(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
9 October 2003 (09.10.2003)

PCT

(10) International Publication Number
WO 03/082940 A1

(51) International Patent Classification[7]**: C08F 255/00**, 257/00, 8/32, 120/56, 26/02, C08J 3/26, C08G 73/00

(21) International Application Number: PCT/US03/09753

(22) International Filing Date: 28 March 2003 (28.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/113,909 28 March 2002 (28.03.2002) US

(63) Related by continuation (CON) or continuation-in-part (CIP) to earlier application:
US 10/113,909 (CIP)
Filed on 28 March 2002 (28.03.2002)

(71) Applicant *(for all designated States except US)*: **HENKEL LOCTITE CORPORATION** [US/US]; 1001 Trout Brook Crossing, Rocky Hill, CT 06067 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **LIU, Puwei** [CN/US]; 9494 Carroll Canyon Road, #5, San Diego, CA 92126 (US). **DERSHEM, Stephen, M.** [US/US]; 9097 Truman Street, San Diego,CA 92129 (US). **YANG, Kang** [US/US]; 8529 Boothbay Place, San Diego, CA 92129 (US). **ALBINO, Carolyn, C.** [US/US]; 10868, Esmond Court, San Diego, CA 92126 (US).

(74) Agents: REITER, Stephen, E. et al.; Foley & Lardner, P.O.Box 80278, San Diego, CA 92138-0278 (US).

(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FILM ADHESIVES CONTAINING MALEIMIDE AND RELATED COMPOUNDS AND METHODS FOR USE THEREOF

(57) Abstract: In accordance with the present invention, there are provided film adhesive compositions comprising at least one macromonomer having at least one unit of ethylenic unsaturation, at least one thermoplastic elastomer co-curable with the macromonomer, and at least one cure initiator, and methods for use thereof. Invention compositions are useful as adhesives in the microelectronics industry. In particular, invention film adhesives may be used to produce microelectronic assemblies with very thin bond lines without compromising adhesive strength.

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FILM ADHESIVES CONTAINING MALEIMIDE AND RELATED COMPOUNDS AND METHODS FOR USE THEREOF

RELATED APPLICATIONS

[0001] This application is a continuation in part of United States Patent Application No. 10/113,909, filed March 28, 2002, now pending, which is incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to film adhesive compositions, and more particularly to the use of film adhesive compositions in stacked die microelectronic packaging applications.

BACKGROUND OF THE INVENTION

[0003] In response to an increasing demand for semiconductor packages that are smaller, yet more functional, the microelectronic packaging industry has recently begun producing packages containing at least two stacked semiconductor dice. Indeed, it is often advantageous to stack multiple dice into the same package in order to increase circuit density without increasing the area occupied on a circuit board by the integrated circuit package.

[0004] Several challenges exist with respect to producing reliable electronic components containing stacked die packages. For example, stacked die packages typically require very thin bond lines between die (e.g., < 15 microns). In addition, it is known that adhesive fillet and resin bleed associated with many adhesive formulations contribute to unreliable component performance. Thus, adhesives used in stacked die applications ideally would provide (at a minimum bond line thickness) superior adhesive strength and conductivity (thermal and electrical) without producing adhesive fillet or resin bleed. One possible approach to address this challenging problem lies in the use of film adhesives.

[0005] Accordingly, there is a need for film adhesives which provide superior adhesive strength and conductivity when dispensed to achieve very thin bond lines in a variety of microelectronic packages, such as, for example, stacked die packages.

SUMMARY OF THE INVENTION

[0006] In accordance with the present invention, there are provided film adhesive compositions comprising at least one macromonomer having at least one unit of ethylenic unsaturation, at least one thermoplastic elastomer co-curable with the macromonomer, and at least one cure initiator. Invention compositions are useful as adhesives in the microelectronics industry. In particular, invention film adhesives may be used to produce microelectronic assemblies with very thin bond lines without compromising adhesive strength.

[0007] In a further aspect of the present invention, there are provided methods employing invention film adhesive compositions for adhesively attaching a device to a substrate, and methods employing invention film adhesive compositions for adhesively attaching at least two semiconductor dice to a substrate in a stacked arrangement.

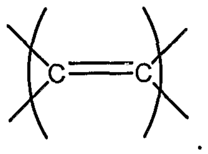
[0008] In a still further aspect of the invention, there are provided assemblies comprising a first article adhered to a second article by invention film adhesive compositions.

DETAILED DESCRIPTION OF THE INVENTION

[0009] In accordance with the present invention, there are provided adhesive compositions comprising at least one macromonomer having at least one unit of ethylenic unsaturation, at least one thermoplastic elastomer co-curable with the macromonomer, and at least one cure initiator.

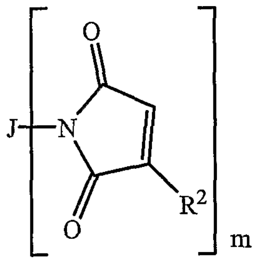
[0010] As employed herein, "macromonomer" refers to a compound having properties suitable for use in invention film adhesive compositions. For example, macromonomers contemplated for use in the practice of the present invention typically are low melting point solids having low vapor pressures. Alternatively, macromonomers contemplated for use in the practice of the present invention may be liquids having a molecular weight of at least about 500 grams/mole.

[0011] As employed herein, “unit of ethylenic unsaturation” refers to unsaturation comprising localized (i.e., non-aromatic) carbon-carbon double bonds, as shown below:

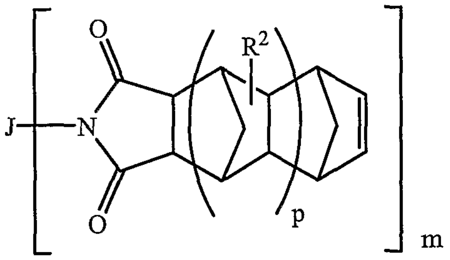


[0012] As employed herein, “co-curable” refers to the ability of a thermoplastic elastomer to undergo copolymerization with a macromonomer to form a three-dimensional polymeric network.

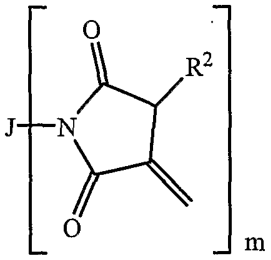
[0013] Macromonomers contemplated for use in the practice of the present invention include, for example, maleimides, nadimides, itaconimides, vinyl compounds, allylated amides, and the like. In one embodiment, maleimide, nadimide, and itaconimide macromonomers contemplated for use in the practice of the present invention include compounds having, respectively, the following structures **I**, **II**, and **III**:



(I)



(II)



(III)

wherein:

$m = 1\text{-}15$,

$p = 0\text{-}15$,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

[0014] In one embodiment, J is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, $-S(O)_2-$, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0015] As employed herein, "hydrocarbyl" comprises any organic radical wherein the backbone thereof comprises carbon and hydrogen only. Thus, hydrocarbyl embraces alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, alkylaryl, arylalkyl, arylalkenyl, alkenylaryl, arylalkynyl, alkynylaryl, and the like.

[0016] As employed herein, "substituted hydrocarbyl" comprises any of the above-referenced hydrocarbyl groups further bearing one or more substituents selected from hydroxy, alkoxy (of a lower alkyl group), mercapto (of a lower alkyl group), cycloalkyl, substituted cycloalkyl, heterocyclic, substituted heterocyclic, aryl, substituted aryl, heteroaryl, substituted heteroaryl, aryloxy, substituted aryloxy, halogen, trifluoromethyl, cyano, nitro, nitrone, amino, amido, —C(O)H, acyl, oxyacyl, carboxyl, carbamate, dithiocarbamoyl, sulfonyl, sulfonamide, sulfuryl, and the like.

[0017] As employed herein, "alkyl" refers to saturated straight or branched chain hydrocarbon radical having in the range of 1 up to about 500 carbon atoms. "Lower alkyl" refers to alkyl groups having in the range of 1 up to about 5 carbon atoms. "Substituted alkyl" refers to alkyl groups further bearing one or more substituents as set forth above.

[0018] As employed herein, "alkenyl" refers to straight or branched chain hydrocarbyl groups having at least one carbon—carbon double bond, and typically having in the range of about 2 up to 500 carbon atoms, and "substituted alkenyl" refers to alkenyl groups further bearing one or more substituents as set forth above.

[0019] As employed herein, "alkynyl" refers to straight or branched chain hydrocarbyl groups having at least one carbon—carbon triple bond, and typically having in the range of about 2 up to 500 carbon atoms, and "substituted alkynyl" refers to alkynyl groups further bearing one or more substituents as set forth above.

[0020] As employed herein, "cycloalkyl" refers to a cyclic ring-containing groups containing in the range of about 3 up to about 8 carbon atoms, and "substituted cycloalkyl" refers to cycloalkyl groups further bearing one or more substituents as set forth above.

[0021] As employed herein, "cycloalkenyl" refers to cyclic ring-containing groups containing in the range of 3 up to 20 carbon atoms and having at least one carbon-carbon double bond, and "substituted cycloalkenyl" refers to cycloalkenyl groups further bearing one or more substituents as set forth above.

[0022] As employed herein, "aryl" refers to aromatic groups having in the range of 6 up to 14 carbon atoms and "substituted aryl" refers to aryl groups further bearing one or more substituents as set forth above.

[0023] As employed herein, "alkylaryl" refers to alkyl-substituted aryl groups and "substituted alkylaryl" refers to alkylaryl groups further bearing one or more substituents as set forth above.

[0024] As employed herein, "arylalkyl" refers to aryl-substituted alkyl groups and "substituted arylalkyl" refers to arylalkyl groups further bearing one or more substituents as set forth above.

[0025] As employed herein, "arylalkenyl" refers to aryl-substituted alkenyl groups and "substituted arylalkenyl" refers to arylalkenyl groups further bearing one or more substituents as set forth above.

[0026] As employed herein, "alkenylaryl" refers to alkenyl-substituted aryl groups and "substituted alkenylaryl" refers to alkenylaryl groups further bearing one or more substituents as set forth above.

[0027] As employed herein, "arylalkynyl" refers to aryl-substituted alkynyl groups and "substituted arylalkynyl" refers to arylalkynyl groups further bearing one or more substituents as set forth above.

[0028] As employed herein, "alkynylaryl" refers to alkynyl-substituted aryl groups and "substituted alkynylaryl" refers to alkynylaryl groups further bearing one or more substituents as set forth above.

[0029] As employed herein, "heterocyclic" refers to cyclic (i.e., ring-containing) groups containing one or more heteroatoms (e.g., N, O, S, or the like) as part of the ring structure, and having in the range of 1 up to 14 carbon atoms and "substituted heterocyclic" refers to heterocyclic groups further bearing one or more substituents as set forth above. Exemplary heterocyclic moieties include saturated rings, unsaturated rings, and aromatic heteroatom-containing ring systems, e.g., epoxy, tetrahydrofuran, oxazoline, oxazine, pyrrole, pyridine, furan, tetrazole, and the like.

[0030] As employed herein, "hydrocarbylene" refers to divalent straight or branched chain hydrocarbyl groups including alkylene groups, alkenylene groups, alkynylene groups, cycloalkylene groups, heterocycloalkylene groups, arylene groups, heteroarylene groups, alkylarylene groups, arylalkylene groups, arylalkenylene groups, arylalkynylene groups, alkenylarylene groups, alkynylarylene groups, and the like; and "substituted hydrocarbylene" refers to hydrocarbylene groups further bearing one or more substituents as set forth above.

[0031] As employed herein, "alkylene" refers to saturated, divalent straight or branched chain hydrocarbyl groups typically having in the range of about 2 up to about 500 carbon atoms, and "substituted alkylene" refers to alkylene groups further bearing one or more substituents as set forth above.

[0032] As employed herein, "alkenylene" refers to divalent straight or branched chain hydrocarbyl groups having at least one carbon—carbon double bond, and typically having in the range of about 2 up to 500 carbon atoms, and "substituted alkenylene" refers to alkenylene groups further bearing one or more substituents as set forth above.

[0033] As employed herein, "alkynylene" refers to divalent straight or branched chain hydrocarbyl groups having at least one carbon-carbon triple bond, and typically having in the range of about 2 up to 500 carbon atoms, and "substituted alkynylene" refers to alkynylene groups further bearing one or more substituents as set forth above.

[0034] As employed herein, "cycloalkylene" refers to divalent ring-containing groups containing in the range of about 3 up to about 8 carbon atoms, and "substituted cycloalkylene" refers to cycloalkylene groups further bearing one or more substituents as set forth above.

[0035] As employed herein, "heterocycloalkylene" refers to divalent cyclic (i.e., ring-containing) groups containing one or more heteroatoms (e.g., N, O, S, or the like) as part of the ring structure, and having in the range of 1 up to 14 carbon atoms and "substituted heterocycloalkylene" refers to heterocycloalkylene groups further bearing one or more substituents as set forth above.

[0036] As employed herein, "cycloalkenylene" refers to divalent ring-containing groups containing in the range of about 3 up to about 8 carbon atoms and having at least one carbon-carbon double bond, and "substituted cycloalkenylene" refers to cycloalkenylene groups further bearing one or more substituents as set forth above.

[0037] As employed herein, "arylene" refers to divalent aromatic groups typically having in the range of 6 up to 14 carbon atoms and "substituted arylene" refers to arylene groups further bearing one or more substituents as set forth above.

[0038] As employed herein, "alkylarylene" refers to alkyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkylarylene" refers to alkylarylene groups further bearing one or more substituents as set forth above.

[0039] As employed herein, "arylalkylene" refers to aryl-substituted divalent alkyl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted arylalkylene" refers to arylalkylene groups further bearing one or more substituents as set forth above.

[0040] As employed herein, "arylalkenylene" refers to aryl-substituted divalent alkenyl groups typically having in the range of about 8 up to 16 carbon atoms and "substituted arylalkenylene" refers to arylalkenylene groups further bearing one or more substituents as set forth above.

[0041] As employed herein, "arylalkynylene" refers to aryl-substituted divalent alkynyl groups typically having in the range of about 8 up to 16 carbon atoms and "substituted arylalkynylene" refers to arylalkynylene group further bearing one or more substituents as set forth above.

[0042] As employed herein, "alkenylarylene" refers to alkenyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkenylarylene" refers to alkenylarylene groups further bearing one or more substituents as set forth above.

[0043] As employed herein, "alkynylarylene" refers to alkynyl-substituted divalent aryl groups typically having in the range of about 7 up to 16 carbon atoms and "substituted alkynylarylene" refers to alkynylarylene groups further bearing one or more substituents as set forth above.

[0044] As employed herein, "heteroarylene" refers to divalent aromatic groups containing one or more heteroatoms (e.g., N, O, S or the like) as part of the aromatic ring, and typically having in the range of 3 up to 14 carbon atoms and "substituted heteroarylene" refers to heteroarylene groups further bearing one or more substituents as set forth above.

[0045] As employed herein, "polysiloxane-polyurethane block copolymers" refer to polymers containing both at least one polysiloxane (soft) block and at least one polyurethane (hard) block.

[0046] When one or more of the above described monovalent or polyvalent groups contain one or more of the above described linkers to form the "J" appendage of a maleimide, nadimide or itaconimide group, as readily recognized by those of skill in the art, a wide variety of linkers can be produced, such as, for example, oxyalkyl, thioalkyl, aminoalkyl, carboxylalkyl, oxyalkenyl, thioalkenyl, aminoalkenyl, carboxyalkenyl, oxyalkynyl, thioalkynyl, aminoalkynyl, carboxyalkynyl, oxycycloalkyl, thiocycloalkyl, aminocycloalkyl, carboxycycloalkyl, oxycloalkenyl, thiocycloalkenyl, aminocycloalkenyl, carboxycycloalkenyl, heterocyclic, oxyheterocyclic, thioheterocyclic, aminoheterocyclic, carboxyheterocyclic, oxyaryl, thioaryl, aminoaryl, carboxyaryl, heteroaryl, oxyheteroaryl, thioheteroaryl, aminoheteroaryl, carboxyheteroaryl, oxyalkylaryl, thioalkylaryl, aminoalkylaryl, carboxyalkylaryl, oxyarylalkyl, thioarylalkyl, aminoarylalkyl, carboxyarylalkyl, oxyarylalkenyl, thioarylalkenyl, aminoarylalkenyl, carboxyarylalkenyl, oxyalkenylaryl, thioalkenylaryl, aminoalkenylaryl, carboxyalkenylaryl, oxyarylalkynyl, thioarylalkynyl, aminoarylalkynyl, carboxyarylalkynyl, oxyalkynylaryl, thioalkynylaryl, aminoalkynylaryl or carboxyalkynylaryl. oxyalkylene, thioalkylene, aminoalkylene, carboxyalkylene, oxyalkenylene, thioalkenylene, aminoalkenylene, carboxyalkenylene, oxyalkynylene, thioalkynylene, aminoalkynylene, carboxyalkynylene, oxycycloalkylene, thiocycloalkylene, aminocycloalkylene, carboxycycloalkylene, oxycycloalkenylene, thiocycloalkenylene, aminocycloalkenylene, carboxycycloalkenylene, oxyarylene, thioarylene, aminoarylene, carboxyarylene, oxyalkylarylene, thioalkylarylene, aminoalkylarylene, carboxyalkylarylene, oxyarylalkylene, thioarylalkylene, aminoarylalkylene, carboxyarylalkylene, oxyarylalkenylene, thioarylalkenylene, aminoarylalkenylene, carboxyarylalkenylene, oxyalkenylarylene, thioalkenylarylene, aminoalkenylarylene, carboxyalkenylarylene, oxyarylalkynylene, thioarylalkynylene, aminoarylalkynylene, carboxy arylalkynylene, oxyalkynylarylene, thioalkynylarylene, aminoalkynylarylene, carboxyalkynylarylene, heteroarylene, oxyheteroarylene, thioheteroarylene, aminoheteroarylene, carboxyheteroarylene, heteroatom-containing di- or polyvalent cyclic moiety, oxyheteroatom-containing di- or polyvalent cyclic moiety, thioheteroatom-containing di- or polyvalent cyclic moiety, aminoheteroatom-containing di- or polyvalent cyclic moiety, carboxyheteroatom-containing di- or polyvalent cyclic moiety, disulfide, sulfonamide, and the like.

[0047] In another embodiment, maleimides, nadimides, and itaconimides contemplated for use in the practice of the present invention have the structures **I**, **II**, or **III** wherein,

$m = 1\text{-}6$,
$p = 0\text{-}6$, and
J is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

(c) a polyalkylene oxide having the structure:

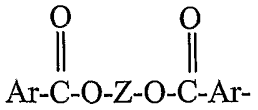
$$[(CR_2)_r-O-]_f-(CR_2)_s-$$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,
$r = 1\text{-}10$,
$s = 1\text{-}10$, and

f is as defined above;

(d) aromatic groups having the structure:



$$\text{Ar-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-O-Z-O-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-Ar-}$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

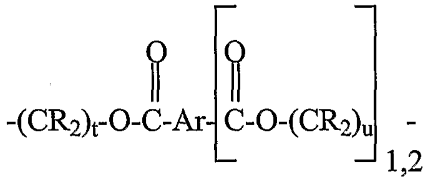
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$$\text{-}[(CR_2)_r\text{-}O\text{-}]_q\text{-}(CR_2)_s\text{-}$$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

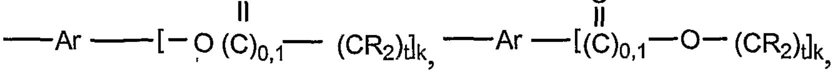
(e) di- or tri-substituted aromatic moieties having the structure:



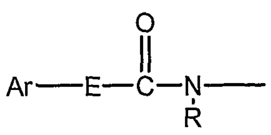
$$\text{-}(CR_2)_t\text{-O-}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-Ar-}\left[\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{-O-}(CR_2)_u\right]_{1,2}\text{-}$$

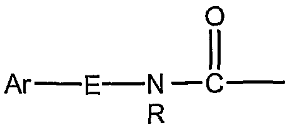
wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

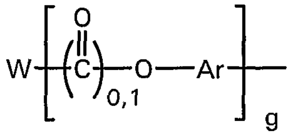
(f) aromatic groups having the structure:



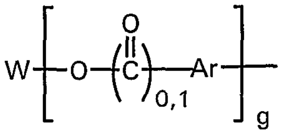
$$\text{—Ar—}[\text{—O}(\overset{\overset{\displaystyle O}{\|}}{\text{C}})_{0,1}\text{—}(CR_2)_t]_k,\ \text{—Ar—}[(\overset{\overset{\displaystyle O}{\|}}{\text{C}})_{0,1}\text{—O—}(CR_2)_t]_k,$$


$Ar{-}E{-}C(=O){-}N(R){-}$,


$Ar{-}E{-}N(R){-}C(=O){-}$,


$W{-}\left[(C(=O))_{0,1}{-}O{-}Ar{-}\right]_g$

or


$W{-}\left[O{-}(C(=O))_{0,1}{-}Ar{-}\right]_g$

wherein:

each R is independently defined as above,

t = 2-10,

k = 1, 2 or 3,

g = 1 up to about 50,

each Ar is as defined above,

E is –O- or -NR^5-, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein,

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

d = 1-10,

e = 1-10, and

f = 1-50; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

r = 1-10,

s = 1-10, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

$R^7\text{-U-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O)-(O-R}^8\text{-O-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O))}_v\text{-U-R}^8\text{-}$

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}$- wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

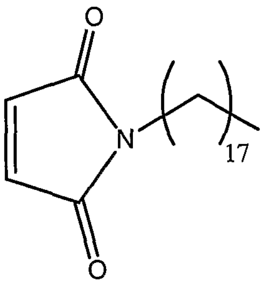
v = 0-50;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

[0048] In another embodiment, J is of sufficient length to render liquid the maleimide, nadimide, itaconimide or combinations of two or more thereof. In some such embodiments, m = 1, 2 or 3, and J is a branched chain alkyl, alkylene or alkylene oxide of sufficient length and branching to render liquid the maleimide, nadimide, itaconimide or combinations of two or more thereof.

[0049] Preferred maleimides, nadimides, and itaconimides contemplated for use in the practice of the present invention include, for example, maleimides, nadimides, and itaconimides having the following structures:



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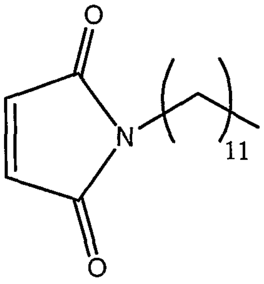

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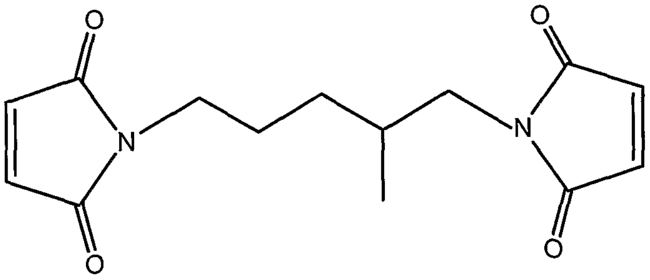

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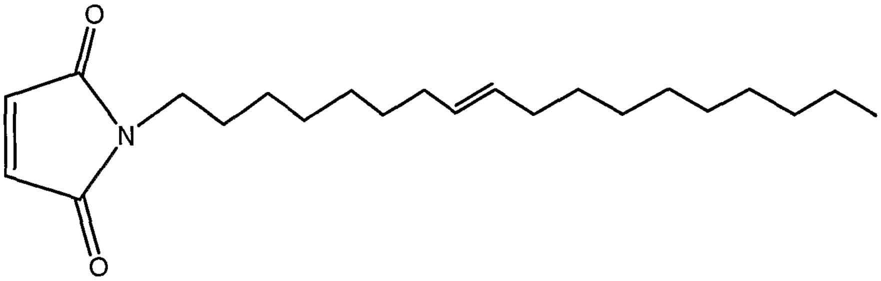

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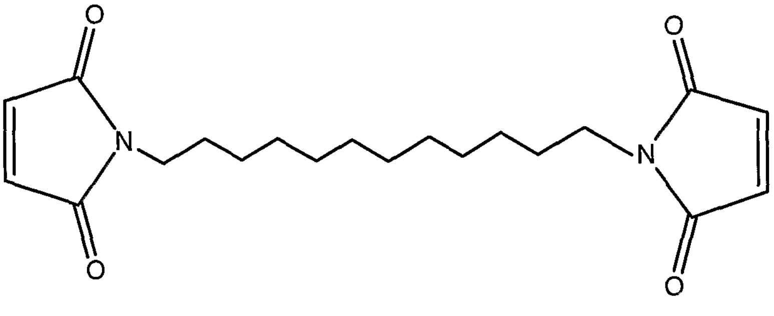

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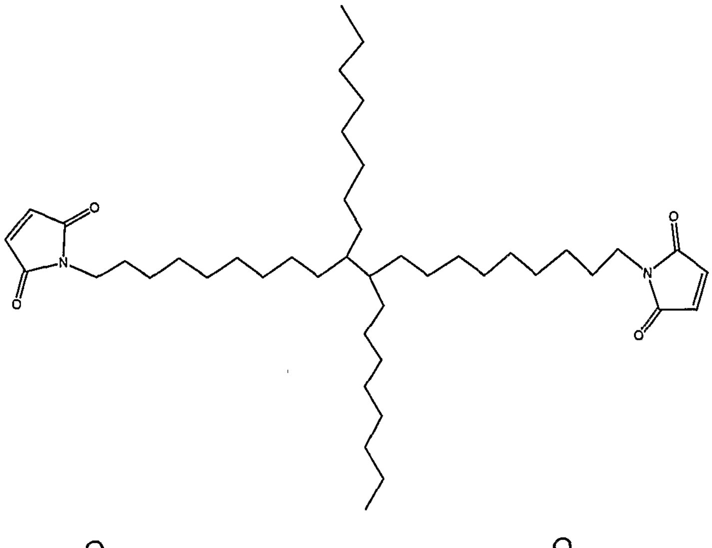
O
N
O
O
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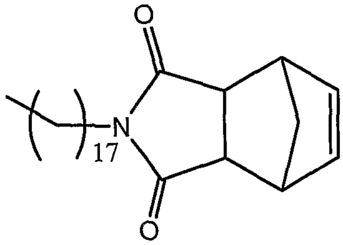
O

,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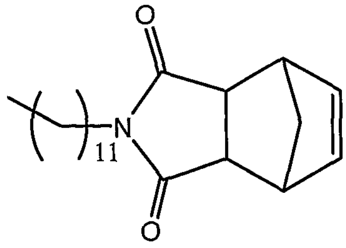
O
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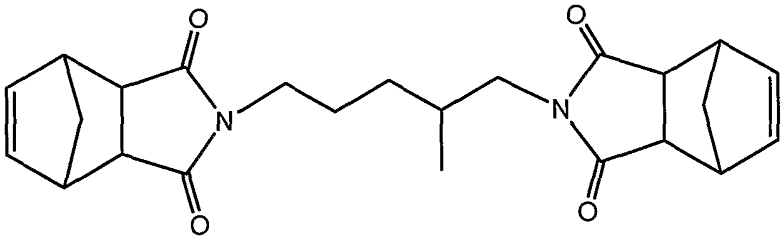
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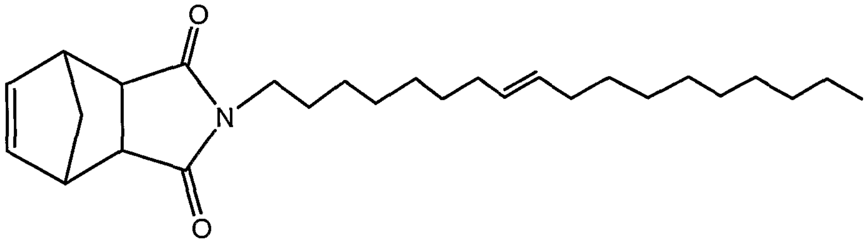
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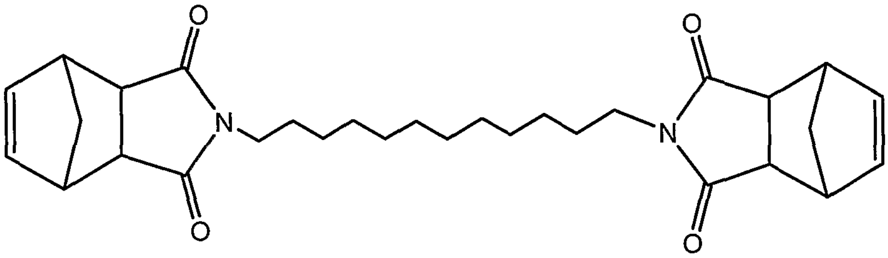
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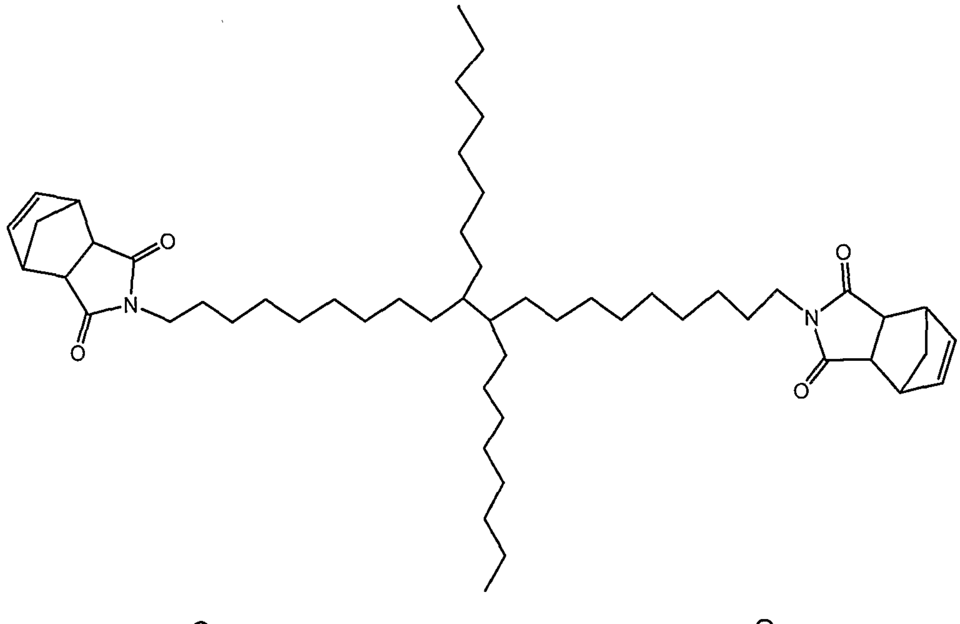

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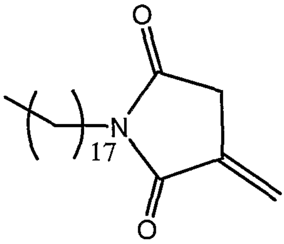

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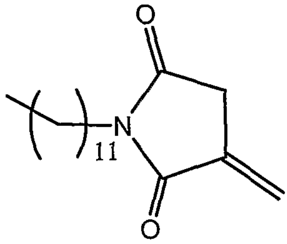

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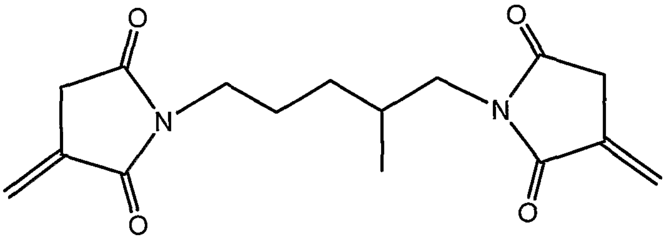

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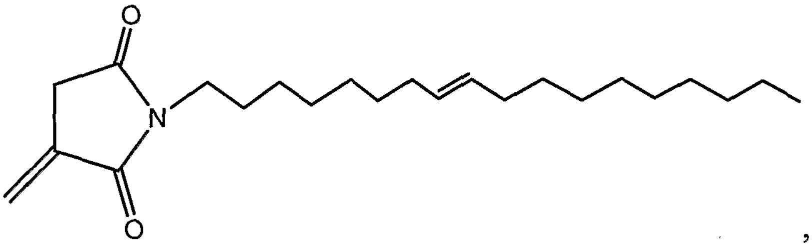

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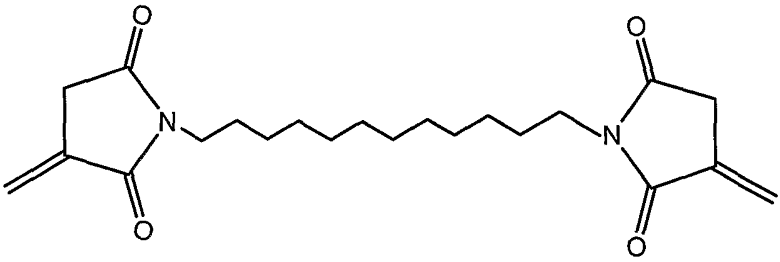

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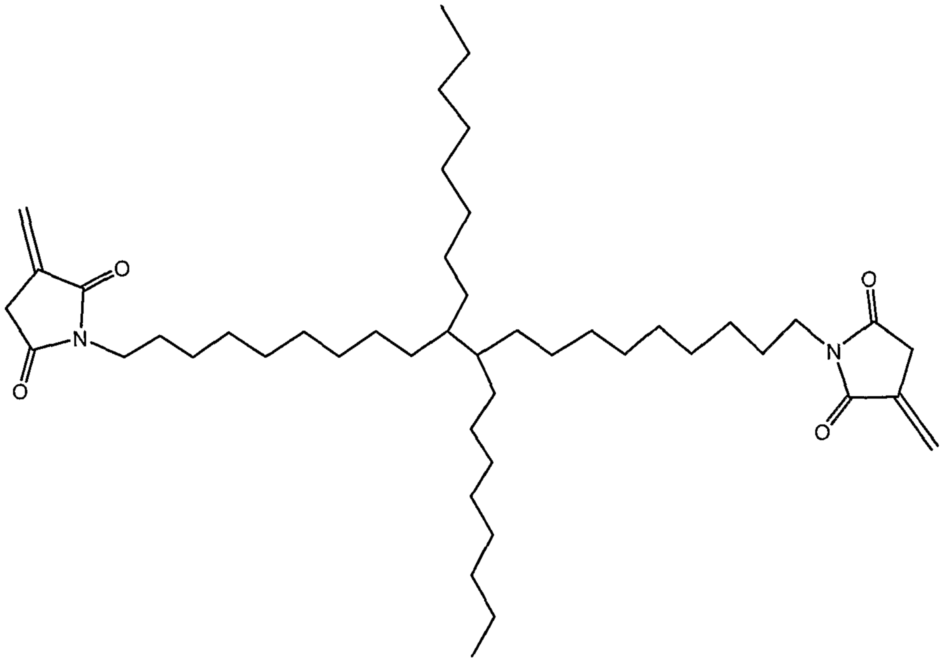


[0050] Vinyl macromonomers contemplated for use in the practice of the present invention include compounds having the following structure:

$$Y\left(Q_{0,1}-CR{=\!=}CHR\right)_q$$

wherein:

q is 1, 2 or 3,

each R is independently selected from hydrogen or lower alkyl,

each Q is independently selected from –O-, -O-C(O)-, -C(O)- or -C(O)-O-, and

Y is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

[0051] In one embodiment, Y is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, $-S(O)_2-$, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0052] In another embodiment, Y is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1-10$,
$e = 1-10$, and
$f = 1-50$;

(c) a polyalkylene oxide having the structure:

$[(CR_2)_r\text{-}O\text{-}]_f\text{-}(CR_2)_s\text{-}$

wherein:

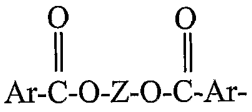
each R is independently hydrogen, alkyl or substituted alkyl,

r = 1-10,

s = 1-10, and

f is as defined above;

(d) aromatic groups having the structure:



$$\mathrm{Ar\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}Z\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ar\text{-}}$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

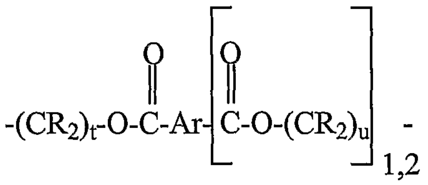
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$\text{-}[(CR_2)_r\text{-}O\text{-}]_q\text{-}(CR_2)_s\text{-}$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

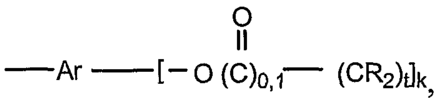
(e) di- or tri-substituted aromatic moieties having the structure:



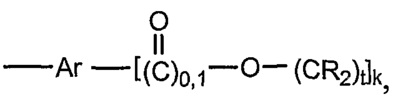
$$\text{-}(CR_2)_t\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}Ar\text{-}\left[\overset{\overset{O}{\|}}{C}\text{-}O\text{-}(CR_2)_u\right]_{1,2}\text{-}$$

wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

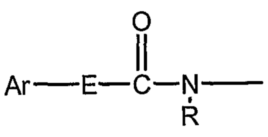
(f) aromatic groups having the structure:



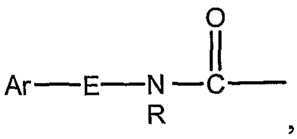
$$-Ar-[-O\overset{O}{\overset{\|}{(C)}}_{0,1}-(CR_2)_t]_k,$$



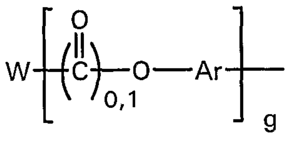
$$-Ar-[\overset{O}{\overset{\|}{(C)}}_{0,1}-O-(CR_2)_t]_k,$$



$$Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-\ ,$$

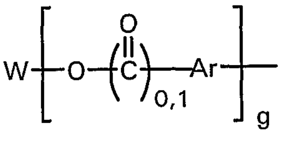


$$Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-\ ,$$



$$W-\left[\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-O-Ar-\right]_g$$

or



$$W-\left[O-\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-Ar-\right]_g$$

wherein:

each R is independently defined as above,

$t = 2\text{-}10$,

$k = 1, 2$ or 3,

$g = 1$ up to about 50,

each Ar is as defined above,

E is –O- or $-NR^5-$, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

d = 1-10,

e = 1-10, and

f = 1-50; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

r = 1-10,

s = 1-10, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

$R^7-U-C(O)-NR^6-R^8-NR^6-C(O)-(O-R^8-O-C(O)-NR^6-R^8-NR^6-C(O))_v-U-R^8-$

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

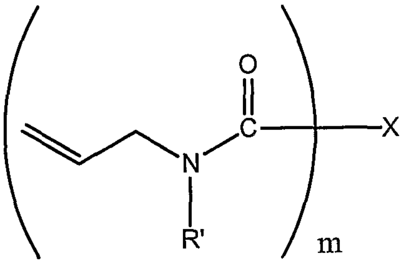
U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}-$ wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

v = 0-50;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

[0053] Allylated amide macromonomers contemplated for use in the practice of the present invention include compounds having the following structure:



wherein:

R' is hydrogen, C_1 up to about C_{18} alkyl or oxyalkyl, allyl, aryl, or substituted aryl,

m is 1-6, and

X is is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

[0054] In one embodiment, X is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, $-S(O)_2-$, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-,

$-O-NR-S(O)-O-$, $-O-NR-S(O)-NR-$, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

[0055] In another embodiment, X is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1-10$,
$e = 1-10$, and
$f = 1-50$;

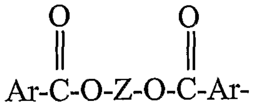
(c) a polyalkylene oxide having the structure:

$[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,
$r = 1-10$,
$s = 1-10$, and
f is as defined above;

(d) aromatic groups having the structure:



$$\text{Ar-}\overset{O}{\overset{\|}{\text{C}}}\text{-O-Z-O-}\overset{O}{\overset{\|}{\text{C}}}\text{-Ar-}$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

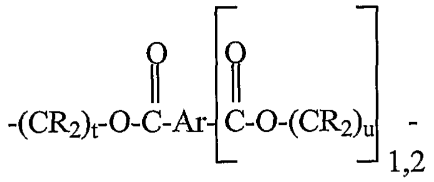
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$$-[(CR_2)_r-O-]_q-(CR_2)_s-$$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

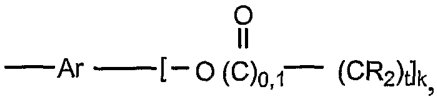
(e) di- or tri-substituted aromatic moieties having the structure:



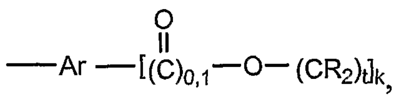
$$-(CR_2)_t-O-\overset{O}{\overset{\|}{C}}-Ar-\left[\overset{O}{\overset{\|}{C}}-O-(CR_2)_u\right]_{1,2}-$$

wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

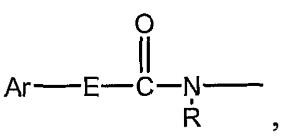
(f) aromatic groups having the structure:



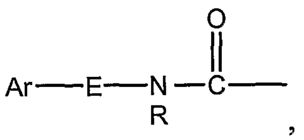
$$-Ar-[-O\overset{O}{\overset{\|}{(C)}}_{0,1}-(CR_2)_t]_k,$$



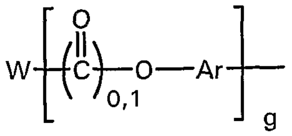
$$-Ar-[\overset{O}{\overset{\|}{(C)}}_{0,1}-O-(CR_2)_t]_k,$$



$$Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-,$$

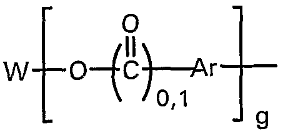


$$Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-,$$



$$W\left[\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-O-Ar\right]_g$$

or



$$W\left[O-\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-Ar\right]_g$$

wherein:

each R is independently defined as above,

$t = 2\text{-}10$,

$k = 1, 2$ or 3,

$g = 1$ up to about 50,

each Ar is as defined above,

E is –O- or $-NR^5-$, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

R^7-U-C(O)-NR^6-R^8-NR^6-C(O)-(O-R^8-O-C(O)-NR^6-R^8-NR^6-C(O))$_v$-U-R^8-

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}$- wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

$v = 0$-50;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

[0056] Thermoplastic elastomers contemplated for use in the practice of the present invention are typically block copolymers. The block copolymers have at least one unit of the general formula (A-B), or (A-B-A), wherein A is a non-elastomeric polymer block and B is an elastomeric polymer block. Block copolymers contemplated for use in the practice of the present invention preferably have low dielectric constants. In addition, thermoplastic elastomers contemplated for use in the practice of the present invention contain pendant and/or terminal units of ethylenic unsaturation, and therefore are able to cure with other components in the adhesive composition, such as the unsaturated macromonomer.

[0057] In one aspect of the invention, the non-elastomeric polymer block (A) is the polymerization product of one or more optionally substituted aromatic hydrocarbons containing at least one unit of ethylenic unsaturation. Aromatic hydrocarbons contemplated for use in the practice of the present invention include, for example, optionally substituted styrene, optionally substituted stilbene, and the like. Substituents contemplated for optional use in the practice of the present invention include for example, alkyl, alkenyl, alkynyl, hydroxy, alkoxy, alkenoxy, and the like. In a preferred embodiment, the aromatic hydrocarbon is optionally substituted styrene.

[0058] The elastomeric polymer block (B) is typically the polymerization or copolymerization product of optionally substituted olefin monomers and/or optionally substituted conjugated diene monomers. Olefin monomers contemplated for use in the practice of the present invention typically contain from 2 up to about 20 carbon atoms. Preferably, the olefin monomers contain from 2 up to about 12 carbon atoms. In a particularly preferred embodiment, the olefin monomers include, for example, ethylene, propylene, butylene, isobutylene, acrylonitrile, (meth)acrylate, and the like. Most preferably, the olefin monomer is acrylonitrile.

[0059] Conjugated diene monomers contemplated for use in the practice of the present invention typically contain from 4 up to about 20 carbon atoms. Preferably, the conjugated diene monomers contain from 4 up to about 12 carbon atoms. In a particularly preferred embodiment, the conjugated diene monomers include, for example, butadiene, isoprene, dimethylbutadiene, and the like. Most preferably, the conjugated diene monomer is butadiene.

[0060] The structure of the elastomeric segments can be optionally modified to increase adhesive strength of invention compositions. For example, the elastomeric segments of the block copolymers (e.g., the polybutadiene segments) may be modified via a thermally induced ene-reaction with maleic anhydride (for a review of the ene-reaction, see, for example, Oppolzer, W., Snieckus, V., *Angew. Chem. Int. Ed. Engl.*, **1978**, *17*, 476). Such modification has a particularly positive impact on hot die-shear values.

[0061] Thermoplastic elastomers contemplated for use in the practice of the present invention include, for example, polystyrene-polybutadiene-polystyrene block copolymers, polystyrene-polyisoprene-polystyrene block copolymers, polystyrene-polydimethylbutadiene-polystyrene block copolymers, polybutadiene-polyacrylonitrile block copolymers, and the like. Preferably, the block copolymer is a polystyrene-polybutadiene-polystyrene block copolymer or a polybutadiene-polyacrylonitrile block copolymer.

[0062] Further examples of the thermoplastic elastomers include poly(olefins), poly(dienes), poly(peptides), poly(esters), poly(ethers), poly(oxides), poly(sulfides), poly(amines), and the like. More specific examples of such thermoplastic elastomers include syndiotactic polybutadiene, alpha-polyisoprene, poly(2-butyl-2-methyl-beta-alanine), poly(decamethylene 4-octendioate), poly(butylvinyl ether), poly(decamethylene oxide), poly(hexamethylene sulfide), poly(ethylene amine), and the like. For additional examples, see R. Miller, Polymer Handbook, chap. 4, 4th ed., J. Bandrup et al., eds., J. Wiley & Sons, New York (1999).

[0063] Adhesive compositions of the invention also contain in the range of 0.2 up to 2 weight % of at least one free radical initiator, wherein weight % (wt %) is based on the total weight of the composition. As employed herein, the term "free radical initiator" refers to any chemical species which, upon exposure to sufficient energy (e.g., light, heat, or the like), decomposes into at least two species which are uncharged, but which each possesses at least one unpaired electron. Preferred free radical initiators contemplated for use in the practice of the present invention are compounds which decompose (i.e., have a half life in the range of about 10 hours) at temperatures in the range of about 70 up to 180° C.

[0064] Free-radical cure initiators contemplated for use in the practice of the present invention include for example, peroxides (e.g., peroxy esters, peroxy carbonates, hydroperoxides, alkylperoxides, arylperoxides, and the like), azo compounds, and the like. Presently preferred peroxides contemplated for use in the practice of the present invention include dicumyl peroxide, dibenzoyl peroxide, 2-butanone peroxide, tert-butyl perbenzoate, di-tert-butyl peroxide, 2,5-bis(tert-butylperoxy)-2,5-dimethylhexane, bis(tert-butyl peroxyisopropyl)benzene, tert-butyl hydroperoxide, and the like. Presently preferred azo compounds contemplated for use in the practice of the present invention include 2,2'-azobis(2-methylpropanenitrile), 2,2'-azobis(2-methylbutanenitrile), 1,1'-azobis(cyclohexanecarbonitrile), and the like.

[0065] Adhesive compositions contemplated for use in the practice of the present invention typically contain in the range of about 10 wt % up to about 95 wt % thermoplastic elastomer, in the range of about 5 wt % up to about 90 wt % macromonomer having at least one unit of ethylenic unsaturation, and in the range of about 0.5 wt % up to about 2.0 wt % a cure initiator, wherein weight % is based on the total weight of the composition. Preferably, the macromonomer having at least one unit of ethylenic unsaturation is present in the range of about 10 wt % up to about 80 wt %.

[0066] Adhesive compositions according to the invention optionally further contain in the range of about 0.1 up to about 10 wt % of at least one coupling agent, based on the total weight of the composition. Preferably, the coupling agent is present in the range of about 0.2 wt % up to about 5 wt %. Coupling agents contemplated for use in the practice of the present invention include siloxanes, silicate esters, metal acrylate salts, titanates, and the like.

[0067] Film adhesive compositions according to the invention may optionally contain a filler. Fillers contemplated for optional use in the practice of the present invention may optionally be conductive (electrically and/or thermally). Electrically conductive fillers contemplated for use in the practice of the present invention include, for example, silver, nickel, gold, cobalt, copper, aluminum, graphite, silver-coated graphite, nickel-coated graphite, alloys of such metals, and the like, as well as mixtures thereof. Both powder and flake forms of filler may be used in the adhesive compositions of the present invention. Preferably, the flake has a thickness of less than about 2 microns, with planar dimensions of about 20 to about 25 microns. Flake employed herein preferably has a surface area of about 0.15 to 5.0 m^2/g and a tap density of about 0.4 up to about 5.5 g/cc. It is presently preferred that powder employed in the practice of the invention has a diameter of about 0.5 to 15 microns. If present, the filler typically comprises in the range of about 1 wt % up to about 95 wt % of the film adhesive composition, wherein weight % is based on the total weight of the composition.

[0068] Thermally conductive fillers contemplated for optional use in the practice of the present invention include, for example, aluminum nitride, boron nitride, silicon carbide, diamond, graphite, beryllium oxide, magnesia, silica, alumina, and the like. Preferably, the particle size of these fillers will be in the range of about 5 up to about 30 microns. Most preferably, the particle size of these fillers will be about 20 microns.

[0069] Electrically and/or thermally conductive fillers are optionally (and preferably) rendered substantially free of catalytically active metal ions by treatment with chelating agents, reducing agents, nonionic lubricating agents, or mixtures of such agents. Such treatment is described in U.S. Patent No. 5,447,988, which is incorporated by reference herein in its entirety.

[0070] Optionally, a filler may be used that is neither an electrical nor thermal conductor. Such fillers may be desirable to impart some other property to the film adhesive composition, such as, for example, reduced thermal expansion of the cured adhesive, reduced dielectric constant, improved toughness, increased hydrophobicity, and the like. Examples of such fillers include perfluorinated hydrocarbon polymers (i.e., TEFLON^{TM}), thermoplastic polymers, thermoplastic elastomers, mica, fused silica, glass powder, and the like.

[0071] In a preferred embodiment, film adhesive compositions contemplated for use in the practice of the present invention contain in the range of about 5 wt % up to about 90 wt% thermoplastic elastomer, in the range of about 5 wt % up to about 90 wt% macromonomer containing at least one unit of ethylenic unsaturation, in the range of about 0.5 wt % up to about 2.0 wt % cure initiator, in the range of about 0.5 wt % up to about 5 wt % coupling agent, and in the range of about 1 wt % up to about 95 wt% filler, wherein weight % is based on the total weight of the composition.

[0072] In a further aspect of the invention, there are provided methods for adhesively attaching a device to a substrate comprising subjecting a sufficient quantity of an invention film adhesive composition positioned between a substrate and a device to conditions suitable to cure the film adhesive composition. Devices contemplated for use in the practice of the present invention include any surface mount component such as, for example, semiconductor die, resistors, capacitors, and the like. Preferably, devices contemplated for use in the practice of invention methods are semiconductor dies. Substrates contemplated for use include metal substrates (e.g., lead frames), organic substrates (e.g., laminates, ball grid arrays, polyamide films), and the like.

[0073] Conditions suitable to cure invention film adhesive compositions comprise subjecting invention film adhesive compositions to a temperature of at least about 60° C but less than about 300° C for about 0.25 up to about 2 minutes. In some such embodiments, the cure temperature is in the range of about 75° C up to about 200 ° C. This rapid, short duration heating can be accomplished in a variety of ways, e.g., with an in-line heated rail, a belt furnace, or the like.

[0074] Alternatively, conditions suitable to cure invention film adhesive compositions comprise subjecting invention film adhesive compositions to a temperature in the range of about 60°C up to about 200°C for a period of about 15 minutes up to about 60 minutes. These conditions can be readily produced in a variety of ways, such, for example, by placing invention film adhesive compositions in a curing oven.

[0075] In still other embodiments, conditions suitable to cure invention film adhesive compositions may further comprise subjecting invention film adhesive compositions to a pre-cure at a temperature high enough to increase the viscosity of the liquid adhesive and reduce tackiness but low enough to prevent a complete cure. Such pre-cured adhesive film compositions may then undergo a final cure as described above to give the fully cured adhesive.

[0076] In a still further aspect of the invention, there are provided methods for adhesively attaching at least two semiconductor dice to a substrate in a stacked arrangement comprising curing a sufficient quantity of an invention adhesive composition positioned between the substrate and each of the die.

[0077] In yet another aspect of the present invention, there are provided assemblies comprising a first article permanently adhered to a second article by a sufficient quantity of an invention adhesive composition.

[0078] The invention will now be described in greater detail by reference to the following non-limiting example.

EXAMPLE

[0079] An adhesive composition according to the present invention was prepared as follows. Invention Film Adhesive Composition 1 was prepared using the styrene-butadiene block copolymer KRATON^{TM} D-1102 as the thermoplastic elastomeric component. Octadecylmaleimide and X-BMI (X-BMI is the 1,20-bismaleimido derivative of 10,11-dioctyl-eicosane) were employed as macromonomers. The maleimides used in the following invention film adhesive compositions were prepared according to the procedure set forth in U.S. Patent No. 5,973,166, the entire contents of which are incorporated by reference herein.

Invention Film Adhesive Composition 1

1.	Octadecylmaleimide	1.0 g
2.	KRATON^{TM} D-1102	2.5 g
3.	X-BMI	1.5 g
4.	Ricon 130[1]	0.2 g
5.	Silane coupling agent[2]	0.2 g
6.	Dicumyl peroxide	0.05 g
7.	Xylene	5.0 g
8.	TEFLON^{TM} filler	6.9 g

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1. Polybutadiene 20 % grafted with maleic anhydride (Sartomer)
2. Proprietary silane-containing coupling agent.

[0080] Preparation of Film Adhesive Composition 1 began by dissolving octadecylmaleimide in xylene. KRATON was added to this solution and allowed to dissolve completely before the remaining components were added.

[0081] A film of Invention Film Adhesive Composition 1 was cast onto a glass substrate and dried overnight. A silicon die was then placed onto the film, and the film-coated substrate was heated to 80°C for 1 to 3 seconds. This assembly was finally cured at 185°C for 30 minutes.

[0082] The film adhesive compositions were tested for room temperature die shear and hot die shear on a calibrated Dage 2400 die shear tester. The results for Invention Film Adhesive Composition 1 are shown below in Table 1, compared to QMI536, a non-film adhesive formulation (prepared according to U.S. Patent No. 5,717,034) comprising the same maleimides as employed for the preparation of Invention Film Adhesive Composition 1. Also included in Table 1 are die shear values after the cured compositions were subjected to 85°C/85% humidity for 24 hrs.

Table 1

	Room Temperature Die Shear (lbs)	**Hot Die Shear (245°C) (lbs)**
QMI536, initial	59.1	24.4
Invention Film Adhesive Composition 1, initial	88.9	25.9
QMI536, 24 hrs. 85/85	52.6	23.9
Invention Film Adhesive Composition 1, 24 hrs. 85/85	79.6	24.6

[0083] The results shown above demonstrate that Invention Film Adhesive Composition 1 has superior adhesive strength compared to an analogous non-film forming composition. .

CLAIMS

WHAT IS CLAIMED IS:

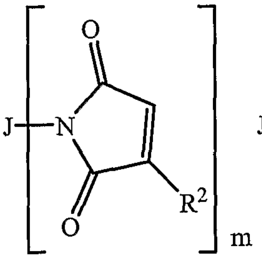
1. An adhesive composition comprising at least one thermoplastic elastomer, at least one macromonomer having at least one unit of ethylenic unsaturation, and at least one cure initiator,

wherein the macromonomer is selected from the group consisting of maleimides, nadimides, itaconimides, allylated amides, and vinyl compounds.

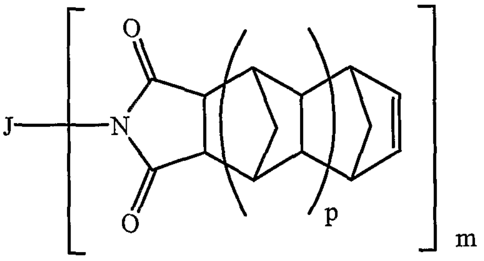
2. An adhesive composition according to claim 1, wherein the composition is capable of curing at a temperature in the range of about 60°C up to about 300°C in a period of time of about 0.25 minutes up to about 2 minutes.

3. An adhesive composition according to claim 1, wherein the macromonomer is a maleimide, a nadimide, an itaconimide, or a mixture of any two or more thereof.

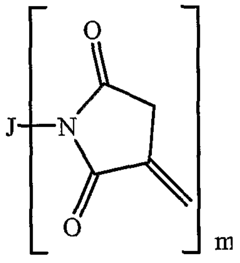
4. An adhesive composition according to claim 3, wherein the maleimide nadimides and itaconimide have, respectively, the following structures, **I**, **II**, and **III**:



(I)



(II)



(III)

wherein:

$m = 1\text{-}15$,

$p = 0\text{-}15$,

each R^2 is independently selected from hydrogen or lower alkyl, and

J is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

5. An adhesive composition according to claim 4, wherein J is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, $-S(O)_2-$, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

6. An adhesive composition according to claim 4, wherein

m = 1-6,
p = 0-6, and
J is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$;

(c) a polyalkylene oxide having the structure:

$[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

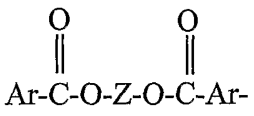
each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

(d) aromatic groups having the structure:



$$Ar-\overset{\displaystyle O}{\overset{\|}{C}}-O-Z-O-\overset{\displaystyle O}{\overset{\|}{C}}-Ar-$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

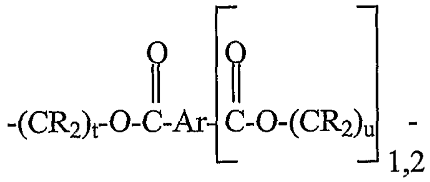
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$-[(CR_2)_r-O-]_q-(CR_2)_s-$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

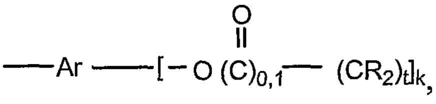
(e) di- or tri-substituted aromatic moieties having the structure:



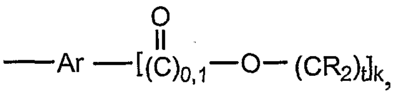
$$-(CR_2)_t-O-\overset{O}{\overset{\|}{C}}-Ar-\left[\overset{O}{\overset{\|}{C}}-O-(CR_2)_u\right]_{1,2}-$$

wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

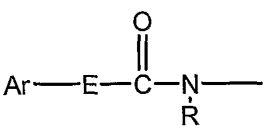
(f) aromatic groups having the structure:



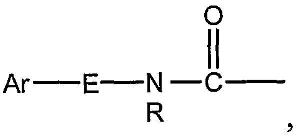
$$-Ar-[-O(\overset{O}{\overset{\|}{C}})_{0,1}-(CR_2)_t]_k,$$



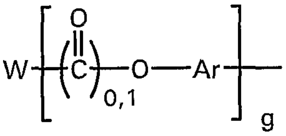
$$-Ar-[(\overset{O}{\overset{\|}{C}})_{0,1}-O-(CR_2)_t]_k,$$



$$Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-\ ,$$

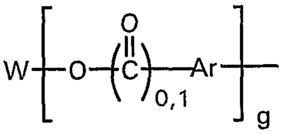


$$Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-\ ,$$



$$W\left[(\overset{O}{\overset{\|}{C}})_{0,1}-O-Ar\right]_g$$

or



$$W\left[O-(\overset{O}{\overset{\|}{C}})_{0,1}-Ar\right]_g$$

wherein:

each R is independently defined as above,

t = 2-10,

k = 1, 2 or 3,

g = 1 up to about 50,

each Ar is as defined above,

E is –O- or -NR^5-, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1-10$,

$e = 1-10$, and

$f = 1-50$; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1-10$,

$s = 1-10$, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

$R^7-U-C(O)-NR^6-R^8-NR^6-C(O)-(O-R^8-O-C(O)-NR^6-R^8-NR^6-C(O))_v-U-R^8-$

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or –$P(L)_{1,2}$- wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

$v = 0-50$;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

7. An adhesive composition according to claim 6, wherein J is of sufficient length to render liquid the maleimide, nadimide, or itaconimide.

8. An adhesive composition according to claim 6, wherein m = 1, 2 or 3, and J is a branched chain alkyl, alkylene or alkylene oxide of sufficient length and branching to render liquid the maleimide, nadimide, itaconimide or combinations of two or more thereof.

9. An adhesive composition according to claim 1, wherein the macromonomer is a vinyl compound.

10. An adhesive composition according to claim 9, wherein the vinyl compound has the following structure:

$$Y\left(Q_{0,1}-CR=CHR\right)_q$$

wherein:

q is 1, 2 or 3,

each R is independently selected from hydrogen or lower alkyl,

each Q is independently selected from –O-, -O-C(O)-, -C(O)- or -C(O)-O-, and

Y is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

11. An adhesive composition according to claim 10, wherein Y is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, -S(O)$_2$-, -O-S(O)$_2$-, -O-S(O)$_2$-O-, -O-S(O)$_2$-NR-, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-,

-NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

12. An adhesive composition according to claim 10, wherein Y is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

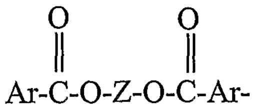
(c) a polyalkylene oxide having the structure:

$[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,
$r = 1\text{-}10$,
$s = 1\text{-}10$, and
f is as defined above;

(d) aromatic groups having the structure:



$$\mathrm{Ar{-}\overset{O}{\overset{\|}{C}}{-}O{-}Z{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar{-}}$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

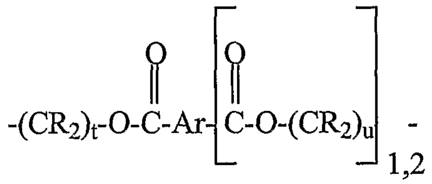
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$-[(CR_2)_r\text{-}O\text{-}]_q\text{-}(CR_2)_s\text{-}$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

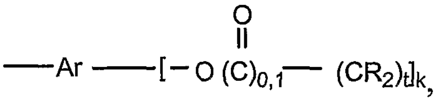
(e) di- or tri-substituted aromatic moieties having the structure:



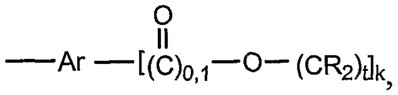
$$\mathrm{-(CR_2)_t{-}O{-}\overset{O}{\overset{\|}{C}}{-}Ar{-}\left[\overset{O}{\overset{\|}{C}}{-}O{-}(CR_2)_u\right]_{1,2}{-}}$$

wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

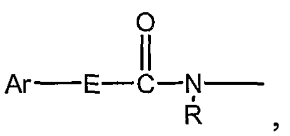
(f) aromatic groups having the structure:



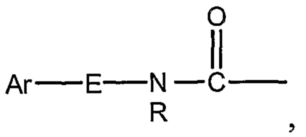
$$\mathrm{-Ar-[-O\,(\overset{O}{\overset{\|}{C}})_{0,1}-(CR_2)_t]_k,}$$



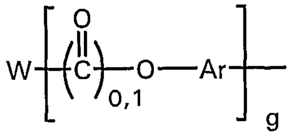
$$\mathrm{-Ar-[(\overset{O}{\overset{\|}{C}})_{0,1}-O-(CR_2)_t]_k,}$$



$$\mathrm{Ar-E-\overset{O}{\overset{\|}{C}}-\underset{R}{N}-,}$$

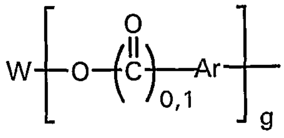


$$\mathrm{Ar-E-\underset{R}{N}-\overset{O}{\overset{\|}{C}}-,}$$



$W\left[\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-O-Ar\right]_g$

or



$W\left[O-\left(\overset{O}{\overset{\|}{C}}\right)_{0,1}-Ar\right]_g$

wherein:

each R is independently defined as above,

$t = 2\text{-}10$,

$k = 1, 2$ or 3,

$g = 1$ up to about 50,

each Ar is as defined above,

E is –O- or $-NR^5-$, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$; or

(iii) a polyalkylene oxide having the structure: $-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

$R^7\text{-U-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O)-(O-R}^8\text{-O-C(O)-NR}^6\text{-R}^8\text{-NR}^6\text{-C(O))}_v\text{-U-R}^8\text{-}$

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or $-P(L)_{1,2}-$ wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

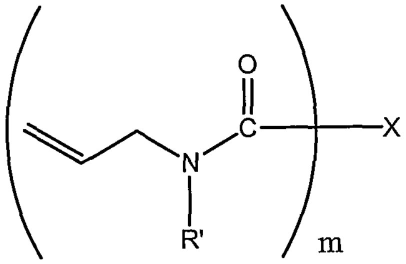
$v = 0\text{-}50$;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

13. An adhesive composition according to claim 1, wherein the macromonomer is an allylated amide.

14. An adhesive composition according to claim 13, wherein the allylated amide has the following structure:



wherein:

R' is hydrogen, C_1 up to about C_{18} alkyl or oxyalkyl, allyl, aryl, or substituted aryl,

m is 1-6, and

X is is a monovalent or a polyvalent moiety comprising organic or organosiloxane radicals, and combinations of two or more thereof.

15. An adhesive composition according to claim 13, wherein, X is a monovalent or polyvalent radical selected from the group consisting of hydrocarbyl, substituted hydrocarbyl, heteroatom-containing hydrocarbyl, substituted heteroatom-containing hydrocarbyl, hydrocarbylene, substituted hydrocarbylene, heteroatom-containing hydrocarbylene, substituted heteroatom-containing hydrocarbylene, polysiloxane, polysiloxane-polyurethane block copolymer, and combinations of two or more thereof, optionally containing one or more linkers selected from the group consisting of a covalent bond, -O-, -S-, -NR-, -O-C(O)-, -O-C(O)-O-, -O-C(O)-NR-, -NR-C(O)-, -NR-C(O)-O-, -NR-C(O)-NR-, -S-C(O)-, -S-C(O)-O-, -S-C(O)-NR-, -S(O)-, $-S(O)_2-$, $-O-S(O)_2-$, $-O-S(O)_2-O-$, $-O-S(O)_2-NR-$, -O-S(O)-, -O-S(O)-O-, -O-S(O)-NR-, -O-NR-C(O)-, -O-NR-C(O)-O-, -O-NR-C(O)-NR-, -NR-O-C(O)-, -NR-O-C(O)-O-, -NR-O-C(O)-NR-, -O-NR-C(S)-, -O-NR-C(S)-O-, -O-NR-C(S)-NR-, -NR-O-C(S)-, -NR-O-C(S)-O-, -NR-O-C(S)-NR-, -O-C(S)-, -O-C(S)-O-, -O-C(S)-NR-, -NR-C(S)-, -NR-C(S)-O-, -NR-C(S)-NR-, $-S-S(O)_2-$, $-S-S(O)_2-O-$, $-S-S(O)_2-NR-$, -NR-O-S(O)-, -NR-O-S(O)-O-, -NR-O-S(O)-NR-, $-NR-O-S(O)_2-$, $-NR-O-S(O)_2-O-$, $-NR-O-S(O)_2-NR-$, -O-NR-S(O)-, -O-NR-S(O)-O-, -O-NR-S(O)-NR-, $-O-NR-S(O)_2-O-$, $-O-NR-S(O)_2-NR-$, $-O-NR-S(O)_2-$, $-O-P(O)R_2-$, $-S-P(O)R_2-$, $-NR-P(O)R_2-$, wherein each R is independently hydrogen, alkyl or substituted alkyl, and combinations of any two or more thereof.

16. An adhesive composition according to claim 13, wherein X is

(a) saturated straight chain alkyl or branched chain alkyl, optionally containing optionally substituted aryl moieties as substituents on the alkyl chain or as part of the backbone of the alkyl chain, and wherein the alkyl chains have up to about 20 carbon atoms;

(b) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,
each R^4 is independently hydrogen, lower alkyl or aryl,
$d = 1\text{-}10$,
$e = 1\text{-}10$, and
$f = 1\text{-}50$;

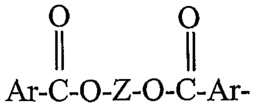
(c) a polyalkylene oxide having the structure:

$$[(CR_2)_r-O-]_f-(CR_2)_s-$$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,
$r = 1\text{-}10$,
$s = 1\text{-}10$, and
f is as defined above;

(d) aromatic groups having the structure:



$$Ar-\overset{\overset{\displaystyle O}{\|}}{C}-O-Z-O-\overset{\overset{\displaystyle O}{\|}}{C}-Ar-$$

wherein each Ar is a monosubstituted, disubstituted or trisubstituted aromatic or heteroaromatic ring having in the range of 3 up to 10 carbon atoms, and Z is:

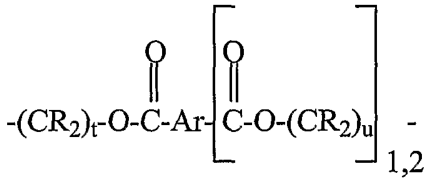
(i) saturated straight chain alkylene or branched chain alkylene, optionally containing saturated cyclic moieties as substituents on the alkylene chain or as part of the backbone of the alkylene chain, or

(ii) polyalkylene oxides having the structure:

$$-[(CR_2)_r-O-]_q-(CR_2)_s-$$

wherein each R is independently defined as above, r and s are each defined as above, and q falls in the range of 1 up to 50;

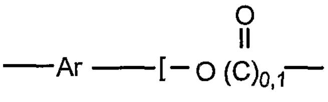
(e) di- or tri-substituted aromatic moieties having the structure:



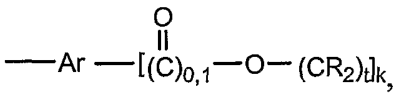
$$-(CR_2)_t-O-\overset{\overset{O}{\|}}{C}-Ar-\left[\overset{\overset{O}{\|}}{C}-O-(CR_2)_u\right]_{1,2}-$$

wherein each R is independently defined as above, t falls in the range of 2 up to 10, u falls in the range of 2 up to 10, and Ar is as defined above;

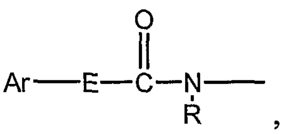
(f) aromatic groups having the structure:



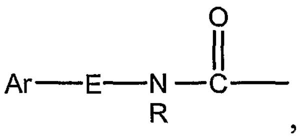
$$-Ar-[-O(\overset{\overset{O}{\|}}{C})_{0,1}-(CR_2)_t]_k,$$



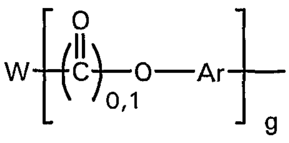
$$-Ar-[(\overset{\overset{O}{\|}}{C})_{0,1}-O-(CR_2)_t]_k,$$



$$Ar-E-\overset{\overset{O}{\|}}{C}-\underset{R}{N}-,$$

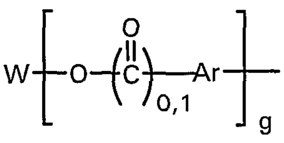


$$Ar-E-\underset{R}{N}-\overset{\overset{O}{\|}}{C}-,$$



$$W\left[(\overset{\overset{O}{\|}}{C})_{0,1}-O-Ar-\right]_g$$

or



$$W\left[-O-(\overset{\overset{O}{\|}}{C})_{0,1}-Ar-\right]_g$$

wherein:

each R is independently defined as above,

t = 2-10,

$k = 1, 2$ or 3,

$g = 1$ up to about 50,

each Ar is as defined above,

E is –O- or $-NR^5-$, wherein R^5 is hydrogen or lower alkyl;

and

W is

(i) straight or branched chain alkyl, alkylene, oxyalkylene, alkenyl, alkenylene, oxyalkenylene, ester, or polyester,

(ii) a siloxane having the structure: $-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-$, $-(C(R^3)_2)_d-C(R^3)-C(O)O-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-O(O)C-(C(R^3)_2)_e-$, or $-(C(R^3)_2)_d-C(R^3)-O(O)C-(C(R^3)_2)_d-[Si(R^4)_2-O]_f-Si(R^4)_2-(C(R^3)_2)_e-C(O)O-(C(R^3)_2)_e-$ wherein:

each R^3 is independently hydrogen, alkyl or substituted alkyl,

each R^4 is independently hydrogen, lower alkyl or aryl,

$d = 1\text{-}10$,

$e = 1\text{-}10$, and

$f = 1\text{-}50$; or

(iii) a polyalkylene oxide having the structure:

$-[(CR_2)_r-O-]_f-(CR_2)_s-$

wherein:

each R is independently hydrogen, alkyl or substituted alkyl,

$r = 1\text{-}10$,

$s = 1\text{-}10$, and

f is as defined above;

optionally containing substituents selected from hydroxy, alkoxy, carboxy, nitrile, cycloalkyl or cycloalkenyl;

(g) a urethane group having the structure:

R^7-U-C(O)-NR^6-R^8-NR^6-C(O)-(O-R^8-O-C(O)-NR^6-R^8-NR^6-C(O))$_v$-U-R^8-

wherein:

each R^6 is independently hydrogen or lower alkyl;

each R^7 is independently an alkyl, aryl, or arylalkyl group having 1 to 18 carbon atoms;

each R^8 is an alkyl or alkyloxy chain having up to about 100 atoms in the chain, optionally substituted with Ar;

U is -O-, -S-, -N(R)-, or –P(L)$_{1,2}$- wherein R as defined above, and wherein each L is independently =O, =S, -OR or -R; and

$v = 0\text{-}50$;

(h) polycyclic alkenyl; or

(i) mixtures of any two or more thereof.

17. An adhesive composition according to claim 1, wherein the thermoplastic elastomer is the polymerization or copolymerization product of optionally substituted olefin monomers and/or optionally substituted conjugated diene monomers.

18. An adhesive composition according to claim 1, wherein the thermoplastic elastomer is a block copolymer.

19. An adhesive composition according to claim 18, wherein the block copolymer has at least one unit of the general formula (A-B), or (A-B-A), wherein A is a non-elastomeric polymer block and B is an elastomeric polymer block.

20. An adhesive composition according to claim 1, wherein the thermoplastic elastomer is present in the range of about 10 wt % up to about 95 wt %, the macromonomer is present in the range of about 5 wt % up to about 90 wt %, and the cure initiator is present in the range of about 0.5 wt % up to about 2.0 wt %, wherein wt % is based on total weight of the composition.

21. An adhesive composition according to claim 20, wherein the macromonomer is present in the range of about 10 wt % up to about 80 wt %, wherein wt % is based on total weight of the composition.

22. An adhesive composition according to claim 1, further comprising a coupling agent.

23. An adhesive composition according to claim 22, wherein the coupling agent is present in the range of about 0.2 wt % up to about 5 wt %, wherein wt % is based on total weight of the composition.

24. An adhesive composition according to claim 1, further comprising a filler.

25. An adhesive composition according to claim 24, wherein the filler is conductive.

26. An adhesive composition according to claim 25, wherein the filler is electrically conductive.

27. An adhesive composition according to claim 25, wherein the filler is thermally conductive.

28. An adhesive composition according to claim 24, wherein the filler is non-conductive.

29. An adhesive composition according to claim 28, wherein the filler is a perfluorinated hydrocarbon polymer.

30. An adhesive composition according to claim 24, wherein the filler is present in the range of about 1 wt % up to about 95 wt %, wherein wt % is based on total weight of the composition.

31. An adhesive composition comprising in the range of about 5 wt % up to about 90 wt % thermoplastic elastomer, in the range of about 5 wt % up to about 90 wt % macromonomer, in the range of about 0.5 wt % up to about 2.0 wt % cure initiator, in the

range of about 0.5 wt % up to about 5 wt % coupling agent, and in the range of about 1 wt % up to about 95 wt % filler, wherein wt % is based on total weight of the composition.

32. A method for adhesively attaching a device to a substrate, the method comprising subjecting an adhesive composition according to claim 1 positioned between the substrate and the device to conditions suitable to cure the adhesive composition.

33. A method according to claim 32, wherein the device is a semiconductor die.

34. A method for adhesively attaching at least two semiconductor dice to a substrate in a stacked arrangement, the method comprising curing an adhesive composition according to claim 1 positioned between the substrate and each of the dice.

35. An assembly comprising a first article permanently adhered to a second article by a cured aliquot of the adhesive composition according to claim 1.

36. An adhesive composition according to claim 1, wherein the macromonomer comprises one or more maleimides, nadimides, or itaconimides attached to an alkyl or alkylene linkage capable of curing at a temperature in the range of about 60°C up to about 300°C in a period of time of about 0.25 minutes up to about 2 minutes.

37. An adhesive composition according to claim 36, wherein the alkyl or alkylene linkage is of sufficient length and branching to render liquid the macromonomer.

38. An assembly comprising a substrate and plurality of semiconductor dice positioned on the substrate in a stacked arrangement, wherein each of the semiconductor die is adhered to either the substrate or another die by a cured aliquot of the adhesive composition according to claim 1, wherein the composition comprises a maleimide, a nadimide, or an itaconimide macromonomer.

39. An adhesive composition comprising at least one macromonomer having at least one unit of ethylenic unsaturation, at least one thermoplastic elastomer co-curable with the at least one macromonomer, and at least one cure initiator, which when dispensed between a device and a substrate and cured for 2 minutes at 200°C, provides a

room temperature die shear of about 90 lbs, wherein the at least one macromonomer is a maleimide, a nadimide, an itaconimide, or mixture of any two or more thereof.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US03/09753

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 255/00, 257/00, 8/32, 120/56, 26/02: C08J 3/26; C08G 73/00
US CL : 525/193, 92G, 280, 282: 526/259, 303.1, 307.2, 305, 310, 312
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 525/193, 92G, 280, 282: 526/259, 303.1, 307.2, 305, 310, 312

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Continuation Sheet

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	*Citation of document, with indication, where appropriate, of the relevant passages*	Relevant to claim No.
X	US 5,717,034 A (DERSHEM et al) 10 February 1998 (10.02.1998), column 2, lines 16-67 and column 3, lines 1-37	1-8, 17, 22, 24, 32-39.
X	EP 0 970 946 A2 (NATIONAL STARCH AND CHEMICAL INVESTMENT HOLDING CORPORATION) 12 January 2000 (12.01.200), entire document, especially, page 3, formula for the allylated amide compounds, page 27 for the vinyl compounds, page 34 for the compounds containing a maleimide moiety, page 27 for an initiator, page 10, line 44 for a coupling agent, page 10, lines 50-53 for a thermoplastic material.	1-39

☐ *Further documents are listed in the continuation of Box C.* ☐ *See patent family annex.*

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search
13 June 2003 (13.06.2003)

Date of mailing of the international search report
21 JUL 2003

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450
Facsimile No. (703)305-3230

Authorized officer
James Seidleck
Telephone No. 703-308-0661

Form PCT/ISA/210 (second sheet) (July 1998)

Continuation of B. FIELDS SEARCHED Item 3:
WEST
macromonomer: maleimide, allylated amide, methacrylate, grafting, adhesive