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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 August 2009 (13.08.2009)

PCT

(10) International Publication Number
WO 2009/099436 A1

(51) International Patent Classification:
C08F 12/28 (2006.01) *C08K 3/00* (2006.01)
C08L 33/24 (2006.01)

(21) International Application Number:
PCT/US2008/052983

(22) International Filing Date:
5 February 2008 (05.02.2008)

(25) Filing Language: English

(26) Publication Language: English

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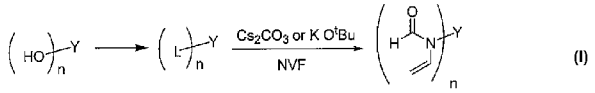
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

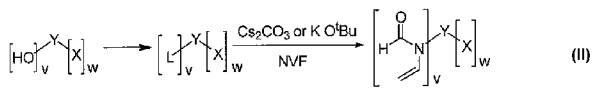
Published:

— *with international search report (Art. 21(3))*

(54) **Title**: CURABLE COMPOSITIONS PREPARED FROM MULTIFUNCTIONAL AND HYBRID N-VINYLFORMAMIDE COMPOUNDS



(I)



(II)

(57) **Abstract**: A curable composition comprises a multi-functional N-vinylformamide compound and/or a hybrid N-vinylformamide compound and an initiator, optionally, an additional curable compound; and optionally, a filler. The hybrid N-vinylformamide compound has a second reactive functionality in addition to N-vinylformamide functionality selected from the group consisting of acrylate, methacrylate, cyanoacrylate, maleimide, cinnamyl, maleate, fumarate, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester, vinyl ether, and combinations of these. These multi-functional and hybrid N-vinylformamide compounds are prepared through an alkylation procedure employing either cesium carbonate or potassium t-butoxide as base to deprotonate, from the nitrogen atom, the hydrogen atom bonded to the nitrogen atom. Reaction schemes include: formulae (I) and (II) in which n = 2 to 100; v is 1 to 100; w is 1 to 10; Y is an aliphatic or aromatic hydrocarbon {including those with heteroatoms); X is a second reactive functionality; and L is a leaving group; and each L and X present can be the same or different.

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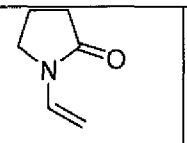
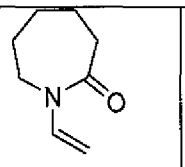
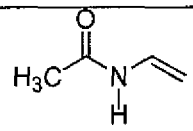
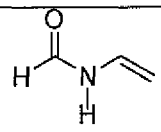
CURABLE COMPOSITIONS PREPARED FROM MULTIFUNCTIONAL AND HYBRID N-VINYLFORMAMIDE COMPOUNDS

BACKGROUND OF THE INVENTION

[0001] This invention relates to a curable composition comprising an N-vinylformamide compound and an initiator.

[0002] N-vinylamides are electron rich monomers, of which commonly known cyclic N-vinylamides are N-vinylpyrrolidinone (NVP) and N-vinyl-caprolactam (NVCL), and commonly known acyclic N-vinylamides are N-vinylacetamide (NVA) and N-vinylformamide (NVF).

[0003] The structures for these compounds are depicted here:

			
NVP	NVCL	NVA	NVF

[0004] The synthesis of N-vinylamides can be accomplished through the vinylation reaction of amide through addition to acetylene, or through a trans-vinylation reaction with vinyl ether or vinyl acetate. N-vinylamides can also be prepared by cracking a vinylamide precursor. The synthesis of multifunctional N-vinylamide derivatives can proceed through a C-alkylation reaction using a lithium base, or through the use of an N-alkylation reaction requiring the use of NaH, which is typically not preferred in industrial manufacturing environments. In another method, NVA can be de-protonated by NaOH in the presence of a phase transfer catalyst to create difunctional monomers that can be used to make polymers with cyclic backbones. Michael addition of N-vinylformamides to acrylonitrile and to acrylates and methacrylates has been used for the synthesis of N-cyanoethyl-N-vinyl-formamide and 3-(N-vinylformamido)propionates, respectively. In both cases, the synthesis was focused on monofunctional substituted N-

vinylamides. The synthetic routes disclosed above relate to either multifunctional N-vinyl-acetamide or N-vinylpyrrolidone, or to monofunctional N-vinylformamides.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Figure 1 is a DSC curing profile of the polymerization of Acrylate I and N-vinylformamide II with VAZO-52 initiator. Figure 2 is a DSC curing profile of the photopolymerization of hexanediol diacrylate (HDDA) and N-vinylformamide II. Figure 3 is a DSC curing profile of the photopolymerization of BMI I and N-vinylformamide II.

SUMMARY OF THE INVENTION

[0006] This invention is a curable composition comprising a multi-functional N-vinylformamide compound and/or a hybrid N-vinylformamide compound; an initiator; optionally, an additional compound (which additional compound can be a monomer, oligomer, or polymer) reactive with the multi-functional or hybrid N-vinylformamide compound; and optionally, a filler.

[0007] The multi-functional N-vinylformamide compounds are prepared through an alkylation reaction between an aliphatic or aromatic hydrocarbon having one or more leaving groups and N-vinylformamide monomer (the monomer starting material, hereinafter "NVF"), employing a base, such as cesium carbonate or potassium t-butoxide, to deprotonate the hydrogen atom bonded to the nitrogen atom on NVF. Other strong bases can be used in this process.

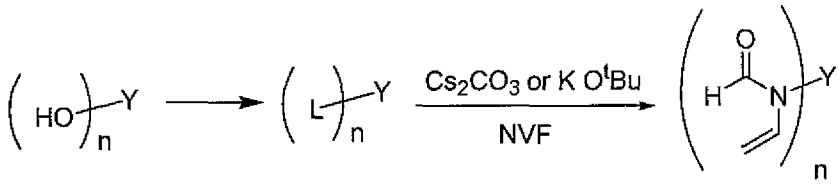
DETAILED DESCRIPTION OF THE INVENTION

[0008] As used in this specification and the claims, a multifunctional N-vinylformamide compound means a compound having at least two N-vinylformamide functionalities and no other reactive functionalities, and a hybrid N-vinylformamide compound means a compound having at least one N-vinylformamide functionality and at least one other reactive functionality. A reactive functionality is one that can react and form a covalent bond with another chemical functionality. In one embodiment, the other reactive functionality is selected from the group consisting of acrylate, methacrylate, cyanoacrylate, maleimide, cinnamyl, maleate, fumarate, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester, vinyl ether, and combinations of these.

[0009] The process for the synthesis of the multifunctional N-vinylformamide compounds and the hybrid N-vinylformamide compounds uses an alkylation procedure in which N-vinyl-formamide is substituted for a leaving group on an aliphatic or aromatic hydrocarbon employing either cesium carbonate or potassium t-butoxide as a base to deprotonate the hydrogen atom

from the nitrogen atom in the starting NVF. Leaving groups well known to those skilled in the art include, but are not limited to, halides, mesylates, and tosylates. The amount of Cs_2CO_3 or KO^tBu used will be sufficient to generate an equimolar amount of nucleophile (after deprotonation of the NVF) to the electrophile (leaving group). In the absence of an excess of NVF, this amount would be equimolar to the amount of NVF. When an excess of NVF is used, the amount of Cs_2CO_3 or KO^tBu will be less than an equimolar amount to the NVF. The choice of such stoichiometry is within the expertise of those skilled in the art.

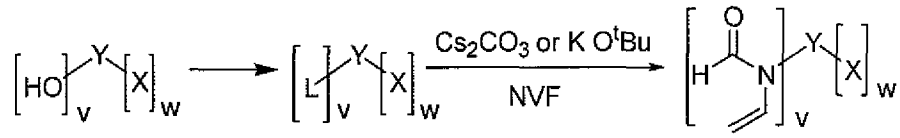
[0010] The synthetic reaction for a multifunctional N-vinylformamide compound proceeds according to the scheme:



in which n is 2 to 100; Y is an aliphatic or aromatic hydrocarbon (including those with heteroatoms); and L is a leaving group. In various embodiments, n is 2 to 25, n is 2 to 10, and n is 2 to 5. The L leaving group is substituted according to well-known reactions for the hydroxyl group on the starting compound, and the resulting compound reacted with an excess of N-vinyl formamide in the presence of Cs_2CO_3 or KO^tBu to form the multifunctional N-vinylformamide compound. Typical reaction conditions are those disclosed in the examples.

[0011] An alternative process for the synthesis of the multifunctional N-vinylformamide compound having at least two N-vinylformamide functionalities comprises reacting an aliphatic or aromatic hydrocarbon having at least one leaving group and at least one N-vinyl-formamide functionality with NVF in the presence of Cs_2CO_3 or KO^tBu.

[0012] This alternative process is also the process used for the synthesis of the hybrid N-vinyl-formamide compound. In the hybrid case the reaction proceeds according to the following scheme, in which L and Y are same as described above, and X is a reactive functionality. A halide, mesylate or tosylate leaving group is substituted for the hydroxyl group on the starting compound using typical reactions known in the art, and the resulting compound reacted with N-vinyl formamide in the presence of Cs_2CO_3 or KO^tBu:



in which v is 1 to 100 and w is 1 to 10. In various embodiments, v is 1 to 25, v is 1 to 10, and v is 1 to 5.

[0013] The X reactive functionality is selected from the group consisting of acrylate, methacrylate, cyanoacrylate, maleimide, cinnamyl, maleate, fumarate, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester, vinyl ether, and combinations of these. Typical reaction conditions are those disclosed in the examples.

[0014] For all of the hybrid N-vinylformamide compounds, each X on the compound can be the same or different; each L on the compound can be the same or different.

[0015] In the above reaction schemes, the conversion of the hydroxyl functionality to a leaving group is known in the art and not part of the inventive process.

[0016] Initiators for curable compositions containing N-vinylformamide compounds are compounds that can produce radical or cationic initiating species, when triggered by heat (thermal initiators) or electromagnetic radiation (photoinitiators). The initiator will be present in an amount of 0.01 to 10% by weight of the total resin.

[0017] Suitable radical thermal initiators include peroxides, such as benzoyl peroxide, lauroyl peroxide, octanoyl peroxide, butyl peroctoate, dicumyl peroxide, acetyl peroxide, para-chlorobenzoyl peroxide and di-t-butyl diperphthalate; 1,1-di-(tert-amyl-peroxy)-cyclohexane; azo compounds such as azoisobutylonitrile, 2,2'-azobispropane, 2,2'-azobis(2-methylbutanenitrile), and m,m'-azoxystyrene. Commercially available azo initiators are those available from Wako Specialty Company, such as those sold under the tradenames VA-044, VA-057, VA-085, V-70, VF-096, V-65, V-601, V-59, V-40, VF-096, V-30, and those available from Akzo Nobel, such as those sold under the tradenames PERKADOX ACCN, PERKADOX AIBN, PERKADOX AMBN-GR, and those available from Dupont, such as those sold under the tradenames VAZO-52, VAZO-64, VAZO-67 and VAZO-88.

[0018] Exemplary radical photoinitiators are disclosed in *Radiation Curing: Science and Technology*, 1992, Plenum Press; New York; S.P. Pappas, Ed. and *Encyclopedia of Polymer*

Science and Engineering, 11, 187, 1988, John Wiley and Sons, New York; H.F. Mark, N.M. Bikales, C.G. Overberger, G. Menges, Eds. One may also select a radical thermal initiator for curing purposes and the exemplary thermal initiators are disclosed in *Principles of Polymerization*, 211, 1991, John Wiley and Sons, New York; G.G. Odian, Ed.

[0019] Suitable cationic photoinitiators are disclosed in *Ionic Polymerizations and Related processes,* 45-60, 1999, Kluwer Academic Publishers; Netherlands; J.E. Puskas et al. (eds.). Preferred cationic photoinitiators include diaryliodonium salts and triarylsulfonium salts. Well known commercially available examples include UV9380C (GE Silicones), PC2506 (Polyset), SR1012 (Sartomer), Rhodorsil 2074 (Rhodia), and UVI-6974 (Dow). Preferred sensitizers for diaryliodonium salts are isopropylthioxanthone (referred to herein as ITX, often sold as a mixture of 2- and 4-isomers) and 2-chloro-4-propoxythioxanthone.

[0020] Suitable cationic thermal initiators, such as thermally generated acids, are also suitable for use where such catalysts, initiators, and curing agents are appropriate. Exemplary catalysts include Brϕnsted acids, Lewis acids, and latent thermal acid generators. Representative examples of Brϕnsted and Lewis acids may be found in literature sources such as Smith, M.B. and March, J. in *March's Advanced Organic Chemistry, Reactions, Mechanisms, and Structures*, 5th Edition, 2001, John Wiley & Sons, Inc., New York, NY. pp. 327-362. Examples of latent thermal acid generators include, but not limited to, diaryliodonium salts, benzylsulfonium salts, phenacylsulfonium salts, N-benzylpyridinium salts, N-benzylpyrazinium salts, N-benzyl-ammonium salts, phosphonium salts, hydrazinium salts, ammonium borate salts, etc.

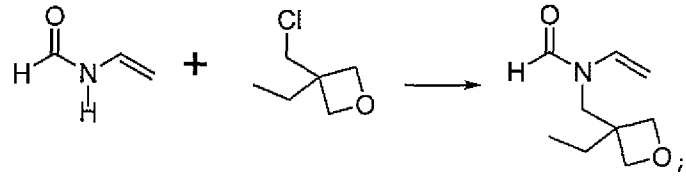
[0021] In another embodiment, the curable composition comprising a multifunctional N-vinylformamide compound and/or a hybrid N-vinylformamide compound, and initiator, will further comprise an additional curable compound reactive with the multifunctional N-vinylformamide compound or hybrid N-vinylformamide compound, which compound can be a monomer, oligomer, or polymer. In various embodiments, the additional curable compound will contain functionality selected from the group consisting of acrylate, methacrylate, maleimide, cyanoacrylate, cinnamyl, maleate, fumarate, maleic anhydride, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester and vinyl ether compounds or resins, and mixtures of those. As needed to progress the reaction, practitioners will understand to include initiators and accelerants as needed.

[0022] Referring to the procedure used in Examples 1, 2, 3 and 4 in this specification, it is

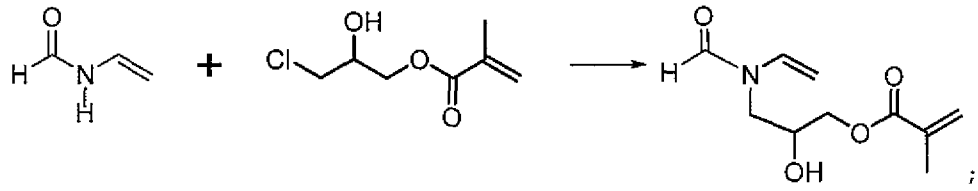
possible to prepare N-vinylformamide compounds that contain at least two N-vinylformamide functionalities per molecule.

[0023] Referring to the procedure used in Examples 6 and 7 in this specification, it is possible to prepare hybrid N-vinylformamide compounds, such as shown in the following exemplary reaction schemes:

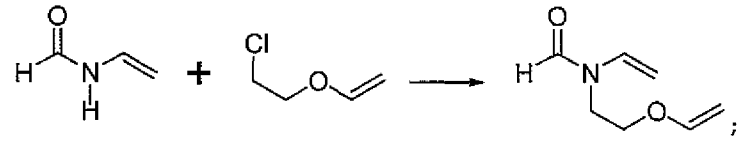
[0024] a compound having both N-vinylformamide and oxetane functionalities, prepared from N-vinyl formamide and chloromethyl-ethyloxetane:



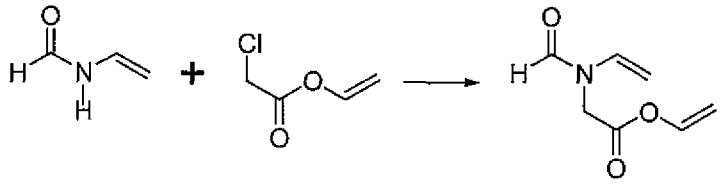
[0025] a compound having both N-vinylformamide and acrylate functionalities, prepared from N-vinyl formamide and 3-chloro-2-hydroxypropyl methacrylate:



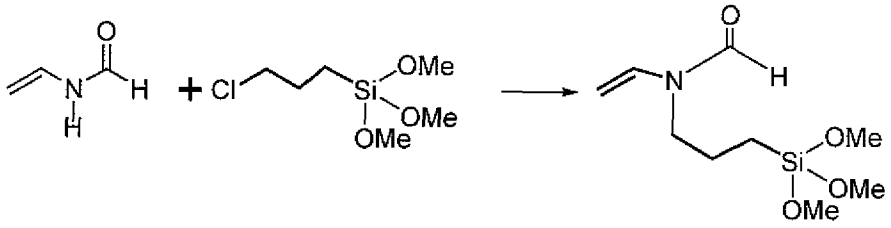
[0026] a compound having both N-vinylformamide and vinyl ether functionalities, prepared from N-vinyl formamide and 2-chloroethyl vinyl ether:



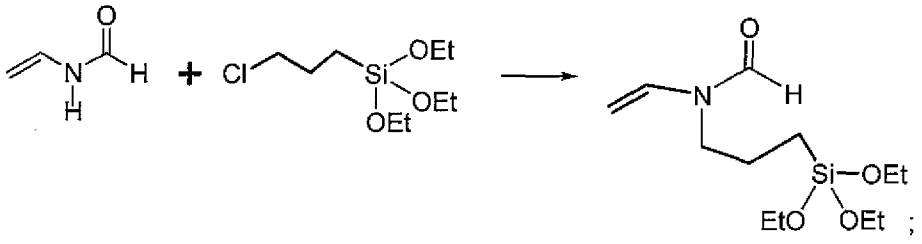
[0027] a compound having both N-vinylformamide and vinyl ester functionalities, prepared from N-vinyl formamide and vinyl chloroacetate:



[0028] a compound having both N-vinylformamide and silane functionalities, prepared from N-vinyl formamide and 3-chloropropyltrimethoxysilane:

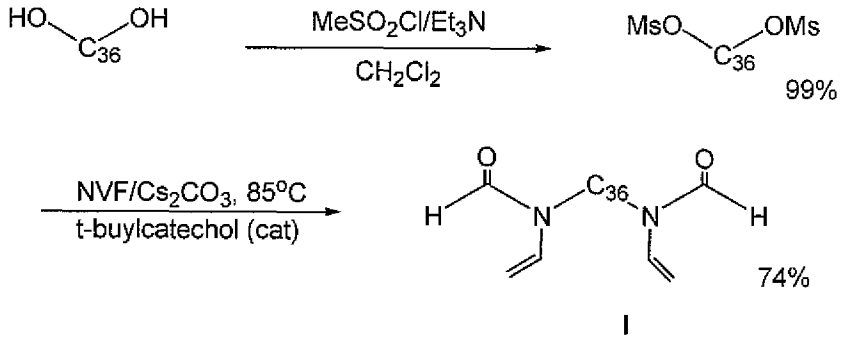


[0029] a compound having both N-vinylformamide and silane functionalities, prepared from N-vinyl formamide and 3-chloropropyltriethoxysilane:



SYNTHETIC EXAMPLES

[0030] **EXAMPLE 1:** SYNTHESIS OF DIFUNCTIONAL N-VINYLFORMAMIDE WITH A C-36 BACKBONE (I)



in which C_{36} is a linear or branched chain hydrocarbon, with or without cyclic moieties, having 36 carbon atoms.

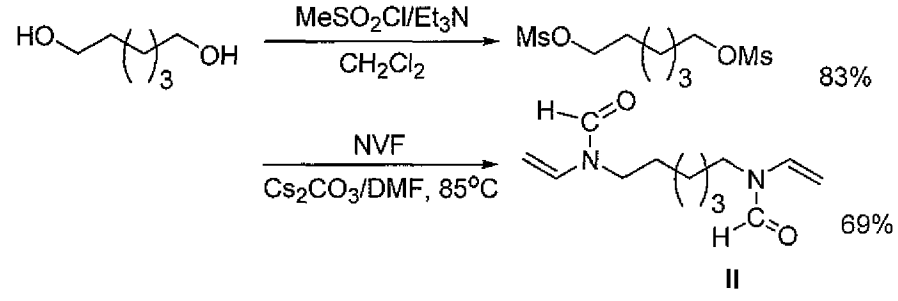
[0031] Preparation of the Mesylate. To a solution of a poly(esterpolyol) (Pripol 2033 from Uniqema) (151g, 0.28mol) in CH_2Cl_2 (1000mL) at 0°C was added triethylamine (118mL, 0.85mol), after which the solution was stirred for 15 minutes. To this mixture was added $MeSO_2Cl$ (48mL, 0.62mol) slowly dropwise over a period of 15 minutes. The mixture was stirred

at the same temperature for one hour and at room temperature for 2.5 hours. CH_2Cl_2 was evaporated off and ethyl acetate (1000mL) was added to the residue. The mixture was washed with water (3×300mL), brine, and dried over anhydrous $MgSO_4$. Solvent evaporation in rotory evaporator followed by removal of residual solvent over Kugelrohr apparatus for three hours furnished the mesylate (189g, 97%). ^1H NMR ($CDCl_3$): δ 0.6-1.8 (69H), 2.95 (6H), 4.1-4.3 (4H). MS (m/z): 694 (M).

[0032] Preparation of N-vinylformamide I. To a solution of NVF (6.08mL, 86.6mmol) in DMF (100mL) were added t-butylcatechol (40mg), and K^{t}OBu (9.7g, 86.4mmol) and the mixture stirred for one hour at room temperature, at which point precipitate was observed. A solution of the mesylate (30g, 43.3mmol) in DMF (25mL) was added slowly dropwise and the resulting mixture was stirred at 85°C for six hours. After cooling to room temperature, ethyl acetate (300mL) was added and the precipitate filtered. The organic layer was washed with water (100mL, 3 times) and brine. Silica gel was added (30g) and the mixture was stirred for one hour, filtered to remove silica gel, and washed with ethyl acetate (100mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated in rotory evaporator and the residual solvent was removed in a Kugelrohr apparatus for three hours at room temperature to afford the desired product (20.5g, 73%). ^1H NMR ($CDCl_3$): δ 0.7-1.8 (69H), 3.4-3.65 (4H), 4.3-4.37 (4H), 6.4-7.3 (2H), 8.1-8.4 (2H). MS (m/z): 642 (M).

[0033] A similar procedure was employed using Cs_2CO_3 in place of K^{t}OBu to give the desired product in 74% yield. ^1H NMR ($CDCl_3$): δ 0.7-1.8 (69H), 3.4-3.65 (4H), 4.3-4.37 (4H), 6.4-7.3 (2H), 8.1-8.4 (2H). MS (m/z): 642 (M).

[0034] EXAMPLE 2. SYNTHESIS OF DIFUNCTIONAL N-VINYLFORMAMIDE WITH A HEXAMETHYLENE BACKBONE (II)



II

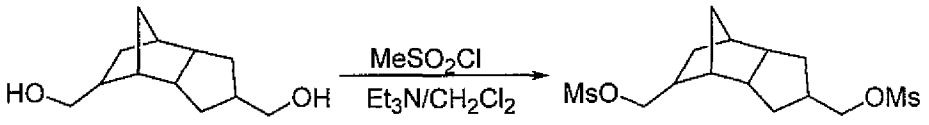
[0035] Preparation of the Mesylate. To a solution of hexanediol (10g, 85mmol) in CH_2Cl_2

(150mL) at 0°C was added triethylamine (30mL, 212mmol) followed by $MeSO_2Cl$ (14.4mL, 186mmol) slowly dropwise. The resulting mixture was stirred at the same temperature for one hour and at room temperature for one hour. CH_2Cl_2 was evaporated and the residue was dissolved in ethyl acetate (250mL) and the organic layer was washed with water several times (to remove the triethylammonium hydrochloride) followed by brine. After solvent evaporation, the residue was dried using Kugelrohr apparatus distillation set up for three hours to give the mesylate (19.3g, 83%). ^1H NMR ($CDCl_3$): δ 1.3-1.8 (8H), 3.0 (6H), 4.1-4.4 (4H).

[0036] Preparation of N-Vinylformamide **II**. To a solution of NVF (12.mL, 175mmol) in DMF (200mL) was added potassium t-butoxide (19.6g, 175mmol) and the mixture stirred for one hour. To this mixture was added hexanediol mesylate (20g, 28.9mmol) in DMF (50mL) and t-butylcatechol (30mg). The resulting mixture was stirred at 85°C for six hours. After cooling to room temperature, ethyl acetate (300mL) was added and the product filtered and washed with ethylacetate (100mL). The filtrate was washed with water (100mL, 3 times) and brine. Silica gel (30g) was added and the mixture stirred for one hour. Silica gel was filtered off and washed with ethyl acetate (100mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated and the product dried in a Kugelrohr apparatus for three hours at room temperature to give the product (15g, 76%). ^1H NMR ($CDCl_3$): δ 1.2-1.8 (8H), 3.3-3.7 (4H), 4.3-4.7 (4H), 6.4-7.3 (2H), 8.1-8.4 (2H). MS (m/z): 224 (M+).

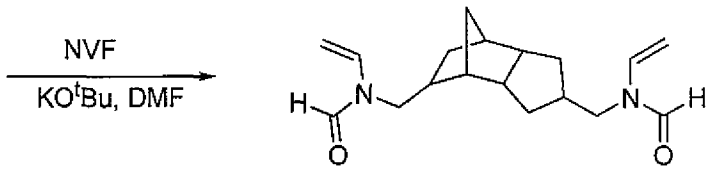
[0037] A similar procedure was employed using Cs_2CO_3 in place of KO^tBu to give the desired product in 69% yield. ^1H NMR ($CDCl_3$): δ 1.2-1.8 (8H), 3.3-3.7 (4H), 4.3-4.7 (4H), 6.4-7.3 (2H), 8.1-8.4 (2H). MS (m/z): 224 (M+).

[0038] EXAMPLE 3. SYNTHESIS OF DIFUNCTIONAL N-VINYLFORMAMIDE WITH A TRICYCLODECANE BACKBONE (**III**)



Tricyclodecanedimethanol

88%



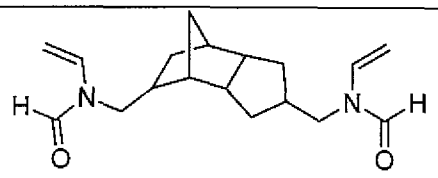
III

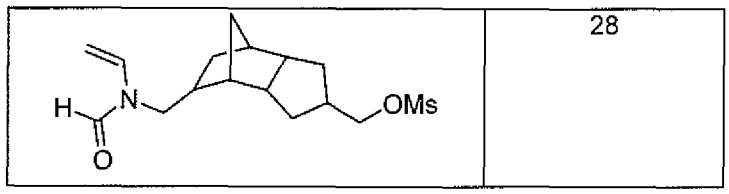
[0039] Preparation of the Mesylate. To a mixture of tricyclodecanedimethanol (21g, 0.1mol) and triethylamine (36mL, 0.26mol) in CH_2Cl_2 (250mL) was added $MeSO_2Cl$ (18.2mL, 0.24mol) at 0°C slowly dropwise. After the addition was complete, the mixture was stirred at the same temperature for one hour and at room temperature for one hour. CH_2Cl_2 was evaporated and water (300mL) was added to the mixture. The product was extracted with ethyl acetate (500mL). The organic layer was washed several times with water to remove the ammonium salts. After drying over anhydrous $MgSO_4$, the solvent was evaporated and the product dried using Kugelrohr distillation set-up to give the mesylate as a colorless solid (33g, 88%). ^1H NMR ($CDCl_3$): δ 1.1-2.4 (14H), 2.6-2.8 (6H), 3.6-3.9 (4H). MS (m/z): 352 (M+).

[0040] Preparation of the N-vinylformamide **III**. To a solution of NVF (4.05mL, 57.7mmol) in DMF (100mL) was added potassium t-butoxide (6.48g, 57.8mmol) and the mixture stirred for one hour. To this mixture was added tricyclodecanedimethanol mesylate (20g, 28.9mmol) in DMF (50mL) and t-butylcatechol (10mg). The resulting mixture was stirred at 120°C for six hours. After cooling to room temperature, ethyl acetate (300mL) was added and the organic layer was washed with water (100mL, 3X) and brine. Silica gel was added (20g) and the mixture stirred for one hour. Silica gel was filtered off and washed with ethyl acetate (100mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated and the product dried in a Kugelrohr apparatus for three hours at room temperature to give the product (20.5g, 73%).

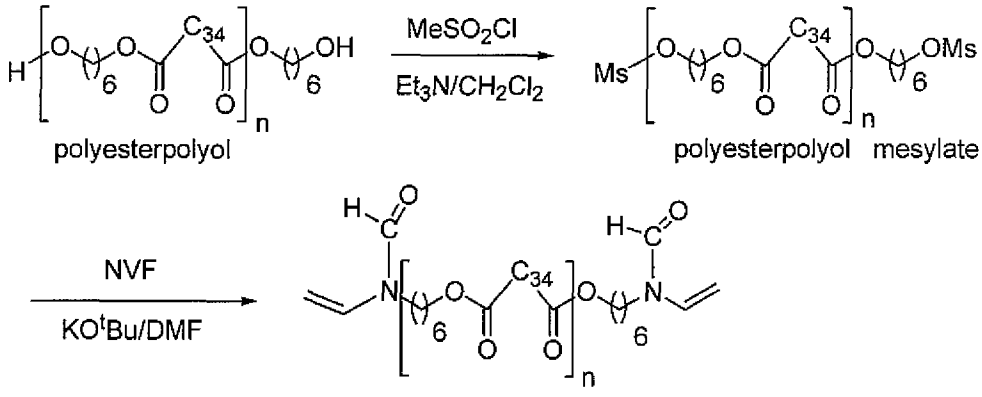
[0041] GC/MS analysis of the product indicated that the product is around 65% pure. Some mono N-vinylformamide compound was also present in the product.

[0042] Component distribution of product

Structure	Percent (area %)
[0043] tricyclodecane-dimethanol	
	65



[0043] EXAMPLE 4. SYNTHESIS OF DIFUNCTIONAL N-VINYLFORMAMIDE WITH A POLYESTERPOLYOL BACKBONE (**IV**)



IV

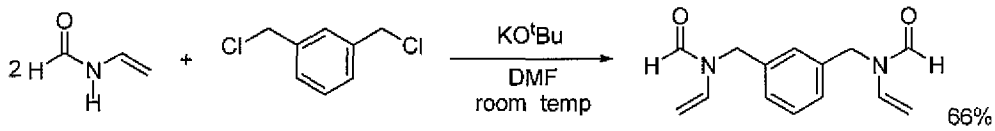
in which C_{34} is a linear or branched hydrocarbon, with or without cyclic moieties, having 34 carbon atoms.

[0044] Preparation of the polyesterpolyol mesylate: To a mixture of polyesterpolyol (sold as Priplast 3196 by Uniqema) (34g, 11.3mol) and triethylamine (6.32mL, 45.3mol) in toluene (200mL) was added $MeSO_2Cl$ (2.63mL, 33.9mmol) at 0°C slowly dropwise. After the addition was complete, the mixture was stirred at room temperature overnight. The mixture was filtered and to the filtrate was added ethyl acetate (200mL). This mixture was washed with water (300mL X 2). To the organic layer was added silica gel (30g) and the mixture was stirred for one hour. Silica gel was filtered and washed with ethyl acetate (100mL). After drying over anhydrous $MgSO_4$, the solvent was evaporated and the product dried using a Kugelrohr distillation set-up to give the mesylate as a colorless solid (30g, 84%). ^1H NMR ($CDCl_3$): δ 0.6-1.7 (m), 2.2(t), 2.95(s), 3.7-4.0(t), 3.95(t), 4.15(t)

[0045] Preparation of the Polyesterpolyol N-vinylformamide **IV:** To a solution of NVF (8.0mL, 113mmol) in DMF (150mL) was added KO^tBu (8.53g, 76mmol). The mixture was stirred at this temperature for two hours at room temperature. t-Butylcatechol (30mg) was added followed by

the polyesterpolyol (Priplast 3196) mesylate (30g, 9.5mmol). The mixture was stirred at 120°C (oil bath temperature) for twelve hours. After cooling to room temperature ethyl acetate (400mL) was added and the precipitate filtered and washed with ethyl acetate (100mL). The organic layer was washed with water (200mL, 3X) and brine. Silica gel was added (30g) and the mixture stirred for one hour. Silica gel was filtered and washed with ethyl acetate (100mL). The organic layer was dried over anhydrous $MgSO_4$, the solvent evaporated and the residual solvent removed using Kugelrohr apparatus for three hours at 50°C to give the product. ^1H NMR ($CDCl_3$): δ 0.6-1.6 (m), 2.0-2.3 (t), 3.2-3.6 (m), 3.7-4.0 (t), 4.2-5.0 (m), 6.3-6.6 (m), 8.2 (s)

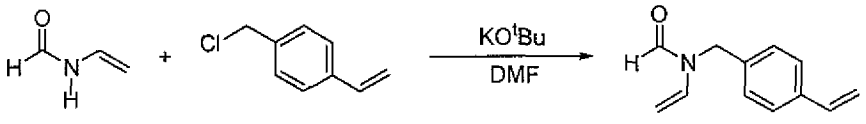
[0046] EXAMPLE 5. SYNTHESIS OF DIFUNCTIONAL N-VINYLFORMAMIDE WITH XYLENE BACKBONE (V)



V

[0047] Into a 500 mL flask was added potassium t-butoxide (0.4mol) followed by DMF (100mL) and NVF (0.4 mol). With stirring, alpha, alpha'-dichloro-m-xylene (0.2mol) was added in small portions to the reaction mixture. The reaction heated up to approximately 100°C. It was allowed to cool to room temperature. Next, water (250mL) was added to the reaction while stirring. The solution was extracted with toluene twice (500mL followed by 250 mL). The toluene solution was combined and extracted with water three times using fresh water (250mL) each time. The organic phase was stored over magnesium sulfate. After filtration and solvent removal, the product was vacuum distilled at 100 °C/200 micron to give 32.2g desired product (66% yield). ^1H NMR ($CDCl_3$): 4.33-4.48 (4H), 4.61-4.74 (4H), 6.58-7.23 (6H), 8.23-8.45 (2H). MS (m/z): 244.

[0048] EXAMPLE 6. SYNTHESIS OF A HYBRID MONOMER WITH BOTH N-VINYLFORMAMIDE AND STYRENE FUNCTIONALITIES (VI)

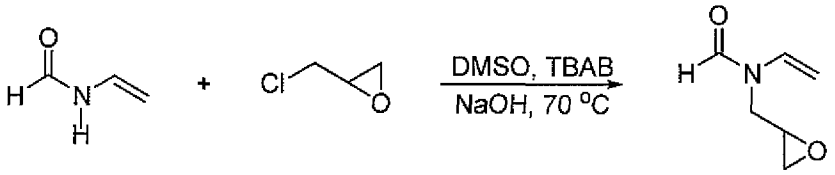


VI

[0049] Into a 500mL flask was added potassium t-butoxide (0.1 mol), N,N-dimethylformamide (DMF) (30 mL), N-vinyl formamide (0.1 mol) and allowed to stir for 20 minutes until clear. 4-Chloromethylstyrene (0.1 mol) was then added and the solution self-heated to 100°C. The

reaction mixture was allowed to cool to room temperature with stirring. The conversions after 10 minutes of addition and after 1.5 hours were found to be the same (by gas chromatography), indicating that the reaction was completed directly after the 4-chloromethyl-styrene addition. After the reaction, water (200 mL) was added to the reaction mixture, and the whole mixture was extracted with toluene (200 mL, 2X). The toluene solutions were combined and extracted with water (200 mL, 3X), and the toluene solvent was removed with a rotary evaporator. The residual toluene and DMF were removed under high vacuum to give the desired product **VI**. ^{1}H NMR ($CDCl_3$): 4.77-4.37 (4H), 5.27-5.20 (1H), 5.77-5.68 (1H), 6.74-6.57 (2H), 7.40-7.14 (4H), 8.30-8.47 (1H). MS (m/z): 187.

[0050] EXAMPLE 7. SYNTHESIS OF A HYBRID MONOMER WITH BOTH N-VINYLFORMAMIDE AND EPOXY FUNCTIONALITIES (**VII**)

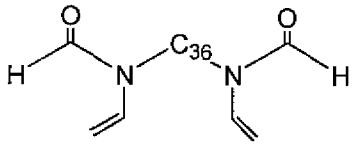


VII

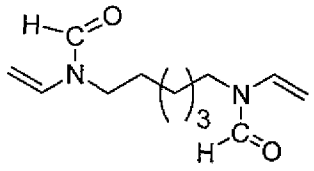
[0051] Into dimethylsulfoxide (DMSO) (50mL) was added NVF (0.1mol), NaOH (0.11mol), epichlorohydrin (0.1mol), and tetrabutylammonium bromide (2mol% based on NVF). The reaction was conducted at 70°C for 2.5 hours. After the reaction cooled down, the mixture was dissolved in toluene and washed with water to remove DMSO. After toluene removal by a rotary evaporator, the resulting product was collected. ^{1}H NMR ($CDCl_3$): δ 2.56-2.66 (1H), 2.78-2.86 (1H), 3.10-3.17 (1H), 3.45-3.55 (1H), 3.82-4.14 (1H), 4.50-4.82 (2H), 6.62-7.30 (1H), 8.10-8.36 (1H). MS (m/z): 127 (M)

[0052] EXAMPLE 8. THERMALLY INITIATED COPOLYMERIZATION OF N-VINYLFORMAMIDE WITH MALEIMIDE OR ACRYLATE

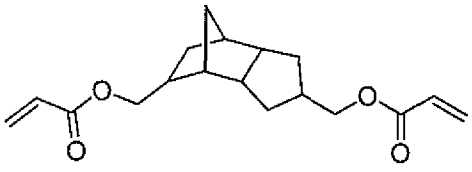
[0053] This example shows that good reactivity can be obtained between N-vinylformamide **I** (from example 1) and acrylates and between N-vinylformamide **II** (from example 2) and maleimides in copolymerization reactions. Peroxide and azo radical initiators were screened in the copolymerization of two N-vinylformamide compounds with acrylate **1** (Sartomer) and a maleimide resin BMI-**1**. The structures of the compounds copolymerized were the following:



I in which C_{36} is a linear or branched chain hydrocarbon, with or without cyclic moieties, having 36 carbon atoms

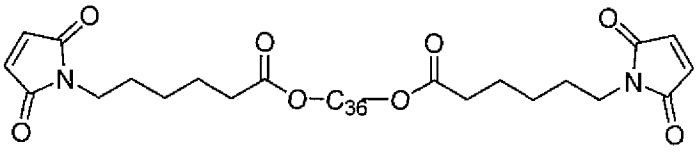


II



Acrylate 1

and



BMI-1

in which C_{36} is a linear or branched chain hydrocarbon, with or without a cyclic moieties, having 36 carbon atoms.

[0054] The Acrylate **1** and BMI-**1** were independently cured with either N-vinylformamide **I** or **II**, using either a peroxide (1,1-di-(tert-amylperoxy)-cyclohexane USP 90MD at 2mol%) or an azo initiator (VAZO-52 (Dupont) or PERKADOX-16 (Akzo Nobel) at 2mol%). In all the resin systems tested, the measured total exotherm of the combined system exceeded the sum of exotherm contributions from each individual resin's homo-polymerization. For example in entry 3, if Acrylate **1** and N-vinylformamide **II** polymerized independently to give two homo-polymers, we would expect to see a total exotherm of roughly 176.5 J/g, of which 170 J/g came from Acrylate **1** and 6.5 J/g from N-vinylformamide **II**. The fact that entry 3 resulted in 407J/g exotherm

indicates that copolymerization has occurred. Attempts to perform the copolymerization of acrylate and N-vinylformamide **II** with other low temperature peroxide initiators such as PERKADOX-16 (Akzo Nobel) gave low conversions (ΔH = 57J/g, entry 5). This indicates that the copolymerization efficacy of N-vinyl-formamides is initiator specific. The copolymerization of Acrylate **1** and N-vinylformamide **II** with an azo initiator showed a fast cure profile with a cure temperature of 106°C (ΔH = 381 J/g, entry 2). With 1,1-di-(tert-amylperoxy) cyclohexane as initiator both N-vinylformamides **I** and **II** co-cured with the Acrylate **1** to give peak temperatures of 129°C and 135°C, respectively (entries 1 and 3, see below). A similar curing behavior was observed with the BMI-**1** (entry 4). The cure profile of Acrylate **1** and N-vinylformamide **II** (flexible backbone) (Figure 1) was especially sharp, indicating that this system may have potential for low temperature snap cure with low temperature initiators (For snap cure, the temperature difference from onset to T_{peak} should be <10°C at ten degrees per minute as measured on a DSC. In examples 2 and 3, onset to T_{peak} = 7°C).

[0055]

CURE DATA FOR COPOLYMERIZATION OF N-VINYLFORMAMIDE WITH BMI-**1** OR ACRYLATE **1**

Entry	Resin System Molar Ratio	Initiator	Peak temp.	ΔH	Onset to T_{peak}
1	Acrylate **1** and N-vinylformamide **I** (1:1)	1,1-di-(tert-amyl-peroxy)-cyclohexane (2mol%) USP 90MD	129°C	275 J/g	15°C
2	Acrylate **1** and N-vinylformamide **II** (1:1)	azo initiator VAZO-52 (2mol%)	106°C	381 J/g	7°C
3	Acrylate **1** and N-vinylformamide **II** (1:1)	1,1-di-(tert-amylperoxy)-cyclohexane (2mol%)	135°C	407 J/g	7°C
4	BMI-**1** and N-vinylformamide **I** (1:1)	1,1-di-(tert-amylperoxy)-cyclohexane (2mol%)	133°C	220 J/g	17°C
5	BMI-**1** and N-vinylformamide **I** (1:1)	azo initiator PERKADOX-16 (2mol%)	110°C	57 J/g	19°C

[0056] EXAMPLE 10. PHOTOINITIATED COPOLYMERIZATION OF N-VINYLFORMAMIDE WITH MALEIMIDE OR ACRYLATE

[0057] N-Vinylformamide **II** (shown above) was investigated as a co-monomer in the photopolymerization of maleimide or acrylate monomers. Curing studies were conducted on a

Perkin-Elmer Diamond DSC equipped with an EXFO Omnicure Series 2000 UV spot cure unit with light intensity output set at 5.2 mW/cm^2. For all the studies, 2.5 wt% DAROCUR 4265 (Ciba Specialty Chemicals) was added as a photoinitiator. The diacrylate used was hexanediol diacrylate (HDDA, Aldrich) and the maleimide used was BMI-**1** (shown above).

[0058] The copolymerization results of N-vinylformamide **II** with HDDA are reported below and shown in the DSC curve in Figure 2. The total exotherm of the 1:1 HDDA : N-vinylamide **II** blend was 305 J/g, exceeding the sum of exotherm contributions (calculated to be 170 J/g) from each individual resin's homo-polymerization under the same conditions (321 J/g for HDDA and 19 J/g for **II**), indicating that copolymerization has occurred.

CURE DATA FOR PHOTOPOLYMERIZATION OF N-VINYLFORMAMIDE WITH ACRYLATE		
Sample	Time to Exotherm Peak (minutes)	ΔH(J/g)
HDDA	0.049	321
1:1 HDDA : N-vinylformamide **II**	0.106	305
N-vinylformamide **II**	0.744	19

[0059] Photopolymerization studies were also conducted on the N-vinylformamide **II** and BMI-**1** resins (Figure 3). BMI-**1**, 3:1 BMI-**1**:N-vinylformamide **II** blend, and N-vinylformamide **II** were each cured with 2.5 wt% DAROCUR 4265 (Ciba Specialty Chemicals). The addition of N-vinylformamide compounds to the BMI-**1** system improved the cure speed, judging by the cure speed (as indicated by shorter Time to Exotherm Peak) and cure exotherm.

CURE DATA FOR PHOTOPOLYMERIZATION OF N-VINYLFORMAMIDE WITH MALEIMIDE		
Sample	Time to Exotherm Peak (minutes)	ΔH(J/g)
BMI-**1**	0.106	127
3:1 BMI-**1**:N-vinylformamide **II**	0.082	168
N-vinylformamide **II**	0.748	19

[0060] EXAMPLE 11. EFFECT OF OXYGEN ON CURING OF ACRYLATE VERSUS BMI/N-VINYLFORMAMIDE SYSTEM

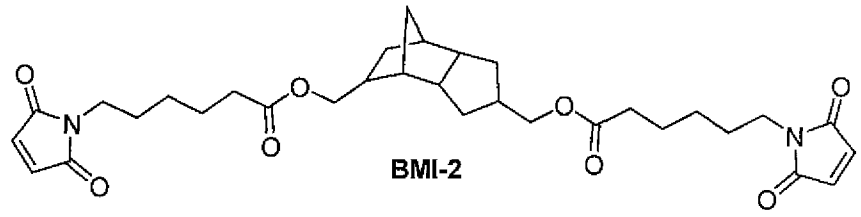
[0061] HDDA and 3:1 BMI-**1**:N-vinylformamide **II** blend samples used in EXAMPLE 10 were cured in air to study the effect of oxygen. PhotoDSC results revealed that the curing of the acrylate and HDDA was significantly delayed in the presence of the oxygen in the air; that is, the

time needed to reach the exotherm peak more than quadrupled in the presence of air compared to the time needed to reach the exotherm peak under nitrogen. In the case of the composition containing a 3:1 molar ratio of BMI-1 to N-vinylformamide **II**, the time to curing peak roughly doubled. The time needed to reach 90% of the total curing exotherm, doubled in the case of HDDA, but increased only 21% for the BMI-**1** and N-vinyl formamide **II** system, when curing was switched from nitrogen to air. (The 3:1 molar ratio was arbitrarily chosen to prove the effect. No study was conducted for an optimized ratio.)

CURE DATA FOR PHOTOPOLYMERIZATIONS IN AIR				
Sample	Time to Exotherm Peak in N_2 (minutes)	Time to Exotherm Peak in air (minutes)	Time to 90% of Total Exotherm in N_2 (minutes)	Time to 90% of Total Exotherm in air (minutes)
HDDA	0.049	0.208	0.433	0.885
3:1 BMI-**1** : N-vinyl-formamide **II**	0.082	0.167	0.927	1.121

[0062] EXAMPLE 12. EFFECT OF N-VINYLFORMAMIDE ON MOISTURE UPTAKE OF MALEIMIDE RESINS

[0063] This example shows the comparison of moisture uptake of cured BMI-**2** and a mixture of BMI-**2** and N-vinylformamide **I** (1:1 by weight, oven cured at 175°C for 30 minutes using 2wt% USP 90MD as the initiator) under 85°C/85% relative humidity exposure. Cured BMI-**2** showed a 1.67% uptake of moisture upon 85°C/85 relative humidity exposure, while a 1:1 mixture (by weight) of BMI-**2** and N-vinylformamide **I** showed a 30% reduction in moisture uptake upon exposure to similar conditions (1.15%).



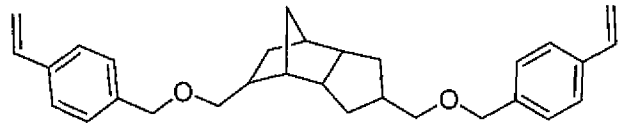
BMI-2

[0064] EXAMPLE 13. STABILITY COMPARISON OF MALEIMIDE FORMULATIONS CONTAINING DIFFERENT ELECTRON-RICH VINYL MONOMERS

[0065] The effect of the addition of electron-rich N-vinylformamide compounds to electron-

deficient maleimide or acrylate resin systems was compared to the effect of the addition of a styrene compound to the same electron-deficient maleimide or acrylate resins system with respect to the resin system's worklife stability. The comparison study indicated that the addition of an N-vinylformamide compound to an electron-deficient monomer provides superior worklife, that is, a longer time to gelation, compared to the addition of a styrenic compound to the same electron-deficient monomer. Both systems were studied in the presence of the radical initiator VAZO-52 (10 hour half life 52°C and the time to gelation recorded. Entry 1, a mixture of Acrylate **1** with N-vinylformamide **II** showed a time to gelation of approximately 12 hours under degassed conditions. In contrast, the Acrylate **1**-Distyrene **1** system (entry 2) showed a time to gelation of approximately six hours under degassed conditions.

Entry	Resin system	Initiator	Cure Temp. (T_c)	ΔH	Time to gelation
1	Acrylate **1** + N-vinylformamide **II** (1:1 by mol)	VAZO-52 (2mol%)	same	same	~12 hours (degassed conditions)
2	Acrylate **1**+ Distyrene **1**(1:1 by mol)	VAZO-52 (2mol%)	80°C	415 J/g	~ 6 hours (degassed conditions)



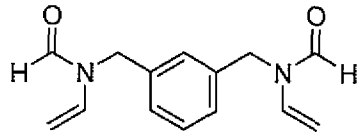
Distyrene 1

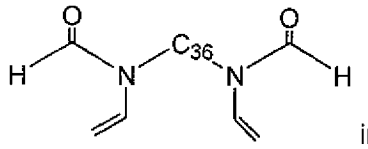
[0066] The compounds prepared by the process of this invention and the compositions comprising those compounds are suitable for use in a variety of adhesives, paints, coatings, inks, and encapsulants applications. Such compositions are particularly suitable for use in electronics packaging applications, such as, in pastes, coatings, or films, for example, in die attach adhesives and underfills.

WHAT IS CLAIMED:

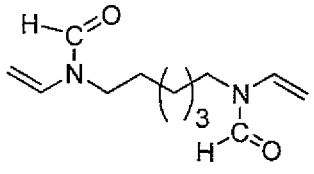
1. A curable composition comprising
   (i) a multifunctional N-vinylformamide compound having at least two N-vinylformamide functionalities on the molecule and no other reactive functionalities;
   (ii) an initiator;
   (iii) optionally, another curable compound reactive with the multifunctional N-vinylformamide compound; and
   (iv) optionally, a filler

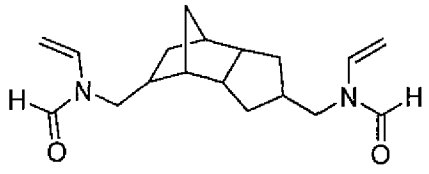
2. The curable composition according to claim 1 in which the multifunctional N-vinylformamide compound is selected from the group consisting of



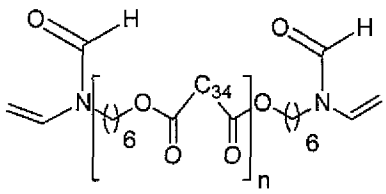


in which C_{36} is a linear or branched chain hydrocarbon, with or without cyclic moieties, having 36 carbon atoms





and

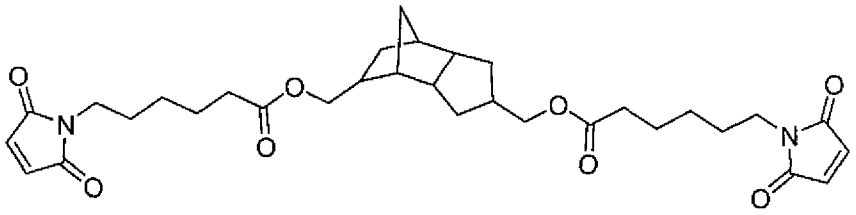


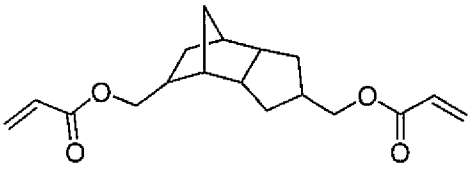
in which n is 1 to 10.

3. The curable composition according to claim 1 in which the additional curable compound is selected from the group consisting of acrylate, methacrylate, maleimide, cyanoacrylate, cinnamyl, maleate, fumarate, maleic anhydride, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester and vinyl ether compounds or resins, and mixtures of these.

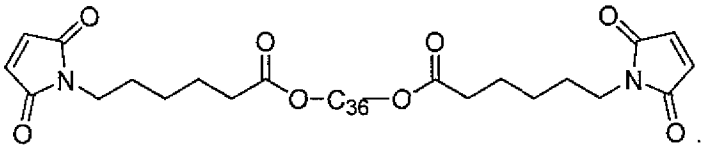
4. The curable composition according to claim 3 in which the additional curable compound is selected from the group consisting of acrylate, methacrylate, and maleimide.

5. The curable composition according to claim 4 in which the additional curable compound is selected from the group consisting of





and



6. A curable composition comprising

(i) a hybrid N-vinylformamide compound having at least one N-vinylformamide functionality and at least one other reactive functionality;

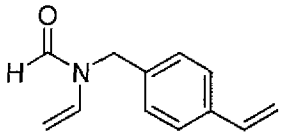
(ii) an initiator;

(iii) optionally, another curable compound reactive with the hybrid N-vinylformamide compound; and

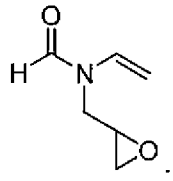
(iv) optionally, a filler.

7. The curable composition according to claim 6 in which the at least one other reactive functionality on the hybrid N-vinylformamide compound is selected from the group consisting of acrylate, methacrylate, cyanoacrylate, maleimide, cinnamyl, maleate, fumarate, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester, vinyl ether, and combinations of these.

8. The curable composition according to claim 6 in which the hybrid N-vinyl-formamide is selected from the group consisting of



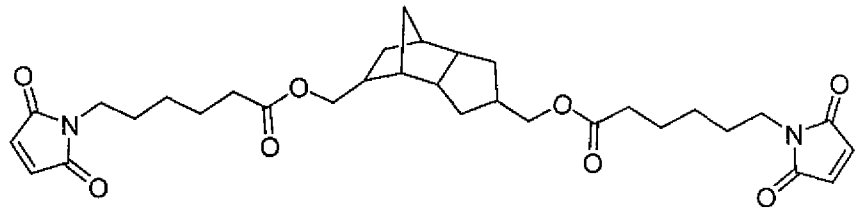
and

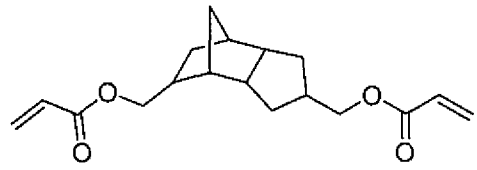


9. The curable composition according to claim 6 in which the additional curable compound is selected from the group consisting of acrylate, methacrylate, maleimide, cyanoacrylate, cinnamyl, maleate, fumarate, maleic anhydride, epoxy, oxetane, silane, styrenic, benzoxazine, oxazoline, vinyl ester and vinyl ether compounds or resins, and mixtures of these.

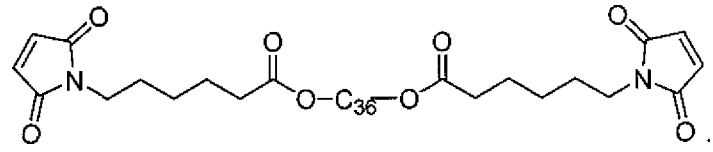
10. The curable composition according to claim 9 in which the additional curable compound is selected from the group consisting of acrylate, methacrylate, and maleimide.

11. The curable composition according to claim 10 in which the additional curable compound is selected from the group consisting of





and



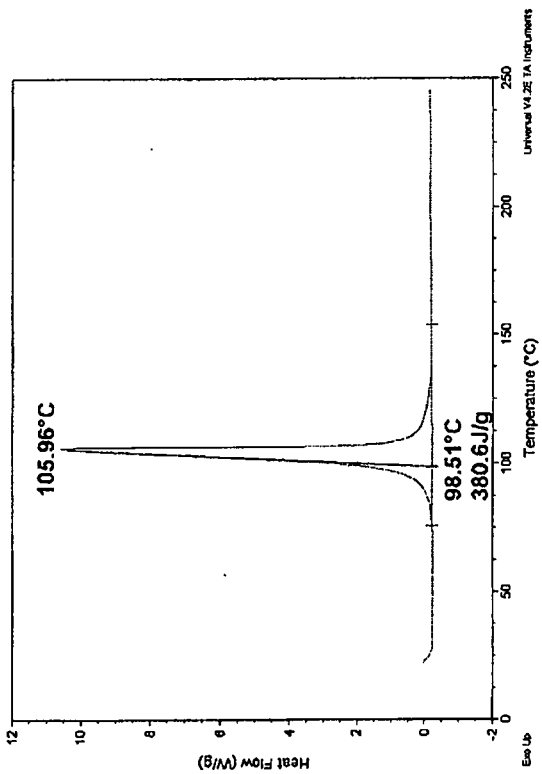


Figure 1
DSC curing profile of Acrylate I and N-Vinylformamide II with VAZO-52 initiator

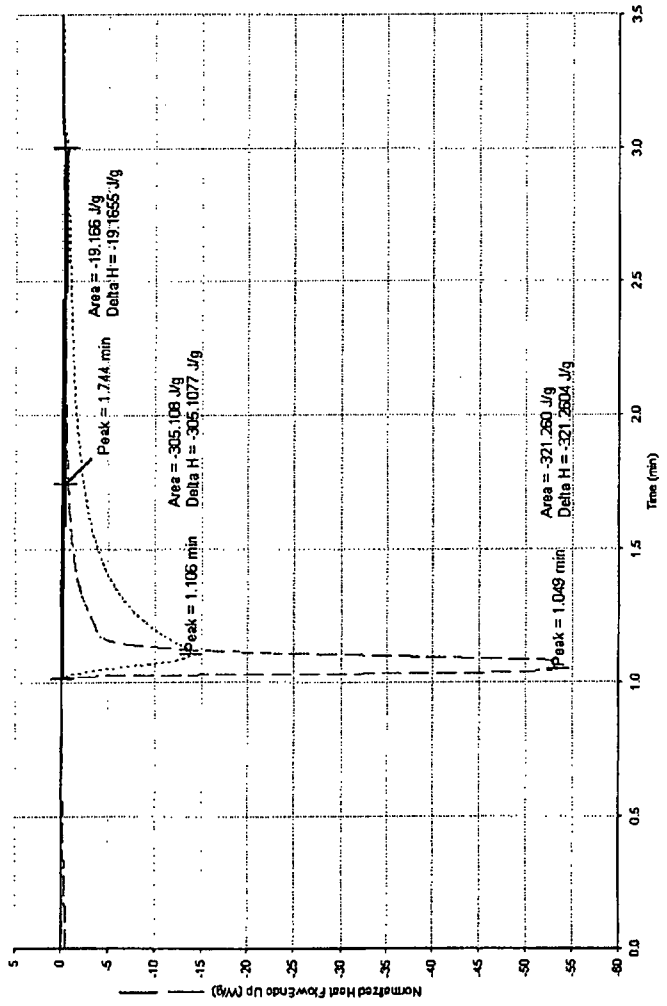


Figure 2: Photopolymerization of Hexanediol Diacrylate (HDDA) and N-vinylformamide II 50/50 (weight mixture)
– – – – – – HDDA
. . . . . 50/50 weight mixture of HDDA and N-vinylformamide II
_____ N-vinylformamide II
UV light shutter on at 1 min, and off at 3 min

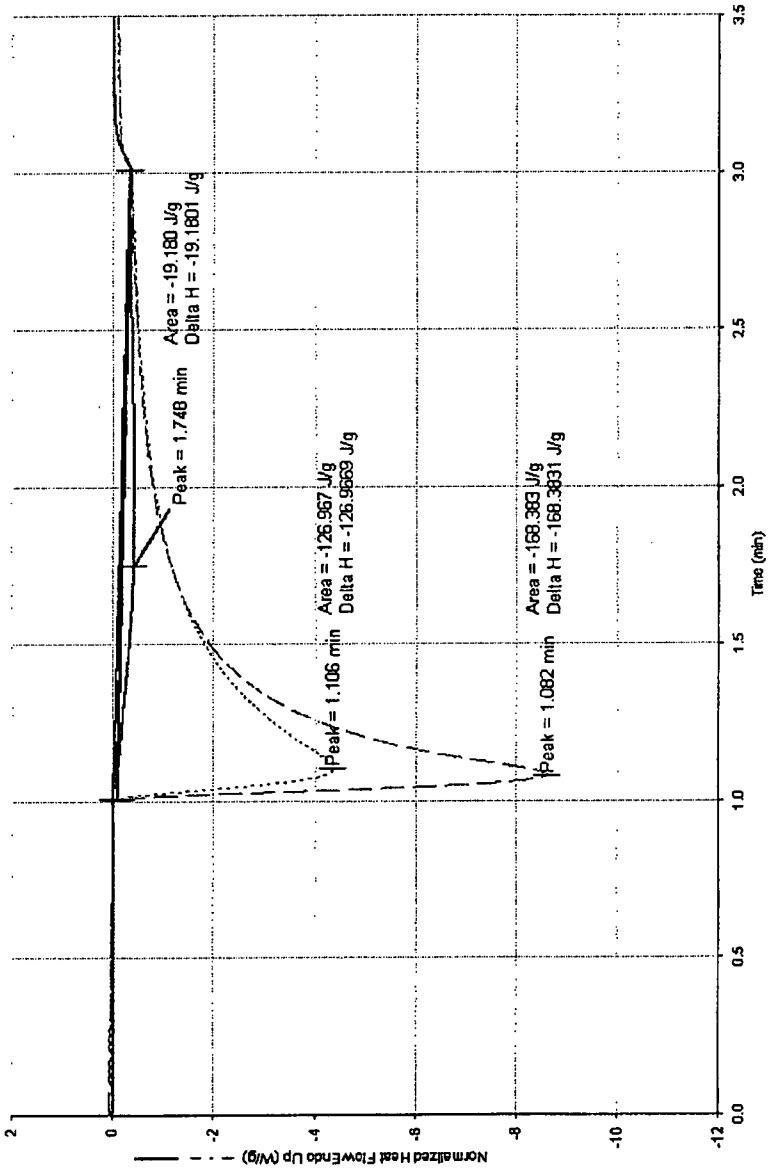


Figure 3: Photopolymerization of
– – – – 3/1 weight blend of BMI-1 and N-vinylformamide II
. . . . . BMI-1
_____ N-vinylformamide II
UV light shutter on at 1 min, and off at 3 min

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/052983

A. CLASSIFICATION OF SUBJECT MATTER

C08F 12/28(2006.01)i, C08L 33/24(2006.01)i, C08K 3/00(2006.01)i

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)

IPC 8 : C08F

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)

eKIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US5338815 A (SHOWA DENKO K.K.) 16 Aug. 1994 Abstract; Column 6 line 38; Claims 1-5	1-5
X	US5407996 A (SHOWA DENKO K.K.) 18 Apr. 1995 Abstract; Column 6 line 27; Claims 1-5	1-5
X	US5788950 A (SHOWA DENKO K.K.) 04 Aug. 1998 Abstract; Column 5 line 36; Claims 1-10	1-5
A	US4205139 A (BASF AG) 27 May 1980 Whole document	1-11

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 SEPTEMBER 2008 (30.09.2008)	**30 SEPTEMBER 2008 (30.09.2008)**

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Telephone No. 82-42-481-5597

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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