groups is in the range from 1:0.1 to about 1:2, and a radical polymerization (photo)initiator, at elevated temperature. These materials would not be expected to yield the same polytriazine materials obtainable from direct polymerization of the polyfunctional cyanates to polytriazines. To our knowledge, no other photoinitiators or photocatalysts for polyfunctional cyanate curing

to polytriazines have been disclosed.

What the prior art has not taught, but what the present invention teaches is the use of organometallic compounds for the curing of cyanate monomers.

5 SUMMARY OF THE INVENTION

The present invention provides energy polymerizable compositions comprising at least one cyanate monomer and oligomers thereof and as curing agent a specified transition metal organometallic compound. The compositions are useful in applications requiring high performance, such as high temperature performance; for composites, particularly structural composites for aircraft; in structural adhesives; in tooling for structural composites; in electronic applications, such as printed wiring boards and semiconductor encapsulants; graphic arts; in injection molding and prepreps; and in high performance binders.

Advantages of compositions of the present invention include:

- 10 Readily available cyanate monomers can be used without the need for preparing monomers containing other polymerizable groups, and with the advantage that the cyanate monomers generally provide superior properties when cured. The compositions are free of hydroxy functionality.

The specified organometallic compounds as catalysts:

provide curing, including radiation curing, at significantly lower temperatures or faster rates than previously described catalysts,

- 20 allow more efficient processing and greater latitude in coating substrates,

provide a fine degree of control of curing temperature by control of catalyst composition, and

are significantly more soluble than many previously described catalysts, making 100% reactive compositions possible.

- The composition of the present invention can be cured by at least one of thermal energy, by 25 electromagnetic radiation, and by accelerated particles. Radiation processing greatly expands the utility and potential applications of cyanate resins; it allows greater flexibility in processing, including curing at faster rates or lower temperatures or two-stage curing (photolysis followed by heating). Radiation processing, particularly utilizing electron beam and photogenerated catalysts, has capability for penetrating and polymerizing thick and pigmented coatings.

- 30 In this application:

"energy polymerizable" means curable by means of electromagnetic radiation (ultraviolet and visible) accelerated particles (including electron beam), and thermal (infrared and heat) means;

- 35 "catalytically-effective amount" means a quantity sufficient to effect polymerization of the curable composition to a polymerized product at least to a degree to cause an increase in the viscosity of the composition;

"organometallic compound" means a salt or covalently bonded compound in which at least one carbon atom of an organic group is bonded to a metal atom (see "Basic Inorganic Chemistry", F.A. Cotton, G. Wilkinson, Wiley, New York, 1976, p. 497);

- 40 "cyanate monomer" means a chemical substance in which at least one -OCN group is bonded to an organic radical R through the oxygen atom, forming an R-OCN bond; and

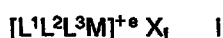
"curing agent" and "catalyst" are terms which are used interchangeably.

DETAILED DESCRIPTION OF THE INVENTION

- 45 The present invention provides, in a preferred embodiment, a thermally polymerizable composition comprising at least one cyanate monomer and a specified organometallic compound as a catalyst or curing agent therefor.

In a second embodiment, this invention provides a photopolymerizable composition comprising at least one cyanate monomer and a specified organometallic compound as a catalyst or curing agent therefor.

- 50 The specified curing agent useful in the energy polymerizable compositions of the invention comprises an organometallic compound having the structure



- 55 wherein

L^1 represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic com-

pounds, each capable of contributing 2 to 24 pi-electrons to the valence shell of M;

L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M;

L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M;

M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VB, VIB, VIIB, and VIII (commonly referred to as transition metals);

e is an integer having a value of 0, 1 or 2, such that the organometallic portion of the molecule is neutral, cationic or dicationic;

X is an anion selected from organic sulfonate and halogenated metal or metalloid groups;

f is an integer of 0, 1, or 2, the number of anions required to balance the charge e on the organometallic portion;

with the proviso that the organometallic compound contains at least one metal-carbon bond; and with the proviso that L^1 , L^2 , L^3 , M, e, X, and f are chosen so as to achieve a stable electronic configuration.

There are restrictions on the sum of electrons donated by the ligands, L^1 , L^2 , L^3 of formula I and the valence electrons possessed by the metal. For most organometallic compounds not involving intramolecular metal-metal bonding, this sum is governed by the "eighteen electron rule" [see J. Chem. Ed., 46, 811 (1969)]. This rule is sometimes called the "nine orbital rule", "the effective number rule", or the "rare gas rule". This rule states that the most stable electronic configurations for organometallic compounds tend to be those in which the sum of the electrons donated by the ligands and the metal is eighteen. Those skilled in the art, however, know that there are exceptions to this rule and that organometallic compounds having a sum of 16, 17, 19, and 20 electrons are also known. Therefore, organometallic compounds not including intramolecular metal-metal bonding as described by formula I, in which complexed metals having a total sum of 16, 17, 18, 19, or 20 electrons in the valence shell, are included within the scope of the invention.

For compounds described in formula I in which intramolecular metal-metal bonding exists, serious departure from the "eighteen electron rule" can occur. It has been proposed [J. Amer. Chem. Soc. 100, 5305 (1978)] that the departure from the "eighteen electron rule" in these transition metal compounds is due to the metal-metal interactions destabilizing the metal p orbitals to an extent to cause them to be unavailable for ligand bonding. Hence, rather than count electrons around each metal separately in a metal cluster, cluster valence electrons (CVE) are counted. A dinuclear compound is seen to have 34 CVEs, a trinuclear compound 48 CVEs, and a tetranuclear compound having tetrahedron, butterfly, and square planar geometry is seen to have 60, 62, or 64 CVEs, respectively. Those skilled in the art, however, know that there are exceptions to this electron counting method and that organometallic cluster compounds having a sum of 42, 44, 46, 50 CVEs for a trinuclear compound and 58 CVEs for a tetranuclear compound are also known. Therefore, di, tri, or tetranuclear organometallic compounds are described by formula I in which the complexed metal cluster, MM, MMM, or MMMM has a sum of 34; 42, 44, 46, 48, 50; 58, 60, 62, or 64 CVEs in the valence shell, respectively, and are included within the scope of this invention.

Ligands L^1 to L^3 are well known in the art of transition metal organometallic compounds. At least one such ligand must be present in the catalyst of the present invention.

Ligand L^1 of general formula I is provided by any monomeric or polymeric compound having an accessible unsaturated group, i.e., an ethylenic, $-C=C-$ group; acetylenic, $-C\equiv C-$ group; or aromatic group which has accessible pi-electrons regardless of the total molecular weight of the compound. By "accessible", it is meant that the compound (or precursor compound from which the accessible compound is prepared) bearing the unsaturated group is soluble or swellable in a reaction medium, such as an alcohol, e.g., methanol; a ketone, e.g., methyl ethyl ketone; an ester, e.g., amyl acetate; a halocarbon, e.g., trichloroethylene; an alkane, e.g., decalin; an aromatic hydrocarbon, e.g., anisole; an ether, e.g., tetrahydrofuran; or that the compound is divisible into very fine particles of high surface area so that the unsaturated group (including aromatic group) is sufficiently close to a metal atom to form a pi-bond between that unsaturated group and the metal atom.

By polymeric compound, is meant, as explained below, that the ligand can be a group on a polymeric chain. Illustrative of ligand L^1 are the linear and cyclic ethylenic and acetylenic compounds having less than 100 carbon atoms (when monomeric), preferably having less than 60 carbon atoms, and from zero to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorous, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, the ligands being those such as, for example, ethylene, acetylene, propylene, methylacetylene, alpha-butene, 2-butene, diacetylene, butadiene, 1,2-dimethylacetylene, cyclobutene, pentene, cyclopentene, hexene, cyclohexene, 1,3-cyclohexadiene, cyclopentadiene, 1,4-cyclohexadiene, cycloheptene, 1-octene, 4-octene, 3,4-dimethyl-3-hexene, and 1-

decene; η^3 -allyl, η^3 -pentenyl, norbornadiene, η^5 -cyclohexadienyl, cycloheptatriene, cyclooctatetraene, and substituted and unsubstituted carbocyclic and heterocyclic aromatic ligands having up to 25 rings and up to 100 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorus, arsenic, selenium, boron, antimony, tellurium, silicon, germanium, and tin, such as, for example, η^5 -cyclopentadienyl, benzene, mesitylene, hexamethylbenzene, fluorene, naphthalene, anthracene, chrysene, pyrene, η^7 -cycloheptatrienyl, triphenylmethane, paracyclophane, 1,4-diphenylbutane, η^5 -pyrrole, η^5 -thiophene, η^5 -furan, pyridine, gamma-picoline, quinaldine, benzopyran, thiochrome, benzoxazine, indole, acridine, carbazole, triphenylene, silabenzene, arsabenzene, stibabenzene, 2,4,6-triphenylphosphabenzene, η^5 -selenophene, dibenzostannepine, η^5 -tellurophene, phenothiarisene, selenanthrene, phenoxaphosphine, phenarsazine, phenatellurazine, η^5 -methylcyclopentadienyl, η^5 -pentamethylcyclopentadienyl, and 1-phenylborabenzene. Other suitable aromatic compounds can be found by consulting any of many chemical handbooks.

As mentioned before, the ligand can be a unit of a polymer, for example, the phenyl group in polystyrene, poly(styrene-co-butadiene), poly(styrene-co-methyl methacrylate), poly(alpha-methylstyrene), polyvinylcarbazole, and polymethylphenylsiloxane; the cyclopentadiene group in poly(vinylcyclopentadiene); the pyridine group in poly(vinylpyridine), etc. Polymers having a weight average molecular weight up to 1,000,000 or more can be used. It is preferable that 1 to 50 percent of the unsaturated or aromatic groups present in the polymer be complexed with organometallic groups.

Each ligand L^1 can be substituted by groups that do not interfere with the complexing of the ligand with the metal atom or which do not reduce the solubility of the ligand to the extent that complexing with the metal atom does not take place. Examples of substituting groups, all of which preferably have less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron, include hydrocarbyl groups such as methyl, ethyl, butyl, dodecyl, tetracosanyl, phenyl, benzyl, allyl, benzyldiene, ethenyl, and ethynyl; hydrocarbyloxy groups such as methoxy, butoxy, and phenoxy; hydrocarbylmercapto groups such as methylmercapto (thiomethoxy), phenylmercapto (thiophenoxy); hydrocarbyloxycarbonyl such as methoxycarbonyl and phenoxycarbonyl; hydrocarbylcarbonyl such as formyl, acetyl, and benzoyl; hydrocarbylcarbonyloxy such as acetoxo, benzoxo, and cyclohexanecarbonyloxy; hydrocarbylcarbonamido, e.g., acetamido, benzamido; azo, boryl; halo, e.g., chloro, iodo, bromo, and fluoro; hydroxy; cyano; nitro; nitroso, oxo; dimethylamino; diphenylphosphino, diphenylarsino; diphenylstibine; trimethylgermyl; tributylstannyl; methylseleno; ethyltelluro; and trimethylsiloxy; condensed rings such as benzo, cyclopenta; naphtho, and indeno;

Each ligand L^2 in formula I is provided by monodentate and polydentate compounds preferably containing up to about 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, non-peroxidic oxygen, phosphorus, arsenic, selenium, antimony, and tellurium, where upon addition to the metal atom, following loss of zero, one, or two hydrogens, the polydentate compounds preferably forming with the metal, M, a 4-, 5-, or 6-membered saturated or unsaturated ring. Examples of suitable monodentate compounds or groups are carbon monoxide, carbon sulfide, carbon selenide, carbon telluride, alcohols such as ethanol, butanol, and phenol; nitrosonium (i.e., NO^+); compounds of Group VA elements such as ammonia, phosphine, trimethylamine, trimethylphosphine, triphenylamine, triphenylphosphine, triphenylarsine, triphenylstibine, tributylphosphite; nitriles such as acetonitrile, benzonitrile; isonitriles such as phenylisonitrile, butylisonitrile; carbene groups such as ethoxymethylcarbene, dithiomethoxycarbene; alkylidenes such as methylidene, ethylidene; suitable polydentate compounds or groups include 1,2-bis(diphenylphosphino)ethane, 1,2-bis(diphenylarsino)ethane, bis(diphenylphosphino)methane, ethylenediamine, propylenediamine, diethylenetriamine, 1,3-diisocyanopropane, and hydridotripyrazolylborate; the hydroxycarboxylic acids such as glycolic acid, lactic acid, salicylic acid; polyhydric phenols such as catechol and 2,2'-dihydroxybiphenyl; hydroxyamines such as ethanolamine, propanolamine, and 2-aminophenol; dithiocarbamates such as diethyldithiocarbamate, dibenzoyldithiocarbamate; xanthates such as ethyl xanthate, phenyl xanthate; the dithiolenes such as bis(perfluoromethyl)-1,2-dithiolene; aminocarboxylic acids such as alanine, glycine and o-aminobenzoic acid; dicarboxylic diamines as oxalamide, biuret; diketones such as 2,4-pentanedione; hydroxyketones such as 2-hydroxyacetophenone; alpha-hydroxyoximes such as salicylaldehyde; ketoximes such as benzil oxime; and glyoximes such as dimethylglyoxime.

Other suitable groups are the inorganic groups such as, for example, CN^- , SCN^- , F^- , OH^- , Cl^- , Br^- , I^- , and H^- and the organic groups such as, for example, acetoxo, formyloxy, and benzoyloxy. As mentioned before, the ligand can be a unit of a polymer, for example the amino group in poly(ethyleneamine); the phosphino group in poly(4-vinylphenyldiphenylphosphine); the carboxylic acid group in poly(acrylic acid); and the isonitrile group in poly(4-vinylphenylisonitrile).

Suitable ligands L^3 in formula I include any group having in its structure an atom with an unshared electron. Suitable groups can contain any number of carbon atoms and hetero atoms but preferably contain less than 30 carbon atoms and up to 10 hetero atoms selected from nitrogen, sulfur, oxygen, phosphorus, arsenic, selenium, antimony, tellurium, silicon, germanium, tin, and boron. Examples of such groups are hydrocarbyl groups such as methyl, ethyl, propyl, hexyl, dodecyl, phenyl, tolyl; unsaturated hydrocarbyl groups such as vinyl, η^1 -allyl, η^1 -butenyl, η^1 -cyclohexenyl; the hydrocarbyl derivatives of a Group IVA element such as trimethylgermyl, triphenylstannyl, and trimethylsilyl, triphenyllead; and organic groups such as formyl, acetyl, propionyl, acryloyl, octadecoyl, benzoyl, toluenesulfonyl, oxalyl, malonyl, o-phthaloyl.

Also suitable as L^3 is any group having in its structure two, three, or four unshared electrons. Examples of such groups are CH_2 , $CHCH_3$, $SiMe_2$, $SiPh_2$ (wherein Ph is phenyl), $SnPh_2$, $GePh_2$, CH , $SiMe$, $SiPh$, $SnPh$, C , Si , and Sn .

M can be any element from the Periodic Groups IVB, VB, VIB, VIIB, and VIII, such as, for example, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pd and Pt.

Each X is provided by organic sulfonates, or halogenated metals or metalloids. Examples of such ions are $CH_3SO_3^-$, $CF_3SO_3^-$, $C_6H_5SO_3^-$, p-toluenesulfonate, p-chlorobenzenesulfonate and related isomers and those in which X has the formula DZ_r , wherein D is a metal from Groups IB to VIII or a metal or metalloid from Groups IIIA to VA of the Periodic Chart of Elements, Z is a halogen atom or hydroxyl group, and r is an integer having a value of 1 to 6. Preferably, the metals are copper, zinc, titanium, vanadium, chromium, manganese, iron, cobalt, or nickel and the metalloids preferably are boron, aluminum, antimony, tin, arsenic, and phosphorus. Preferably, the halogen, Z, is chlorine or fluorine. Illustrative of suitable anions are BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , $FeCl_4^-$, $SnCl_5^-$, SbF_5^- , AlF_6^- , $GaCl_4^-$, InF_4^- , and TiF_6^- . Preferably, the anions are $CF_3SO_3^-$, BF_4^- , PF_6^- , SbF_6^- , SbF_5OH^- , AsF_6^- , and $SbCl_6^-$.

Covalently bonded organometallic compounds useful in the present invention are available from Strem Chemical Company (Newburyport, MA) or can be prepared by literature methods known to those skilled in the art, see for example Inorg. Chem. 17, 1003 (1978), Chem. Ber. 102, 2449 (1969), J. Organomet. Chem. 135, 373 (1977), and Inorg. Chem. 18, 553 (1979). Organometallic complex salts useful in the present invention are available from Strem Chemical Company or can be prepared as disclosed in EP 109851, EP 094914, and EP 094915.

Illustrative examples of organometallic compounds according to formula I include metal carbonyls such as $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Fe_2(CO)_9$; metal-metal bonded binuclear compounds such as $[CpFe(CO)_2]_2$, $Mn_2(CO)_{10}$, $[CpMo(CO)_3]_2$, $[CpW(CO)_3]_2$, $Re_2(CO)_{10}$, $Co_2(CO)_8$, $Cp(CO)_3W-Mo(CO)_3Cp$, $Cp(CO)_3Mo-Mn(CO)_5$, $Cp(CO)_3Mo-Re(CO)_5$, $(CO)_5Mn-Fe(CO)_2Cp$, $Cp(CO)_3W-Mn(CO)_5$, $Cp(CO)_3W-Re(CO)_5$, $Cp(CO)_3Mo-Co(CO)_4$, $Cp(CO)_3W-Co(CO)_4$, $Cp(CO)_3Mo-Fe(CO)_2Cp$, $Cp(CO)_3W-Fe(CO)_2Cp$, $[CpMo(CO)_2PPh_3]_2$, $Mn_2(CO)_9PPh_3$, $Mn_2(CO)_8(PPh_3)_2$, $(CO)_5Mn-Re(CO)_5$, $Mn_2(CO)_8(1,10\text{-phenanthroline})$, $Re_2(CO)_8(1,10\text{-phenanthroline})$, $Re_2(CO)_8(2,2'\text{-biquinoline})$, $[CpNi(CO)]_2$, $[Cp^*Fe(CO)_2]_2$, $Cp(CO)_2Fe-Fe(CO)(PPh_3)Cp$, $Cp(CO)_3Mo-Mo(CO)_2(PPh_3)Cp$; metal clusters such as $Co_4(CO)_{12}$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ru_3(CO)_{11}PPh_3$, $Ru_3(CO)_{10}(Ph_2P-CH_2CH_2-PPh_2)$, $Fe_2Ru(CO)_{12}$, $Ir_4(CO)_{12}$; compounds containing a metal-Group IVA bond such as $CpFe(CO)_2SnPh_3$, $CpFe(CO)_2GePh_3$, $[CpFe(CO)_2]_2SnPh_2$, $CpMo(CO)_3SnPh_3$, $(CO)_5MnSnPh_3$, $[(CO)_5Mn]_2SnPh_2$, $CpFe(CO)_2PbPh_3$, $CpFe(CO)_2CH_2Ph$, $CpFe(CO)_2(COPh)$, $CpFe(CO)_2(SiPh_3)$, $(CO)_5MnPbPh_3$, $(CO)_5ReSnPh_3$, $CpPtMe_3$, $(MeCp)PtMe_3$, $(Me_3SiCp)PtMe_3$, $CpW(CO)_3Me$, $[CpFe(CO)_2]_4Si$; salts of organometallic complex cations such as $Cp(CO)_3Fe(1+)PF_6(1-)$, $Cp(CO)_2(CS)Fe(1+)-BF_4(1-)$, $Cp(CO)(Ph_3Sb)_2Fe(1+)PF_6(1-)$, $Cp(CO)_3Ru(1+)FeCl_4(1-)$, $Cp(CO)_2(Ph_3Sb)Fe(1+)SbF_6(1-)$, $(MeCp)(CO)_2(NO)Mn(1+)SbF_6(1-)$, $(MeCp)(\eta^3\text{-allyl})(CO)_2Mn(1+)BF_4(1-)$, $Cp(CO)_4Mo(1+)PF_6(1-)$, $(\eta^5\text{-pentadienyl})(CO)_3Fe(1+)BF_4(1-)$, $(\eta^5\text{-cyclohexadienyl})(CO)_3Fe(1+)AsF_6(1-)$, $(\eta^5\text{-cyclohexadienyl})(\eta^1\text{-ethylidene})(CO)(Ph_3P)Fe(1+)BF_4(1-)$, $Cp(\eta^5\text{-ethoxymethylcarbene})(CO)(Ph_3P)Fe(1+)BF_4(1-)$, $Cp(\eta^5\text{-dithiomethoxycarbene})(CO)_2Fe(1+)PF_6(1-)$, $Cp(CO)_2(\eta^5\text{-methylisonitrile})Fe(1+)AsF_6(1-)$, $(\eta^6\text{-toluene})(CO)_3Mn(1+)SbF_6(1-)$, $(\eta^6\text{-mesitylene})(CO)_3Re(1+)SbF_6(1-)$, $(\eta^7\text{-cycloheptatrienyl})(CO)_3Cr(1+)PF_6(1-)$, $(\eta^7\text{-cycloheptatrienyl})(CO)_3W(1+)AsF_6(1-)$, $Cp(\eta^2\text{-1-pentene})(CO)_2Fe(1+)BF_4(1-)$, $(\eta^6\text{-benzene})CpFe(1+)PF_6(1-)$, $(\eta^6\text{-mesitylene})CpFe(1+)BF_4(1-)$, $(\eta^6\text{-naphthalene})CpFe(1+)SbF_6(1-)$, $(\eta^6\text{-acetophenone})(MeCp)Fe(1+)AsF_6(1-)$, $Cp_2Co(1+)PF_6(1-)$, $Cp_2Fe(1+)SbF_6(1-)$, $bis(\eta^5\text{-chlorocyclopentadienyl})Ni(1+)PF_6(1-)$, $bis(\eta^6\text{-benzene})Cr(1+)SbF_6(1-)$, $(CO)_4(Ph_3P)Co(1+)PF_6(1-)$, $(CO)_3(Ph_3P)_2Ir(1+)PF_6(1-)$, $(\eta^3\text{-allyl})(CO)_5Cr(1+)BF_4(1-)$, $(CO)_5(NO)Mo(1+)PF_6(1-)$, $(\eta^3\text{-allyl})(CO)_4Fe(1+)SbF_6(1-)$, $(CO)_5Re(1+)SbF_6(1-)$, $bis(\eta^6\text{-hexamethylbenzene})Mn(1+)BF_4(1-)$, $bis(\eta^6\text{-mesitylene})vanadium(1+)PF_6(1-)$, $(\eta^7\text{-cycloheptatrienyl})CpMn(1+)AsF_6(1-)$, $(\eta^8\text{-cyclooctatetraenyl})CpCr(1+)PF_6(1-)$, $(\eta^6\text{-fluorene})CpFe(1+)PF_6(1-)$, $(\eta^6\text{-1-phenylborabenzene})CpCo(1+)PF_6(1-)$, $Cp(\eta^5\text{-N-methylpyrrolyl})Fe(1+)PF_6(1-)$, $(\eta^6\text{-2,3,4,5-tetrathiomethoxybenzene})CpFe(1+)AsF_6(1-)$, $[(\eta^6\text{-1,2,3,3a,13b,13a})benzo(10,11)chryseno(2,3-d)(1,3)\text{-dioxide}](MeCp)Fe(1+)PF_6(1-)$, $bis(\eta^5\text{-acetylcyclopentadienyl})Fe(1+)BF_4(1-)$, $(\eta^3\text{-1-methylallyl})(CO)_4Fe(1+)PF_6(1-)$, $(\eta^3\text{-1,3-dimethylallyl})(CO)_4Fe(1+)SbCl_6(1-)$; salts of organometallic complex dications such

as bis(eta⁶-hexamethylbenzene)Co(2+)[AsF₆(1-)]₂, bis(eta⁶-mesitylene)Fe(2+)[SbF₆(1-)]₂, bis(eta⁶-hexamethylbenzene)Ni(2+)[SbF₆(1-)]₂, bis(eta⁶-hexamethylbenzene)Fe(2+)[PF₆(1-)]₂, [(eta⁶-1,2,3,4,5,6)(eta⁶-7,8,9,10,11,12)biphenyl]Cp₂Fe₂(2+)[BF₄(1-)]₂, [(eta⁶-1,2,3,4,4a,9a)(eta⁶-5,6,7,8,8a,5a)fluorene]Cp₂Fe₂(2+)[PF₆(1-)]₂, [(eta⁶-1,2,3,4,4a,12a)(eta⁶-7,8,9,10,10a,6a)chrysene]bis(eta⁶-benzene)Cr₂(2+)[SbF₆(1-)]₂, (CO)-
 5 2 bis[(diphenylphosphino)ethane]Cp₂Fe₂(2+)[PF₆(1-)]₂, [(eta⁶-4,5,5a,28c,28b,3a)(eta⁶-8a,8b,20d,22a,22b,24c)1H, 14H-dipyrano(3,4,5-gh:3',4',5'-g'h')anthra(2'',1'',9'':4,5,6;6'',5'',10'':4',5',6')diisoquino-(2,1-a:2',1'-a)l)dipyrimidine]Cp₂Fe₂(2+)[SbF₆(1-)]₂, [(eta⁶-1,2,3,3a,16c,16b)(eta⁶-9,10,11,11a,13c,8b)-cycloocta(1,2,3,4-def:5,6,7,8-d'e'f')diphenanthrene]bis(eta⁵-acetyl cyclopentadienyl)Fe(2+)[BF₄(1-)]₂; and other organometallic compounds such as (MeCp)Mn(CO)₃, CpMn(CO)₃, CpFe(CO)₂Cl, [(p-cymene)RuCl₂]₂,
 10 (eta⁶-benzene)Cr(CO)₃, Re(CO)₅Br, Cp₂Fe, Cp₂TiCl₂; wherein

Me is methyl

Ph is phenyl

Cp is eta⁵-cyclopentadienyl

Cp* is eta⁵-pentamethylcyclopentadienyl

15 MeCp is eta⁵-methylcyclopentadienyl

Me₃SiCp is eta⁵-trimethylsilylcyclopentadienyl

The cyanate monomers that can be polymerized using the curing agent of the present invention contain at least one -OCN group, and are of the general formula

20 Q(OCN)_p II

wherein p can be an integer from 1 to 7, and wherein Q comprises at least one of 1) a mono-, di-, tri-, or tetravalent aromatic hydrocarbon containing 5 to 30 carbon atoms, 2) 1 to 5 aliphatic or polycyclic aliphatic mono- or divalent hydrocarbon groups containing 7 to 20 carbon atoms, 1) and 2) optionally comprising 1 to
 25 10 heteroatoms selected from the group consisting of non-peroxidic oxygen, sulfur, non-phosphino phosphorus, non-amino nitrogen, halogen, silicon, and 3) a mono- or divalent fluorocarbon group having 3 to 12,500 carbon atoms and 5 to 25,000 fluorine atoms preferably corresponding to the formulae III and IV:

30 F₃C(CFX)_aA(CFX)_bCH₂- III

where A is a carbon-to-carbon bond, in which case a is an integer from 1 to 30 and b is zero, or A is -O-(CFX-CF₂-O)_c in which case a is an integer from 1 to 10, b is one, and c is an integer from 1 to 100, and X is fluorine or perfluoroalkyl having 1 to 10 carbon atoms;

35 -CH₂(CFX)_aB(CFX)_bCH₂- IV

where B is 1) a carbon-to-carbon bond, in which case a is an integer of 1 to 30 and b is zero, or 2) B is [(CFX)_dO(CFX)_u]_v, in which case a and b are zero, d and u are integers of 1 to 30, and v is an integer of 1 to 20, or 3) B is (OCF₂-CFX)_wO(CFX)_hO(CFX-CF₂O)_i, in which case a and b are 1, h is an integer of 1 to 10, and w and i are integers of 1 to 100, or 4) B is [(CF₂CH₂)_j(CF₂-CFX)_k]_m, in which case a and b are each integers of 1 to 10, j and k are integers whose ratio j/k is 1/1 to 1/10, m is an integer of 1 to 100, and (CF₂CH₂) and (CF₂-CFX) are randomly distributed units; and where X is fluorine or perfluoroalkyl of 1 to 10 carbon atoms.

In the practice of this invention, a combination of cyanate monomers can be used whereby such
 45 combination is comprised of one or more cyanates of Formula II and oligomers thereof, where p is 2 to 7 and oligomers thereof, and optionally one or more monofunctional cyanates (e.g. Formula II where p is one). Examples of cyanates are as follows: cyanatobenzene, 1,3- and 1,4-dicyanatobenzene, 2-tert-butyl-1,4-dicyanatobenzene, 2,4-dimethyl-1,3-dicyanatobenzene, 2,5-di-tert-butyl-1,4-dicyanatobenzene, tetramethyl-1,4-dicyanatobenzene, 4-chloro-1,3-dicyanatobenzene, 1,3,5-tricyanatobenzene, 2,2'- or 4,4'-
 50 dicyanatobiphenyl, 3,3',5,5'-tetramethyl-4,4'-dicyanatobiphenyl, 1,3-, 1,4-, 1,5-, 1,6-, 1,8-, 2,6-, or 2,7-dicyanatonaphthalene, 1,3,6-tricyanatonaphthalene, bis(4-cyanatophenyl)methane, bis(3-chloro-4-cyanatophenyl)methane, 2,2-bis(4-cyanatophenyl)propane, 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane, 2,2-bis(3,5-dibromo-4-cyanatophenyl)propane, bis(4-cyanatophenyl)ether, bis(p-cyanatophenoxyphenoxy)-benzene, di(4-cyanatophenyl)ketone, bis(4-cyanatophenyl)thioether, bis(4-cyanatophenyl)sulfone, tris(4-
 55 cyanatophenyl)phosphite, and tris(4-cyanatophenyl)phosphate. Also useful are cyanic acid esters derived from phenolic resins (U. S. Patent No. 3,962,184), cyanated novolak derived from novolak (U. S. Patent No. 4,022,755), cyanated bisphenol type polycarbonate oligomer derived from bisphenol types polycarbonate oligomer (U. S. Patent No. 4,026,913), cyanato-terminated polyarylene ethers (U. S. Patent No. 3,595,900),

dicyanate esters free of ortho hydrogen atoms (U. S. Patent No. 4,740,584), mixtures of di- and tricyanates (U. S. Patent No. 4,709,008), polyaromatic cyanates containing polycyclic aliphatic diradicals such as XU71787™, Dow Chemical Co. (U. S. Patent No. 4,528,366), fluorocarbon cyanates (U. S. Patent No. 3,733,349), and other novel cyanate compositions (U. S. Patents 4,195,132 and 4,116,946).

Polycyanate compounds obtained by reacting a phenolformaldehyde precondensate with a halogenated cyanide are also useful.

The curing agent can be present in the range of 0.01 to 20, preferably 0.1 to 10 weight percent of the total composition.

The present invention also provides a process for the polymerization of cyanate monomers, comprising the steps of:

- (a) providing at least one cyanate monomer and oligomers thereof;
- (b) adding to the monomer a catalytically effective amount of a curing agent comprising the specified organometallic compound mentioned above, and a solvent in the amount of zero to 99 weight percent (and all permutations of the order of mixing the aforementioned components), thereby forming a polymerizable mixture, and
- (c) allowing the mixture to polymerize or adding energy to the mixture to effect polymerization.

In a further aspect, there is also provided a method for preparing coated articles containing the cured composition of the invention comprising the steps of:

- (a) providing a substrate,
- (b) coating an energy polymerizable mixture as described above onto at least one surface of said substrate by methods known in the art, such as bar, knife, reverse roll, knurled roll, or spin coatings, or by dipping, spraying, and brushing, with or without a coating solvent, and
- (c) applying energy (after evaporation of solvent if present) to the article to effect the polymerization of the coating.

In a still further aspect, there are also provided shaped articles comprising the polymerizable mixture of the invention. The articles can be provided, for example, by techniques such as molding, injection molding, casting, and extrusion. Applying energy to the mixture causes polymerization and provides the cured shaped article.

It may be desirable to add solvent to solubilize components and aid in processing. Solvent, preferably organic solvent, in an amount up to 99 weight percent, but preferably in the range of 0 to 90 weight percent, most preferably in the range of 0 to 75 weight percent, of the polymerizable composition can be used.

Representative solvents include acetone, methyl ethyl ketone, tetrahydrofuran, cyclopentanone, methyl cellosolve acetate, methylene chloride, nitromethane, methyl formate, acetonitrile, gamma-butyrolactone, and 1,2-dimethoxyethane (glyme). In some applications, it may be advantageous to sorb the curing agent onto an inert support such as silica, alumina, or clays, as described in U.S. Patent No. 4,677,137.

In general, thermally induced polymerization of cyanate monomers with organometallic compounds may be carried out at 80 to 250°C (preferably 80 to 150°C). In general, radiation-induced polymerization of cyanate monomers with latent curing agents comprising an organometallic compound can be carried out at 25 to 300°C, preferably at 80 to 125°C for the majority of energy curable compositions, although low temperature (e.g., 25 to 80°C) or elevated temperature (e.g., 125 to 300°C, preferably 125 to 200°C) can be used to subdue the exotherm of polymerization or to accelerate the polymerization, respectively.

Temperature of polymerization and amount of curing agent (catalyst) will vary and be dependent on the particular curable composition used and the desired application of the polymerized or cured product. The amount of curing agent to be used in this invention should be sufficient to effect polymerization of the monomers or precursors (i.e., a catalytically-effective amount) under the desired use conditions. Such amount generally will be in the range of 0.01 to 20 weight percent, and preferably 0.1 to 10.0 weight percent, based on the weight of curable composition.

For the radiation-sensitive compositions of the invention any source of radiation including electron beam radiation and radiation sources emitting active radiation in the ultraviolet and visible region of the spectrum (e.g., 200 to 800 nm) can be used. Suitable sources of radiation include mercury vapor discharge lamps, carbon arcs, tungsten lamps, xenon lamps, lasers, sunlight, etc. The required amount of exposure to effect polymerization is dependent upon such factors as the identity and concentration of the organometallic compound, the particular cyanate monomer, the thickness of the exposed material, type of substrate, intensity of the radiation source and amount of heat associated with the radiation. Thermal polymerization using direct heating or infrared electromagnetic radiation, as is known in the art, can be used to cure cyanate monomers according to the teachings of this invention.

It is within the scope of this invention to include two-stage polymerization (curing), which is well known in the art, by first activating the curing agent by irradiating the curable compositions and subsequently

thermally curing the activated precursors so obtained, the irradiation temperature being below the temperature employed for the subsequent heat-curing. These activated precursors may normally be cured at temperatures which are substantially lower than those required for the direct thermal curing, with an advantage in the range from 50 to 150°C. This two-stage curing also makes it possible to control the polymerization in a particularly simple and advantageous manner.

It may be desirable to protect the polymerizable composition of the invention from light and heat as by use of shielding or filters known in the art until polymerization and cure are desired.

Adjuvants such as solvents, pigments, abrasive granules, stabilizers, light stabilizers, antioxidants, flow agents, bodying agents, flattening agents, colorants, inert fillers, binders, blowing agents, fungicides, bacteriocides, surfactants, plasticizers, and other additives as known to those skilled in the art can be added to the compositions of this invention. These can be added in an amount effective for their intended purpose. Generally, the amount of such adjuvants is in the range of 0.001 to 99.9 weight percent.

Compositions of this invention may be applied, preferably as a liquid, to a substrate such as steel, aluminum, copper, cadmium, zinc, glass, ceramic, paper, wood, or various plastic films such as poly(ethylene terephthalate), plasticized poly(vinylchloride), poly(propylene), and poly(ethylene), and irradiated.

In a preferred embodiment, the polymerizable composition can be used as a resin in graphic arts preparations. By polymerizing part of the coating, for example by irradiation through a mask or by use of a thermal imaging device, those portions which have not been polymerized may be washed with a solvent to remove the unpolymerized portions while leaving the polymerized, insoluble portions in place. Thus, compositions of this invention may be used in the production of articles useful in the graphic arts such as printing plates and printed circuits. Methods of producing printing plates and printed circuits from photopolymerizing compositions are well known in the art (see for example British Patent Specification No. 1,495,746).

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. In the Examples, Cp means η^5 -cyclopentadienyl, Ph means phenyl, Me means methyl, and NBD means η^4 -norbornadiene.

EXAMPLE 1

A number of salts of organometallic complex cations of the general formula $(\eta^5\text{-pentadienyl})M(\eta^5\text{-arene})^+$ where M = Fe or Ru were evaluated as catalysts in the polymerization of an aromatic dicyanate, namely 2,2-bis(4-cyanatophenyl)propane (Hi-Tek Polymers, Inc., Louisville, KY). Thermal catalytic activity was assayed by differential scanning calorimetry (DSC) and photocatalytic activity was assayed by differential photocalorimetry (DPC) using a thermal analyzer Model 9900, differential scanning calorimeter, Model 912, differential photocalorimeter, Model 930, all available from E. I. duPont de Nemours and Company, Inc., Wilmington, DE.

Samples were prepared by weighing solid 2,2-bis(4-cyanatophenyl)propane (approximately 0.3 g) and catalyst (approximately 0.005 g) into polystyrene vials, a plexiglass ball was added and the samples were ground in a WIG-L-BUG™ (Crescent Dental) vibrating grinder/mixer.

For DSC experiments, small quantities (5 - 10 mg) of the resulting powder samples were weighed into aluminum liquid sample pans which were hermetically sealed in a sample press. No effort was made to protect the samples from air. The sealed sample pans were placed in the DSC cell; two samples were run concurrently. The samples were heated from ambient temperature to 400°C at a rate of 10°C per minute. The data, heat flow (watts/g) vs. temperature (°C), was analyzed by the curve fitting software supplied with the Model 9900 thermal analyzer to give the onset temperature, peak temperature, and total energy (J/g) for the endotherms and exotherms of interest.

All samples showed an endotherm with approximate onset and peak temperatures of 80 and 84°C, respectively. This corresponds to the melting of 2,2-bis(4-cyanatophenyl)propane and may be used as an internal standard for these experiments. The samples then showed exotherms, the software handled data of which showed various shapes at various temperatures which correspond to the polymerization of 2,2-bis(4-cyanatophenyl)propane. These curves were compared to those obtained for the monomer in the absence of any catalyst. Representative samples were ramped to 400°C a second time and in all cases a flat line was obtained for the DSC curve. This was taken as evidence for complete polymerization in the initial DSC runs.

For DPC experiments, small quantities (6 - 12 mg) of the powder samples were weighed into aluminum liquid sample pans; no effort was made to protect the samples from air. The open sample pans were placed in the DPC cell; two samples were run concurrently. The samples were heated from ambient temperature to 400°C at a rate of 10°C per minute. Above approximately 250°C, downward sloping baselines were

obtained, presumably due to sample volatilization. During the course of the heating, the samples were irradiated through the quartz DPC cell cover with the unfiltered light from a 200 watt medium pressure Hg lamp. The irradiation system contained a feedback mechanism to insure that the samples received a constant light flux. The DPC cell was purged with a gentle stream of nitrogen. The data, heat flow (watts/g) vs. temperature ($^{\circ}\text{C}$), was analyzed by the curve fitting software supplied with the Model 9900 thermal analyzer to give the onset temperature, peak temperature, and total energy (J/g) for the endotherms and exotherms of interest. This is the standard method to treat DSC data; these trials were essentially DSC runs with concurrent irradiation. All samples showed an endotherm with approximate onset and peak temperatures of 80 and 84 $^{\circ}\text{C}$, respectively. This corresponded to the melting of 2,2-bis(4-cyanatophenyl)propane and may be used as an internal standard for these experiments. The samples then showed exotherms, the software handled data of which showed various shapes at various temperatures which corresponded to the polymerization of 2,2-bis(4-cyanatophenyl)propane. These curves were compared to those obtained for the monomer in the absence of any catalyst.

In both trials, the sample pans at the end of each run generally contained a hard, glassy polymer with colors ranging from almost black to pale amber. The results of the DSC and DPC studies, expressed in terms of the onset and peak (indicated in parentheses) temperatures for the polymerization, are summarized in Table I, below.

Table I

Catalyst	Mol%	Wt%	Thermal onset (peak) ($^{\circ}\text{C}$)	Photo onset (peak) ($^{\circ}\text{C}$)
None (Comparative)	0.0	0.0	307(327)	283(302)
[CpRu(η^5 -benzene) $^+$]PF $_6^-$	0.6	0.9	236(261)	233(264)
[Cp $^+$ Fe(η^5 -toluene) $^+$]PF $_6^-$	0.3	0.4	238(250)	124(173)
[CpFe(η^5 -pyrene) $^+$]PF $_6^-$	0.8	1.4	117(134)	86(110)
[CpFe(η^5 -naphthalene) $^+$]AsF $_6^-$	0.4	0.8	124(131)	83(110)
[CpFe(η^5 -fluorene) $^+$]PF $_6^-$	0.4	0.6	186(195)	86(114)
[CpFe(η^5 -benzene) $^+$]AsF $_6^-$	1.4	1.9	177(199)	90(114)
[CpFe(η^5 -mesitylene) $^+$]SbF $_6^-$	0.7	1.3	175(189)	84(111)

Lower onset and peak temperatures for polymerization are evidence of more efficient catalysts.

The above data show that the salts of organometallic complex cations were active catalysts for the thermal polymerization of dicyanates and that the catalysts were more effective in the presence of light. Additionally, the data show that the nature of the arene and pentadienyl ligands affected the thermal catalytic activity of the salts. In addition, the data show that the nature of the metal affected the catalytic activity of the salts.

Cp $^+$ means η^5 -pentamethylcyclopentadienyl

EXAMPLE 2

Five salts of organometallic complex cations of the general formula CpFe(η^5 -mesitylene) $^+$ X $^-$ where X = BF $_4$, AsF $_6$, PF $_6$, SbF $_6$, or CF $_3$ SO $_3$ were evaluated as catalysts following the procedure of Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table II, below.

Table II

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (Comparative)	0.0	0.0	307(327)	283(302)
[CpFe(eta ⁶ -mesitylene) ⁺]BF ₄ ⁻	0.5	0.6	179(194)	105(131)
[CpFe(eta ⁶ -mesitylene) ⁺]AsF ₆ ⁻	0.5	0.8	177(204)	87(115)
[CpFe(eta ⁶ -mesitylene) ⁺]CF ₃ SO ₃ ⁻	0.8	1.2	174(196)	87(114)
[CpFe(eta ⁶ -mesitylene) ⁺]PF ₆ ⁻	0.6	0.9	191(197)	85(113)
[CpFe(eta ⁶ -mesitylene) ⁺]SbF ₆ ⁻	0.7	1.3	175(189)	84(111)

The data of Table II show that the catalytic activity of the salts of organometallic complex cations was not greatly affected by the anionic counterion.

EXAMPLE 3

Three organometallic complexes of the general formula (eta⁵-pentadienyl)Fe(L²)₃⁺ wherein L² is a ligand as described in Formula I were evaluated as catalysts following the procedure of Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table III, below.

Table III

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
[(eta ⁵ -C ₅ H ₇)Fe(CO) ₃ ⁺]PF ₆ ⁻	0.6	0.8	203(216)	98(140)
[CpFe(CO) ₃ ⁺]PF ₆ ⁻	0.8	1.0	155(187)	86(140)
[CpFe(CO) ₂ (PPh ₃) ⁺]AsF ₆ ⁻	0.3	0.7	199(224)	90(114)

This example shows that the (eta⁵-pentadienyl)Fe(L²)₃⁺ complexes were effective thermal and photocatalysts for the curing of polyfunctional cyanates. Furthermore the nature of the ligands attached to the Fe affected the thermal and photocatalytic ability of the complexes.

EXAMPLE 4

Four neutral organometallic compounds were evaluated as catalysts following the procedure in Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table IV, below.

Table IV

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
[Cp*Fe(CO) ₂] ₂	0.6	1.0	106(123)	97(118)
[CpFe(CO) ₂] ₂	0.6	0.8	101(110)	89(102)
CpFe(CO) ₂ SnPh ₃	0.4	0.7	173(187)	89(122)
CpFe(CO) ₂ Cl	1.8	1.4	88(99)	81(90)

The data of Table IV show that the neutral organometallic compounds were effective thermal and photocatalysts for the curing of polyfunctional cyanates. Furthermore, the data show the nature of the ligands attached to Fe affected the thermal and photocatalytic ability of the complexes. Cp* see Example 1

EXAMPLE 5

Six neutral organometallic carbonyl compounds were evaluated as catalysts following the procedure in Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table V, below.

TABLE V

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
W(CO) ₆	2.5	3.2	177(229)	192(226)
Ru ₃ (CO) ₁₂	0.4	0.9	172(222)	181(226)
Re ₂ (CO) ₁₀	2.2	5.2	176(181)	124(156)
Mn ₂ (CO) ₁₀	1.5	2.1	145(150)	95(122)
Fe ₃ (CO) ₁₂	1.2	2.8	88(94)	90(95)
Fe ₂ (CO) ₉	1.2	1.5	83(88)	83(97)

The data of Table V show that the metal carbonyl complexes were active catalysts for the thermal polymerization of dicyanates and that they were effective in the presence of light. Additionally, it is apparent from this example that the nature of the metal affected the catalytic activity of the complexes.

EXAMPLE 6

Five neutral organometallic compounds were evaluated as catalysts following the procedure in Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table VI, below.

Table VI

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
[CpW(CO) ₃] ₂	0.4	0.9	168(220)	151(188)
(eta ⁵ -benzene)Cr(CO) ₃	1.5	1.2	149(207)	114(150)
(MeCp)Mn(CO) ₃	8.2	6.5	169(253)	103(157)
[CpMo(CO) ₃] ₂	1.1	1.8	129(145)	101(141)
CpMn(CO) ₃	3.4	1.7	240(270)	99(132)

The data of Table VI show that the neutral organometallic compounds were active catalysts for the thermal polymerization of dicyanates and that they were more effective in the presence of light. Additionally, the data of Table VI show that the nature of the metal and the nature of the polyene affected the thermal and photocatalytic activity of the complexes.

EXAMPLE 7

Four organometallic compounds containing halogen ligands were evaluated as catalysts following the procedure in Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table VII, below.

Table VII

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
$[(\eta^5\text{-C}_6\text{H}_5)\text{Ru}(\text{CH}_3\text{CN})_2\text{Cl}^+]\text{AsF}_6^-$	0.3	0.6	225(269)	224(260)
$(\text{CO})_5\text{ReBr}$	0.9	1.3	189(234)	185(217)
$(\text{Cp})_2\text{Ti}(\text{Cl})_2$	1.2	1.0	208(227)	163(186)
$[(\eta^5\text{-p-cymene})\text{Ru}(\text{Cl})_2]_2$	0.6	1.2	142(162)	144(162)

The data of Table VII show that halogen containing organometallic compounds were active catalysts for the thermal polymerization of dicyanates and that they were effective in the presence of light. Additionally, it is apparent from these data that the nature of the metal and the nature of the ancillary ligands affected the catalytic activity of the complexes.

EXAMPLE 8

Nine other organometallic compounds were evaluated as catalysts following the procedure in Example 1. Hard, glassy polymers with colors ranging from almost black to pale amber were again obtained. The results are summarized in Table VIII, below.

Table VIII

Catalyst	Mol%	Wt%	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
None (comparative)	0.0	0.0	307(327)	283(302)
$[(\text{Cp})_2\text{Co}^+]\text{PF}_6^-$	0.7	0.9	240(295)	226(280)
$[(\text{MeCp})\text{Mn}(\text{CO})_2\text{NO}^+]\text{PF}_6^-$	1.1	1.5	265(299)	223(262)
$[(\text{NBD})\text{Rh}(\text{PPh}_3)_2^+]\text{PF}_6^-$	0.3	1.0	206(263)	211(271)
$(\text{Cp})_2\text{Fe}$	3.8	2.6	161(193)	164(192)
$[(\eta^5\text{-hexamethylbenzene})_2\text{Fe}^{+2}][\text{PF}_6^-]_2$	0.5	1.1	222(236)	150(186)
$\text{CpPt}(\text{CH}_3)_3$	3.5	3.9	137(177)	140(180)
$\text{CpW}(\text{CO})_3\text{CH}_3$	1.1	1.4	183(210)	137(197)
$[(\text{Cp})_2\text{Fe}^+]\text{AsF}_6^-$	0.7	0.9	105(150)	110(153)
$[(\text{CpFe})_2(\eta^5\text{-fluorene})^{+2}][\text{AsF}_6^-]_2$	0.3	1.0	160(174)	87(114)

The data of Table VIII provide further examples of organometallic compounds, including salts of organometallic complex dications, which were effective thermal and photocatalysts for the cyclotrimerization of cyanates.

The data also show that complexes containing metal-alkyl sigma bonds were effective catalysts.

EXAMPLE 9

Six samples were prepared as in Example 1. Sample A contained bis(4-cyanato-3,5-dimethylphenyl)-methane alone.

Sample B contained

bis(4-cyanato-3,5-dimethylphenyl)methane (0.3010g) and $\text{CpFe}(\eta^5\text{-mesitylene})^+\text{CF}_3\text{SO}_3^-$ (0.0036g).

Sample C contained

bis(4-cyanato-3,5-dimethylphenyl)methane (0.3772g) and $\text{CpFe}(\text{CO})_2\text{SnPh}_3$ (0.0033g).

Sample D contained 1,1'-bis(cyanato)biphenyl alone.

Sample E contained 1,1'-bis(cyanato)biphenyl (0.1494g) and $\text{CpFe}(\eta^5\text{-mesitylene})^+\text{CF}_3\text{SO}_3^-$ (0.0015g).

Sample F contained 1,1'-bis(cyanato)biphenyl (0.1290g) and $\text{CpFe}(\text{CO})_2\text{SnPh}_3$ (0.0022g).

Three samples were prepared by dissolving catalysts into a liquid dicyanate resin (ESR-310™, Hi-Tek Polymers, Inc.). Sample G contained ESR-310 alone. Sample H contained ESR-310 (1.4804g) and $\text{Fe}_2(\text{CO})_9$ (0.0048g). Sample I contained ESR-310 (1.2001g) and $\text{CpFe}(\text{CO})_2\text{Cl}$ (0.0030g). All nine samples were evaluated for catalytic activity following the procedure in Example 1. Hard, glassy polymers with colors

ranging from almost black to pale amber were again obtained. The results are summarized in Table IX, below.

Table IX

<u>Sample</u>	<u>Catalyst</u>	<u>Monomer</u>	Thermal onset (peak) (°C)	Photo onset (peak) (°C)
A	None	bis(4-cyanato- 3,5-dimethyl- phenyl)methane	286(340)	293(318)
B	CpFe(η^6 - mesitylene) ⁺ CF ₃ SO ₃ ⁻	bis(4-cyanato- 3,5-dimethyl- phenyl)methane	202(217)	109(155)
C	CpFe(CO) ₂ - SnPh ₃	bis(4-cyanato- 3,5-dimethyl- phenyl)methane	231(242)	109(140)
D	None	1,1'-bis- (cyanato)- biphenyl	153(187)	160(185)
E	CpFe(η^6 - mesitylene) ⁺ CF ₃ SO ₃ ⁻	1,1'-bis (cyanato)- biphenyl	158(185)	128(134)

Sample	Catalyst	Monomer	Thermal	Photo
			onset (peak) (°C)	onset (peak) (°C)
F	CpFe(CO) ₂ - SnPh ₃	1,1'-bis- (cyanato)- biphenyl	130(160)	128(134)
G	None	ESR-310	223(289)	257(298)
H	Fe ₂ (CO) ₉	ESR-310	92(110)	87(101)
I	CpFe(CO) ₂ Cl	ESR-310	97(110)	86(104)

The data of Table IX show that a variety of cyanate monomers were cured thermally and photochemically by the organometallic catalyst system.

EXAMPLE 10

A sample containing 10 mg of [CpFe(CO)₂]₂, 1.0 g of 2,2-bis(4-cyanatophenyl)propane, and 1.0 ml of gamma-butyrolactone was prepared and placed in a 90 °C oven. The sample was periodically observed and was found to form a solid polymeric mass within 52 minutes. This example demonstrated that [CpFe(CO)₂]₂ was a thermal catalyst for the polymerization of cyanate monomers and that the polymerization could be carried out in the presence of solvent.

EXAMPLE 11

A sample containing 10 mg of CpFe(eta⁶-pyrene)⁺PF₆⁻ and 1.0 g 2,2-bis(4-cyanatophenyl)propane was heated gently to 90 °C for two minutes to give a homogeneous solution of cyanate monomer and catalyst. The sample was placed in a 120 °C oven and observed periodically. The sample was found to form a solid polymeric mass within 60 minutes. This example demonstrated that CpFe(eta⁶-pyrene)⁺PF₆⁻ was a thermal catalyst for the polymerization of cyanate monomers and that the polymerization could be carried out on 100% solids compositions.

EXAMPLE 12

A sample containing 1.0 g of 2,2-bis(4-cyanatophenyl)propane, 1.0 ml of gamma-butyrolactone, and 10 mg of CpFe(eta⁶-mesitylene)⁺PF₆⁻, was placed in a vial under subdued light. The sample was gently warmed (in the dark) to complete dissolution of the solids and then was irradiated with light from a Kodak Carousel™ Projector (Eastman Kodak Co., Rochester, NY) while being held at approximately 100 °C in an oven.

The sample cured to a solid mass within 45 minutes. An identical sample was held at approximately 100 °C in the dark; no increase in viscosity could be detected visually after 4 hours which was taken as evidence that little or no polymerization had occurred. This example demonstrated the photochemical component in the catalysis of the polymerization of cyanate monomers by CpFe(eta⁶-mesitylene)⁺PF₆⁻. It also showed that the photocuring could be carried out in the presence of solvent and that visible light was useful in the polymerization.

EXAMPLE 13

A sample containing 1.0 g of 2,2-bis(4-cyanatophenyl)propane, 1.0 ml of gamma-butyrolactone, and 10 mg of $\text{CpFe}(\eta^6\text{-fluorene})^+\text{PF}_6^-$, was placed in a vial under subdued light. The sample was gently warmed (in the dark) to complete dissolution of the solids and then was irradiated with light from a Kodak Carousel Projector while being held at approximately 100 °C in an oven. The sample cured to a solid mass within 45 minutes. An identical sample was held at approximately 100 °C in the dark; no increase in viscosity could be detected visually after 4 hours which was taken as evidence that little or no polymerization had occurred. This example demonstrated the photochemical component in the catalysis of the polymerization of cyanate monomers by $\text{CpFe}(\eta^6\text{-fluorene})^+\text{PF}_6^-$. It also showed that the photocuring could be carried out in the presence of solvent and that visible light was useful in the polymerization.

EXAMPLE 14

A stock solution of 2.0g of 2,2-bis(4-cyanatophenyl)propane and 2.0g of tetrahydrofuran (THF) was prepared. Three samples were then prepared and sealed as follows: (A) 1.0g of stock solution and 0.02g of $(\text{MeCp})\text{Mn}(\text{CO})_3$; (B) 1.0g of stock solution and 0.02g of $(\text{MeCp})\text{Mn}(\text{CO})_3$; and (C) 1.0g of stock solution. Samples (A) and (C) were irradiated for 15 minutes at room temperature using two GE Blak-ray 15 watt blacklights (primary wavelength 366nm) (General Electric Co., Schenectady, NY) and sample (B) was placed in the dark at room temperature. The solution in sample (A) changed color from yellow to purple while samples (B) and (C) remained unchanged. All three samples were then heated in the dark by placing them in a 100 °C water bath. Sample (A) was cured to a solid material in 20 minutes while samples (B) and (C) were unchanged after 3.5 hours. This example demonstrated that the curing of cyanate monomers could be accomplished in two stages; photochemical activation of the catalyst species followed by a later thermal curing step. It further demonstrated that the two stage curing could be carried out in the presence of solvent and that ultraviolet light was useful in the polymerization.

EXAMPLE 15

Two samples, each 0.5 g, were prepared containing 1 part $(\text{MeCp})\text{Mn}(\text{CO})_3$ and 200 parts 2,2-bis(4-cyanatophenyl)propane and placed in glass vials. Each sample was gently warmed (in the dark) to complete dissolution of the solids and gave pale yellow homogeneous solutions. One sample was irradiated for 10 minutes at room temperature using two GE Blak-ray 15 watt black lights (primary wavelength 366nm) and one sample was kept in the dark at room temperature. Both were then placed in an 85 °C oven and were observed periodically. The sample which had been irradiated cured to a solid polymeric mass within 45 minutes while the sample which was not irradiated was still fluid after four hours. This example demonstrated that the curing of cyanate monomers could be accomplished in two stages; photochemical activation of the catalyst species followed by a later thermal curing step. It further demonstrated that the two stage curing could be carried out with 100% solids compositions and that ultraviolet light was useful in the polymerization.

EXAMPLE 16

Two samples, 0.5 g each, were prepared containing 1 part $\text{CpFe}(\eta^6\text{-mesitylene})^+\text{PF}_6^-$ and 200 parts 2,2-bis(4-cyanatophenyl)propane and placed in glass vials. Each sample was heated in an oven at 120 °C for 3 minutes, to form a light yellow, fluid, homogeneous solution. One sample was removed from the oven and irradiated for 1 minute using a Kodak Carousel projector ("A" stage), then returned to the oven ("B" stage). The irradiated sample cured to a glassy black solid in 6 minutes, while the sample which was not irradiated was unchanged after 45 minutes at 120 °C. This example demonstrated that the photocuring of cyanate monomers could be accomplished in two stages; photochemical activation of the catalyst species followed by a later thermal curing step. It further demonstrated that the two stage curing could be carried out on 100% solids compositions and that visible light was useful in the process.

EXAMPLE 17

A 3.3 g sample containing 1 part $\text{CpFe}(\eta^6\text{-mesitylene})^+\text{PF}_6^-$ and 200 parts 2,2-bis(4-cyanatophenyl)propane was prepared in a glass vial. This was placed in an oven at 120 °C for 6 minutes yielding a light yellow, homogeneous, fluid (i.e., processable) solution. This solution was poured into a cylindrical poly-

tetrafluoroethylene (Teflon™, DuPont) mold (which had been heated to 120°C) and was irradiated for 1 minute with a Kodak Carousel projector. The mold was returned to the oven at 120°C; the sample cured in 5.5 minutes to give a black, glassy, cylinder. This example demonstrated that the two stage curing process could be used to prepare shaped articles. It further demonstrated that the process could be carried out with 100% solids compositions and that visible light was useful in the process.

EXAMPLE 18

An ethyl acetate solution (5.0 ml) containing 1.0 g of partially trimerized bis(4-cyanatophenyl)thioether resin, (AroCy T-30™, Hi-Tek Polymers, Inc.), was prepared and (MeCp)Mn(CO)₃ (0.01 g) was added. The resulting mixture was coated on an aluminum Alodined™ brand, Q-panel (Q-panel Company, Cleveland, Ohio) using a #22 wire wound bar. The panel was placed in a 100°C oven for one minute to evaporate the solvent, and yielded a tack-free coating. A #1-T Resolution Guide (Stouffer Graphic Arts Equipment Company, South Bend, Ind.) was placed on top of the coating and the construction was irradiated at ambient (room) temperature for 3 minutes with two GE Blak-ray 15 watt blacklights. The Resolution Guide was removed and the exposed Q-panel was placed in a 100°C oven for 5 minutes. The panel was then rinsed with methyl ethyl ketone, leaving a negative image of the Resolution Guide.

This example demonstrated that coatings of cyanate monomers could be cured using the neutral organometallic compounds of the present invention and that the curing could be accomplished in two stages. It further demonstrated that the coatings could be accomplished in an image-wise fashion.

EXAMPLE 19

A methyl ethyl ketone (MEK) solution (5.0 ml) containing 1.0 g of partially trimerized 2,2-bis(4-cyanatophenyl)propane resin (AroCy B-50™, Hi-Tek Polymers, Inc.) was prepared and CpFe(eta⁶-mesitylene)⁺CF₃SO₃⁻ (0.006 g) was added. The mixture was coated on an Alodined aluminum Q-panel using a #20 wire wound bar. The panel was air dried in the dark for one hour to evaporate the MEK and give a tack-free coating. The coating was exposed through a 21 step sensitivity guide (Stouffer Graphic Arts Equipment Company) for 4 minutes with two GE Blak-ray 15 watt blacklights. The exposed sample was placed in a 110°C oven for 5 minutes. The panel was then rinsed with MEK, leaving a negative image of the sensitivity guide (eight solid steps, one ghost).

This example demonstrated that coatings of cyanate resins could be cured by the salts of organometallic complex cations of the present invention and that the curing could be accomplished in an image-wise fashion in two stages.

EXAMPLE 20

An MEK solution (5.0 ml) containing 1.0 g of partially trimerized 2,2-bis(4-cyanatophenyl)propane resin (AroCy B-50) was prepared and CpFe(CO)₂SnPh₃ (0.01 g) was added. The mixture was coated on poly(vinylidene chloride)-primed polyester film (Scotch Par™, 3M, St. Paul, MN) using a #20 wire wound bar. The film was air dried in the dark for one hour to evaporate the MEK and give a tack-free coating. The coating was exposed through a #1-T Resolution Guide for 5 minutes with two GE Blak-ray 15 watt blacklights. The exposed film was placed in a 110°C oven for 5 minutes. The film was then rinsed with MEK, leaving a negative image of the Resolution Guide.

This example demonstrated that coatings of cyanate resins on polymeric substrates could be cured by the organometallic catalysts of the present invention and that the curing could be accomplished in an image-wise fashion in two stages.

Claims

1. An energy polymerizable composition comprising at least one of a cyanate monomer and oligomers thereof and as curing agent an organometallic compound, wherein said organometallic compound has the formula:



wherein

L¹ represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different



tetrafluoroethylene (Teflon™, DuPont) mold (which had been heated to 120°C) and was irradiated for 1 minute with a Kodak Carousel projector. The mold was returned to the oven at 120°C; the sample cured in 5.5 minutes to give a black, glassy, cylinder. This example demonstrated that the two stage curing process could be used to prepare shaped articles. It further demonstrated that the process could be carried out with

EXAMPLE 18

An ethyl acetate solution (5.0 ml) containing 1.0 g of partially trimerized bis(4-cyanatophenyl)thioether resin, (AroCy T-30™, Hi-Tek Polymers, Inc.), was prepared and (MeCp)Mn(CO)₃ (0.01 g) was added. The resulting mixture was coated on an aluminum Alodined™ brand, Q-panel (Q-panel Company, Cleveland, Ohio) using a #22 wire wound bar. The panel was placed in a 100°C oven for one minute to evaporate the solvent, and yielded a tack-free coating. A #1-T Resolution Guide (Stouffer Graphic Arts Equipment Company, South Bend, Ind.) was placed on top of the coating and the construction was irradiated at ambient (room) temperature for 3 minutes with two GE Blak-ray 15 watt blacklights. The Resolution Guide was removed and the exposed Q-panel was placed in a 100°C oven for 5 minutes. The panel was then rinsed with methyl ethyl ketone, leaving a negative image of the Resolution Guide.

This example demonstrated that coatings of cyanate monomers could be cured using the neutral organometallic compounds of the present invention and that the curing could be accomplished in two stages. It further demonstrated that the coatings could be accomplished in an image-wise fashion.

EXAMPLE 19

A methyl ethyl ketone (MEK) solution (5.0 ml) containing 1.0 g of partially trimerized 2,2-bis(4-cyanatophenyl)propane resin (AroCy B-50™, Hi-Tek Polymers, Inc.) was prepared and CpFe(eta⁶-mesitylene)+CF₃SO₃⁻ (0.006 g) was added. The mixture was coated on an Alodined aluminum Q-panel using a #20 wire wound bar. The panel was air dried in the dark for one hour to evaporate the MEK and give a tack-free coating. The coating was exposed through a 21 step sensitivity guide (Stouffer Graphic Arts Equipment Company) for 4 minutes with two GE Blak-ray 15 watt blacklights. The exposed sample was placed in a 110°C oven for 5 minutes. The panel was then rinsed with MEK, leaving a negative image of the sensitivity guide (eight solid steps, one ghost).

This example demonstrated that coatings of cyanate resins could be cured by the salts of organometallic complex cations of the present invention and that the curing could be accomplished in an image-wise fashion in two stages.

EXAMPLE 20

An MEK solution (5.0 ml) containing 1.0 g of partially trimerized 2,2-bis(4-cyanatophenyl)propane resin (AroCy B-50) was prepared and CpFe(CO)₂SnPh₃ (0.01 g) was added. The mixture was coated on poly(vinylidene chloride)-primed polyester film (Scotch Par™, 3M, St. Paul, MN) using a #20 wire wound bar. The film was air dried in the dark for one hour to evaporate the MEK and give a tack-free coating. The coating was exposed through a #1-T Resolution Guide for 5 minutes with two GE Blak-ray 15 watt blacklights. The exposed film was placed in a 110°C oven for 5 minutes. The film was then rinsed with MEK, leaving a negative image of the Resolution Guide.

This example demonstrated that coatings of cyanate resins on polymeric substrates could be cured by the organometallic catalysts of the present invention and that the curing could be accomplished in an image-wise fashion in two stages.

Claims

1. An energy polymerizable composition comprising at least one of a cyanate monomer and oligomers thereof and as curing agent an organometallic compound, wherein said organometallic compound has the formula:



wherein

L¹ represents none, or 1 to 12 ligands contributing pi-electrons that can be the same or different



selected from substituted and unsubstituted acyclic and cyclic unsaturated compounds, polymers, and groups and substituted and unsubstituted carbocyclic aromatic and heterocyclic aromatic compounds, each capable of contributing 2 to 24 pi-electrons to the valence shell of M;

L^2 represents none, or 1 to 24 ligands that can be the same or different contributing an even number of sigma-electrons selected from mono-, di-, and tri-dentate ligands, each donating 2, 4, or 6 sigma-electrons to the valence shell of M;

L^3 represents none, or 1 to 12 ligands that can be the same or different, each contributing no more than one sigma-electron each to the valence shell of each M;

M represents 1 to 4 of the same or different metal atoms selected from the elements of Periodic Groups IVB, VB, VIB, VIIB, and VIII (commonly referred to as transition metals);

e is an integer having a value of 0, 1 or 2;

X is an anion selected from organic sulfonate and halogenated metal or metalloid groups;

f is an integer of 0, 1 or 2, the number of anions required to balance the charge e on the organometallic portion;

with the proviso that the organometallic compound contains at least one metal-carbon bond; and with the proviso that L^1 , L^2 , L^3 , M, e, X, and f are chosen so as to achieve a stable configuration.

2. The composition according to Claim 1 wherein said cyanate monomer has the formula:



wherein p is an integer from 1 to 7, and wherein Q comprises at least one of 1) a mono-, di-, tri-, or tetravalent aromatic hydrocarbon group containing 5 to 30 carbon atoms, 2) 1 to 5 aliphatic or polycyclic aliphatic mono- or divalent hydrocarbon groups containing 7 to 20 carbon atoms, and 3) a mono- or divalent fluorocarbon group having 3 to 12,500 carbons and 5 to 25,000 fluorine atoms.

3. The composition according to claim 2 wherein when Q is said aromatic hydrocarbon or said polycyclic aliphatic hydrocarbon, it further comprises 1 to 10 hetero atoms selected from the group consisting of non-peroxidic oxygen, sulfur, non-phosphino phosphorus, non-amino nitrogen, halogen, and silicon.

4. The composition according to Claims 1 to 3 wherein said cyanate monomer is 2,2-bis(4-cyanatophenyl)propane or oligomers thereof.

5. The composition according to Claim 3 wherein Q corresponds to a fluorocarbon group of Formula III or IV:



wherein A is a carbon-to-carbon bond, in which case a is an integer from 1 to 30 and b is zero, or A is $-O-(CFX-CF_2-O)_c-$, in which case a is an integer 1 to 10, b is one, and c is an integer 1 to 100; and X is fluorine or perfluoroalkyl having 1 to 10 carbon atoms;



wherein B is 1) a carbon-to-carbon bond, in which case a is an integer of 1 to 30 and b is zero, or 2) B is $[(CFX)_dO(CFX)_u]_v$, in which case a and b are zero, d and u are integers of 1 to 30, and v is an integer of 1 to 20, or 3) B is $(OCF_2-CFX)_wO(CFX)_hO(CFX-CF_2O)_i$, in which case a and b are 1, h is an integer of 1 to 10, and w and i are integers of 1 to 100, or 4) B is $[(CF_2CH_2)_j(CF_2-CFX)_k]_m$, in which case a and b are integers of 1 to 10, j and k are integers whose ratio j/k is 1/1 to 1/10, m is an integer of 1 to 100, and (CF_2CH_2) and (CF_2-CFX) are randomly distributed units; and where X is fluorine or perfluoroalkyl of 1 to 10 carbon atoms.

6. The composition according to Claims 1 to 5 wherein said organometallic compound is selected from the group consisting of (eta⁵-methylcyclopentadienyl)-manganesetricarbonyl, bis[(eta⁵-cyclopentadienyl)irondicarbonyl], (eta⁵-cyclopentadienyl)iron(triphenyltin)dicarbonyl, (eta⁵-cyclopentadienyl)irondicarbonylchloride,



(η^5 -cyclopentadienyl)(η^6 -mesitylene)iron(+1)
trifluoromethylsulfonate(-1),
(η^5 -cyclopentadienyl)-
(η^6 -mesitylene)iron(+1)hexafluorophosphate(-1).

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7. The composition according to Claims 1 to 6 which has been cured by at least one of thermal energy, electromagnetic radiation, and accelerated particles.

8. The composition according to Claims 1 to 7 which is a shaped article, coating, film, or photoresist.

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9. The composition according to Claims 1 to 8 wherein said curing agent is present in an amount in the range of 0.01 to 20 weight percent of the total composition.

10. A method comprising the steps of:

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a) providing a polymerizable mixture according to Claim 1, and

b) effecting polymerization of said mixture by at least one of thermal energy, radiation, and accelerated particles, said polymerization optionally being effected by a two-stage process comprising first activating said polymerizable composition by irradiation to provide activated precursors, and then thermally curing the activated precursors, said irradiation temperature being below the temperature used in the thermal curing.

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Patentansprüche

25

1. Energiepolymerisierbare Zusammensetzung mit einem Cyanatmonomer und/oder Oligomeren desselben und mit einer metallorganischen Verbindung als Härtemittel, wobei die metallorganische Verbindung die Formel



30

hat, in der

L^1 nichts darstellt oder 1 bis 12 Pi-Elektronen beitragende Liganden, die gleich oder verschieden sein können und aus den substituierten und nichtsubstituierten azyklischen und zyklischen ungesättigten Verbindungen, Polymeren und Gruppen und substituierten und nichtsubstituierten carboxyklischen aromatischen und heterozyklischen aromatischen Verbindungen ausgewählt sind und von denen jeder zu der Valenzschale von M 2 bis 24 Pi-Elektronen beitragen kann;

35

L^2 nichts darstellt oder 1 bis 24 und eine gerade Anzahl von Sigma-Elektronen beitragende Liganden, die gleich oder verschieden sein können und aus ein-, zwei- und dreizähligen Liganden ausgewählt sind und von denen jeder zu der Valenzschale von M 2, 4 oder 6 Sigma-Elektronen beiträgt, oder 1 bis 12 Liganden, die gleich oder verschieden sein können und von denen jeder höchstens ein Sigma-Elektron zu der Valenzschale jedes M beiträgt.

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L^3 nichts darstellt oder 1 bis 12 Liganden, die gleich oder verschieden sein können und zu der Valenzschale jedes M höchstens ein Sigma-Elektron beiträgt;

M 1 bis 4 gleiche oder verschiedene Metallatome darstellt, die aus den Elementen der Gruppen IVb, Vb, Vlb, VIb und VIII des Periodensystems (gewöhnlich als Übergangsmetalle bezeichnet) ausgewählt sind;

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s eine ganze Zahl mit dem Wert 0, 1 oder 2 ist;

X ein Anion ist, das aus den organischen Sulfonatgruppen und den halogenierten Metall- oder Metalloidgruppen ausgewählt ist; und

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Z eine ganze Zahl mit dem Wert 0, 1 oder 2 ist und die Anzahl der Anionen darstellt, die zum Ausgleich der Ladung e des metallorganischen Teils erforderlich ist;

wobei die metallorganische Verbindung mindestens eine Metall-Kohlenstoff-Bindung enthält und L^1 , L^2 , L^3 , M, e, X und f so gewählt sind, daß eine stabile Konfiguration erhalten wird.

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2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Cyanatmonomer die Formel





hat, in der

p eine ganze Zahl m von 1 bis 7 ist und

Q mindestens eine der folgenden Anteile darstellt: 1) eine ein-, zwei-, drei- oder vierwertige aromatische Kohlenwasserstoffgruppe mit 5 bis 30 Kohlenstoffatomen, 2) 1 bis 5 aliphatische oder polyzyklische aliphatische ein- oder zweiwertige Kohlenwasserstoffgruppen mit 7 bis 20 Kohlenstoffatomen und 3) eine ein- oder zweiwertige Fluorkohlenstoffgruppe mit 3 bis 12 500 Kohlenstoffatomen und 5 bis 25 000 Fluoratomen.

3. Zusammensetzung nach Anspruch 2, in der, wenn Q der genannte aromatische Kohlenwasserstoff oder der genannte polyzyklische aliphatische Kohlenwasserstoff ist, es ferner 1 bis 10 Heteroatome enthält, die aus der Gruppe ausgewählt sind, die aus dem nichtperoxidischen Sauerstoff, Schwefel, Nichtphosphino-Phosphor, Nichtamino-Stickstoff, Halogen und Silicium ausgewählt sind.

4. Zusammensetzung nach Anspruch 1 bis 3, in der das Cyanatmonomer 2,2-Bis(4-cyanatophenyl)propan ist oder aus Oligomeren desselben besteht.

5. Zusammensetzung nach Anspruch 3, in der Q einer Fluorkohlenstoffgruppe der Formel III oder IV entspricht:



in der A eine Kohlenstoff-Kohlenstoff-Bindung ist, in welchem Fall a eine ganze Zahl von 1 bis 30 und b gleich null ist, oder A $-O-(CFX-CF_2-O)_c$ ist, in welchem Fall a eine ganze Zahl von 1 bis 100 ist, b gleich eins ist und c eine ganze Zahl von 1 bis 100 ist; und X Fluor oder Perfluoralkyl mit 1 bis 20 Kohlenstoffatomen ist;



in der B 1) eine Kohlenstoff-Kohlenstoff-Bindung ist, in welchem Fall a eine ganze Zahl von 1 bis 30 und b gleich null ist, oder 2) $B[(CFX)_dO(CFX)_u]_v$ ist, in welchem Fall a und b gleich null sind, d und u ganze Zahlen von 1 bis 30 sind und v eine ganze Zahl von 1 bis 20 ist, oder 3) $B(OXF_2CFX)_wO(CFX)_hO(CFX-CF_2O)_i$ ist, in welchem Fall a und b gleich 1 sind, h eine ganze Zahl von 1 bis 10 ist und w und i ganze Zahlen von 1 bis 100 ist, oder 4) $B[(CF_2CH_2)_j(CF_2-CFX)_k]_m$ ist, in welchem Fall a und b ganze Zahlen von 1 bis 10 sind, j und k ganze Zahlen sind, deren Verhältnis j/k 1/1 bis 1/10 beträgt, m eine ganze Zahl von 1 bis 100 ist und (CF_2CH_2) und (CF_2-CFX) zufällig verteilte Einheiten sind, und X Fluor oder Perfluoralkyl mit 1 bis 10 Kohlenstoffatomen ist.

6. Zusammensetzung nach Anspruch 1 bis 5, in der die metallorganische Verbindung aus der Gruppe ausgewählt ist, die aus

(Eta⁵-methylcyclopentadienyl)mangantricarbonyl,
Bis[(eta⁵-cyclopentadienyl)eisendicarbonyl],
(Eta⁵-cyclopentadienyl)eisen(triphenylzinn)dicarbonyl,
(Eta⁵-cyclopentadienyl)eisendicarbonylchlorid,
(Eta⁵-cyclopentadienyl)(eta⁶-mesitylen)eisen(+1)trifluormethyl-sulfonat(-1),
(Eta⁵-cyclopentadienyl)- und
(Eta⁶-mesitylen)eisen(+1)hexafluorphosphat(-1) besteht.

7. Zusammensetzung nach Anspruch 1 bis 6, die durch Wärmeenergie, elektromagnetische Strahlung und/oder beschleunigte Teilchen gehärtet worden ist.

8. Zusammensetzung nach Anspruch 1 bis 7, die ein Formkörper oder Überzug, eine Feinfolie oder ein Photolack ist.

9. Zusammensetzung nach Anspruch 1 bis 8, in der das Härtemittel in einer Menge im Bereich von 0,01 bis 20 Gew.-% der Gesamtzusammensetzung enthalten ist.

10. Verfahren mit folgenden Schritten:

a) es wird ein polymerisierbares Gemisch nach Anspruch 1 beschafft, und



b) das Gemisch wird durch Wärmeenergie, Strahlung und/oder beschleunigte Teilchen polymerisiert, wobei die Polymerisation gegebenenfalls in einem zweistufigen Verfahren erfolgt, in dem zum Erzeugen von aktivierten Vorstufen die polymerisierbare Zusammensetzung zunächst durch Bestrahlen aktiviert wird und die aktivierten Vorstufen dann wärmegehärtet werden, wobei die Bestrahlungstemperatur unter der zum Wärmehärten angewendeten Temperatur liegt.

Revendications

1. Composition polymérisable sous l'effet d'une énergie, comprenant au moins un cyanate monomère ou l'un de ses oligomères, et comme agent de durcissement un composé organométallique, où le composé organométallique a la formule :



dans laquelle :

L^1 représente zéro, ou de 1 à 12 ligands contribuant pour des électrons pi, qui peuvent être identiques ou différents et choisis parmi l'ensemble comprenant les composés, polymères et groupes insaturés, éventuellement substitués, acycliques ou cycliques, et les composés aromatiques carboxyliques éventuellement substitués et les composés aromatiques hétérocycliques, chacun d'eux étant à même de contribuer pour 2 à 24 électrons pi à la couche de valence de M ;

L^2 représente zéro, ou de 1 à 24 ligands pouvant être identiques ou différents, et contribuant pour un nombre pair d'électrons sigma, choisis parmi l'ensemble comprenant les ligands mono-, di- et tridentés, chacun donnant 2, 4 ou 6 électrons sigma à la couche de valence de M ;

L^3 représente zéro, ou de 1 à 12 ligands pouvant être identiques ou différents, chacun contribuant pour au plus un électron sigma à la couche de valence de chaque M ;

M représente 1 à 4 atomes métalliques, identiques ou différents, choisis parmi les éléments des groupes IVB, VB, VIB, VIIB et VIII du Tableau Périodique (couramment appelés "métaux de transition") ;

e est un entier valant 0, 1 ou 2 ;

X est un anion choisi parmi l'ensemble comprenant les groupes sulfonates organiques et les groupes métaux ou métalloïdes halogénés ;

f est un entier valant 0, 1 ou 2, et est le nombre d'anions dont on a besoin pour équilibrer la charge e sur la portion organométallique ;

du moment que le composé organométallique contient au moins une liaison métal-carbone ; et du moment que L^1 , L^2 , L^3 , M, e, X et f sont choisis de façon à donner une configuration stable.

2. Composition selon la revendication 1, dans laquelle ledit cyanate monomère a la formule



dans laquelle p est un entier de 1 à 7, et Q comprend au moins un groupe choisi parmi l'ensemble comprenant

1) un groupe hydrocarboné aromatique mono-, di-, tri- ou tétravalent comprenant de 5 à 30 atomes de carbone,

2) des groupes hydrocarbonés aliphatiques ou aliphatiques polycycliques, mono- ou divalents, contenant de 7 à 20 atomes de carbone, et

3) un groupe fluorocarboné mono- ou divalent ayant de 3 à 12 500 atomes de carbone et de 5 à 25 000 atomes de fluor.

3. Composition selon la revendication 2, dans laquelle, quand Q est ledit hydrocarbure aromatique ou ledit hydrocarbure aliphatique polycyclique, il comprend en outre de 1 à 10 hétéroatomes choisis parmi l'ensemble comprenant l'oxygène non-péroxyde, le soufre, le phosphore non-phosphino, l'azote non-amino, les halogènes et le silicium.

4. Composition selon les revendications 1 à 3, dans laquelle ledit cyanate monomère est le 2,2-bis(4-cyanatophényl)propane ou ses oligomères.



5. Composition selon la revendication 3, dans laquelle Q correspond à un groupe fluorocarboné de formule III ou IV :



où A est une liaison carbone-carbone, auquel cas a est un entier de 1 à 30 et b vaut 0, ou encore A est $-O-(CFX-CF_2-O)_c$, auquel cas a est un entier de 1 à 10, b vaut 1 et c est un entier de 1 à 100 ; et X est le fluor ou un radical perfluoralkyle ayant de 1 à 10 atomes de carbone ;



où B est

1) une liaison carbone-carbone, auquel cas a est un entier de 1 à 30, et b) vaut 0, ou bien

2) B est $[(CFX)_dO(CFX)_u]_v$, auquel a et b valent chacun zéro, d et u sont chacun des entiers de 1 à 30, et v est un entier de 1 à 20, ou bien

3) B est $(COF_2-CFX)_wO(CFX)_hO(CFX-CF_2O)_i$, auquel cas a et b valent chacun 1, h est un entier de 1 à 10, et w et i sont chacun des entiers de 1 à 100, ou encore

4) B est $[(CF_2CH_2)_j(CF_2-CFX)_k]_m$, auquel cas a et b sont chacun des entiers de 1 à 10, j et k sont chacun des entiers dont le rapport j/k est compris entre 1/1 et 1/10, m est un entier de 1 à 100, et les motifs (CF_2CH_2) et (CF_2-CFX) sont répartis au hasard ; et où X est le fluor ou un radical perfluoralkyle ayant de 1 à 10 atomes de carbone.

6. Composition selon les revendications 1 à 5, dans laquelle ledit composé organométallique est choisi parmi l'ensemble comprenant les composés suivants : $(\eta^5\text{-méthylcyclopentadiényl})\text{-mananèsetricarbonyle}$, $\text{bis}[(\eta^5\text{-cyclopentadiényl})\text{ferdicarbonyle}]$, $(\eta^5\text{-cyclopentadiényl})\text{fer-(triphenylétain)dicarbonyle}$, chlorure de $(\eta^5\text{-cyclopentadiényl})\text{ferdicarbonyle}$, trifluorométhylsulfonate(-1) de $(\eta^5\text{-cyclopentadiényl})(\eta^5\text{-mésitylène})\text{fer(+1)}$, hexafluorophosphate(-1) de $(\eta^5\text{-cyclopentadiényl})(\eta^5\text{-mésitylène})\text{fer(+1)}$.

7. Composition selon les revendications 1 à 6, qui a été durcie par au moins une technique choisie parmi l'ensemble comprenant l'énergie thermique, les rayonnements électromagnétiques et les particules accélérées.

8. Composition selon les revendications 1 à 7, qui est un article façonné, un revêtement, un film ou une photoréserve.

9. Composition selon les revendications 1 à 8, dans laquelle ledit agent de durcissement est présent en une quantité de 0,01 à 20 % en poids par rapport à la composition totale.

10. Procédé comprenant les étapes consistant :

a) à préparer un mélange polymérisable selon la revendication 1, et

b) à effectuer une polymérisation de ce mélange par au moins une technique choisie parmi l'ensemble comprenant l'énergie thermique, les rayonnements et les particules accélérées, cette polymérisation étant éventuellement mise en oeuvre dans le cadre d'un procédé en deux étapes qui consiste à activer d'abord, par une irradiation, ladite composition polymère pour obtenir des précurseurs activés, puis à procéder à un durcissement thermique des précurseurs activés, la température d'irradiation étant inférieure à la température utilisée pour le durcissement thermique.