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(54) Titre : RESINES DE NEUTRALISATION D'ACIDE ET LEURS COMPOSITIONS DENTAIRES DURCISSABLES
(54) Title: ACID-NEUTRALIZING RESINS AND HARDENABLE DENTAL COMPOSITIONS THEREOF

(57) **Abrégé/Abstract:**

Disclosed herein is a dental composition comprising: a. 0.5-10% wt/wt of non-polymerizable acid-neutralizing resin (I) or 0.5-99% wt/wt of an acid-neutralizing polymerizable resin (II) or a mixture of (I) and (II), featuring a moiety that is capable to effectively neutralizing an acid group, where the neutralized acid group is a carboxylic acid, a sulphonc acid, a phosphonic acid or a phosphoric acid, b. 5-90% wt/wt of mixed conventional polymerizable resins; c. 0.01-5.00% of initiators and other additives; d. 0-90% wt/wt of a plurality of filler particles ranged from 10 nm-50 micron.

Abstract

Disclosed herein is a dental composition comprising: a. 0.5-10% wt/wt of non-polymerizable acid-neutralizing resin (I) or 0.5-99% wt/wt of an acid-neutralizing polymerizable resin (II) or a mixture of (I) and (II), featuring a moiety that is capable to effectively neutralizing an acid group, where the neutralized acid group is a carboxylic acid, a sulphonic acid, a phosphonic acid or a phosphoric acid, b. 5-90% wt/wt of mixed conventional polymerizable resins; c. 0.01-5.00% of initiators and other additives; d. 0-90% wt/wt of a plurality of filler particles ranged from 10 nm-50 micron.

ACID-NEUTRALIZING RESINS AND HARDENABLE DENTAL COMPOSITIONS THEREOF

TECHNICAL FIELD

[001] Disclosed herein are a class of acid-neutralizing resins and hardenable or curable compositions containing such resins.

BACKGROUND

[002] Chemical polymerization of vinyl or acrylate based resins via a free radical polymerization mechanism at ambient temperature is traditionally achieved using a binary, redox curing system consisting of a peroxide and an aromatic tertiary amine. On the other hand, light-activated polymerization proceeds via the generation of free radicals from the activation of a photoinitiator, usually an α -diketone, to its excited triplet state. This is followed by the reduction of the activated photoinitiator by an amine accelerator to form an intermediate excited complex (exciplex), which releases the free radicals on dissociation. There was evidence to suggest that bond strengths of resin composites to dentin were influenced by the compatibility of the polymerization modes between adhesive systems and resin composites (Swift EJ, May KN, Wilder AD. *Journal of Prosthodontics*, 7: 256-60, 1998). A report further revealed that common light-cured, self-etching adhesive systems were incompatible with chemical-cured composites (Miller MB et al. *Realty* 13(1), 182-7, 1999), to the extent that no effective bonding was achieved for some systems. However, the systems that bonded poorly to the chemically cured composites exhibited high shear bond strengths with the use of light-cured resin composites. Generally, the nature of incompatibility of self-etching adhesives with chemical-cured resins is attributed to the *in situ* reaction between the basic component

(amine cointiator) of the dual-cure restorative and the acid components of the adhesive system. More specifically, these acid components of the bonding agent are able to readily protonate the tertiary aromatic amine, which could be found in the self-curing resin composite as part of the organic redox catalyst. The protonated amine (quaternary aromatic amine) became inactive and/or not reactive towards the peroxide. Consequently, initiating radicals were able to be generated under ambient conditions. Overall, such a catalyst pair would have a loss in efficiency, and the rate and degree of functional group conversion are significantly diminished compromising the performance of the dental adhesive. In order to avoid such an unwanted amine protonation reaction, the dental restoratives to be used in combination have to be limited to those of the photo-curable type only.

[003] Although light-cured resin composites have largely superseded the use of chemical-cured composites in esthetic dental applications, chemically activated composites still have important applications in contemporary restorative dentistry. The longer working time of chemically cured composites has been adopted in the 'directed shrinkage technique' for posterior resin composite restorations. In this technique, a slow setting, chemically cured composite was used either in bulk or as a basal layer to relieve the stress developed in a restoration by the flow of the partially polymerized material. Chemically cured resins are frequently used as restorative materials in areas that are not easily penetrable by light, and as auto- or dual-curing resin cements for luting of crown and bridges, inlays and onlays along with endodontic posts. In order to facilitate the use of light curing self-etching bonding agents with dual curing or chemically curing composites, a self-curing activator is required to overcome the incompatibility of the acid containing adhesive with the amine in the redox catalyst of the chemically cured system. In the Prime&Bond NT® Dual-Cure

bonding system available from DENTSPLY International, Inc., the regular light-cure bonding agent, Prime&Bond NT® is mixed with Self-Cure Activator prior to use. The Prime&Bond NT® Dual-Cure exhibits excellent bond strength when bonding a dual-cure cement, e.g. Calibra® available from DENTSPLY International, Inc., in chemical-cure mode.

[004] The Self-Cure Activator developed specifically for Prime&Bond NT® does not necessarily work as well with other simplified adhesives. More importantly, Self-Cure Activator has to be mixed with a simplified adhesive prior to use, which is an extra step for clinicians. There is a real need to simplify the system. It was thought that cement incorporating a base could neutralize acids in a simplified adhesive to mitigate or eliminate the issue of deactivation of amine in the cement. As a result, the incompatibility of a simplified adhesive and resin cement in self-cure mode may be reduced or eliminated.

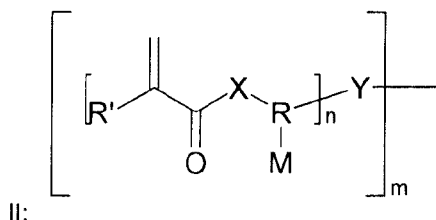
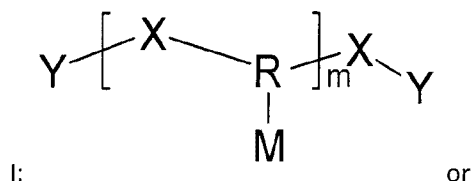
[005] Osada et al (*Dental materials Journal*, 21 (11): 1044-50, 2005) reported that addition of an anion exchange resin to the amine component of self-cured resin was an effective means of enhancing the bond strength on dentin and to prevent amine neutralization through the acid groups of self-etching primer adhesives. The drawback with this approach is that flexural modulus of cement with anion exchange resin drops off. More critically, anion exchange resin is polymerized beads with diameter 1-2 mm, which would result in cement with film thickness too large for any clinical usage.

SUMMARY

[006] Disclosed herein is a method of making an acid-neutralizing resins, a resin composition having an acid-neutralizing capability and polymerizable or hardenable dental compositions for application in dental restorations. More specifically this disclosure is related to a method to prepare such reactive resins containing proper moieties that are capable

effectively neutralizing stronger acids to prevent the amine co-initiator existing in any formulated dental restoratives from similar neutralizing reaction. Furthermore such acid-neutralizing resins can be either polymerizable or nonpolymerizable, and it can be further formulated in a variety of hardenable dental compositions, including but not limited to dental adhesives, dual-cure dental cements and dental composites. Thus in this disclosure is a method of effectively neutralizing any residual acid either from cured dental primer or from dental adhesives by dental compositions containing acid-neutralizing polymerizable resin, and consequently sound bonding of dental restoratives to tooth substitutes is readily achieved.

[007] Representative formulas of such base resins may be as follows:



R': H or Me;

X: O, S, NH, NR₁ (R₁=CH₃, C₂H₅)

R and Y: independently of each other, have C1-C24, linear and/or branched alkylene residue, or aromatic/substituted residue;

M: alpha-substituted tertiary amine, pyridine or substituted pyridine, imidazole and/or substituted imidazole, pyrrole and/or substituted pyrrole, piperidine and/or substituted piperidine, pyrazole and/or substituted pyrazole, oxazole and/or substituted oxazole, thiazole and/or substituted thiazole, isoxazole and/or substituted isoxazole, isothiazole and/or substituted isoxazole, thiadiazole indole and/or substituted thiadiazole indole, indolizine and/or substituted indolizine, triazole and/or substituted triazole, tetrazole and/or substituted tetrazole, pentazole and/or substituted pentazole, quinoline and/or substituted quinoline, isoquinoline and/or substituted isoquinoline, pyridazine and/or substituted pyridazine, pyrimidine and/or substituted, pyrazine and/or substituted pyrazine, cinnoline and/or substituted cinnoline, phthalazine pyrimidine and/or substituted phthalazine, quinazoline and/or substituted quinazoline, quinoxaline and/or substituted quinoxaline, phenazine and/or substituted triazines, triazines and/or substituted triazines or any combination of these

n=1-10 and m=1-10

[008] This disclosure relates to resin compositions of acid-neutralizing resins and further hardenable or curable compositions containing the said resins. The hardenable or curable compositions are preferably dental compositions, included but not limited to adhesives, cements and composites. This disclosure relates particularly to a method of effectively neutralizing the excess acids in any cured primers, self-etching adhesives or any other adhesive systems so as to allow subsequently adequate curing for good bonding between such adhesive systems and the dual-cure restoratives. Disclosed herein are compositions of such acid-neutralizing resins and the method to utilize such acid-neutralizing resins in formulated compositions that become capable of effectively neutralizing any residual acid and

at the same time effectively preventing the similar neutralizing reaction from the amine coinitiators that existed in standard dual-cure restoratives. Thus a significant enhancement in term of hardening or curing process, especially at the interface between the acidic surface and restorative materials should be readily achieved, which consequently results in improved compatibility and more specifically improved bonding strength.

[008a] In an embodiment, there is provided a dental composition comprising:

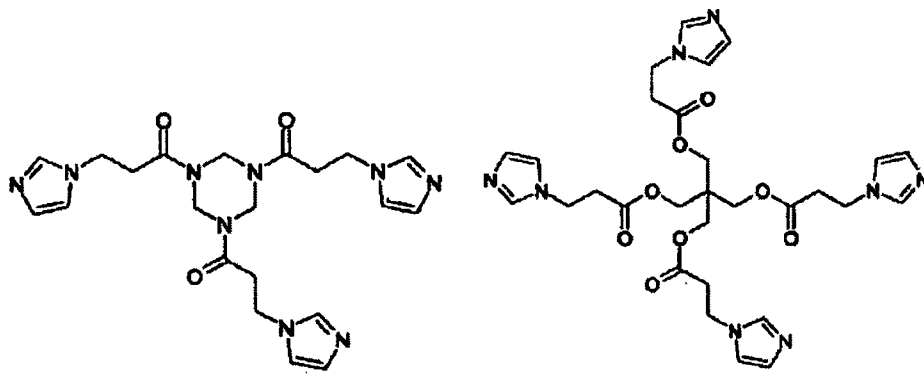
a. 0.5-10% wt/wt of non-polymerizable acid-neutralizing resin (I) or 0.5-94.99% wt/wt of an acid-neutralizing polymerizable resin (II) or a mixture of (I) and (II), featuring a moiety that is capable to effectively neutralizing an acid group, where the neutralized acid group is a carboxylic acid, a sulphonic acid, a phosphonic acid or a phosphoric acid,

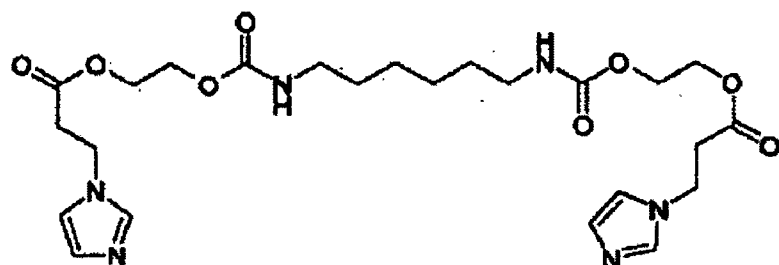
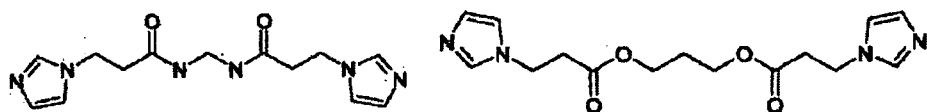
b. 5-90% wt/wt of mixed conventional polymerizable resins;

c. 0.01-5.00% of initiators and other additives;

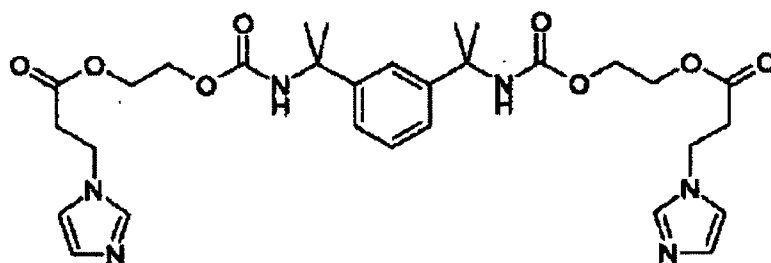
d. 0-90% wt/wt of a plurality of filler particles ranged from 10 nm-50 micron;

wherein the non-polymerizable acid-neutralizing resin (I) is selected from the group consisting of

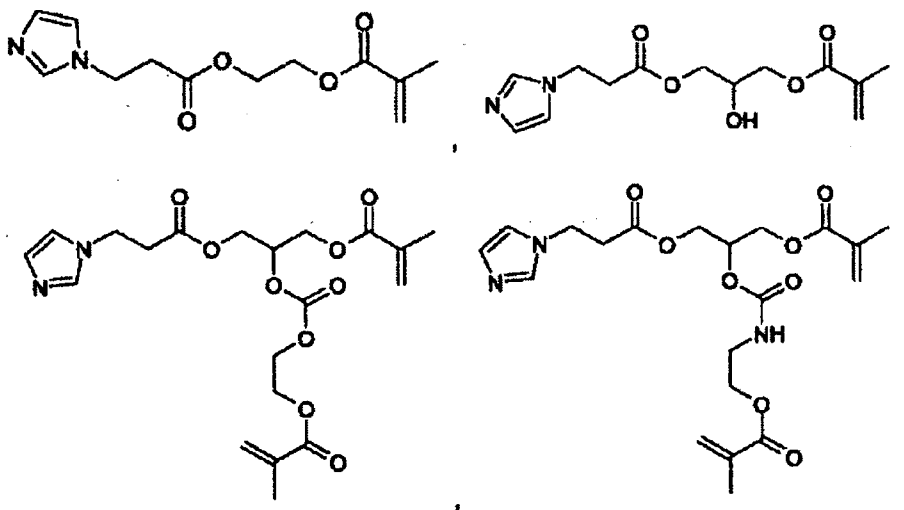


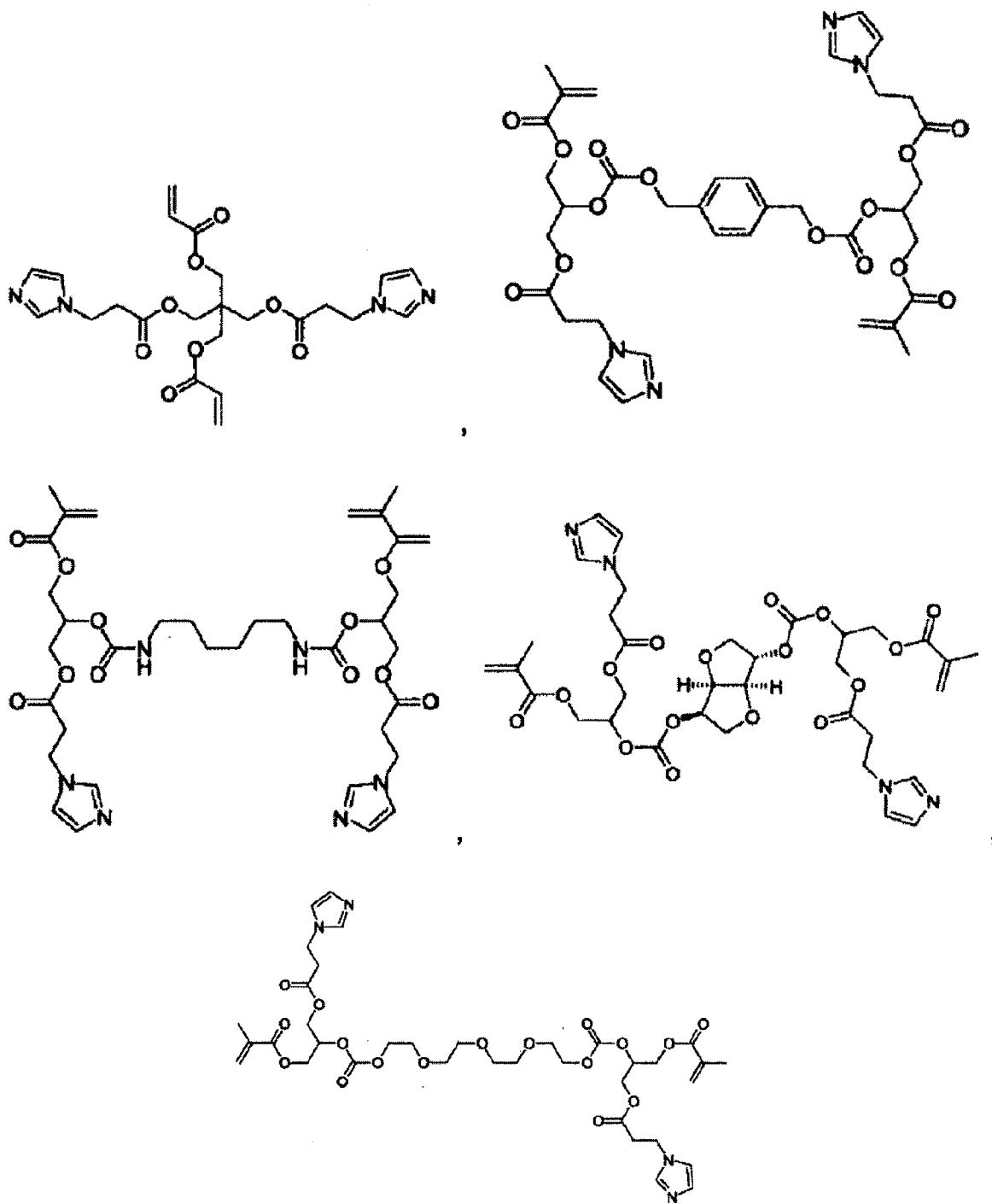


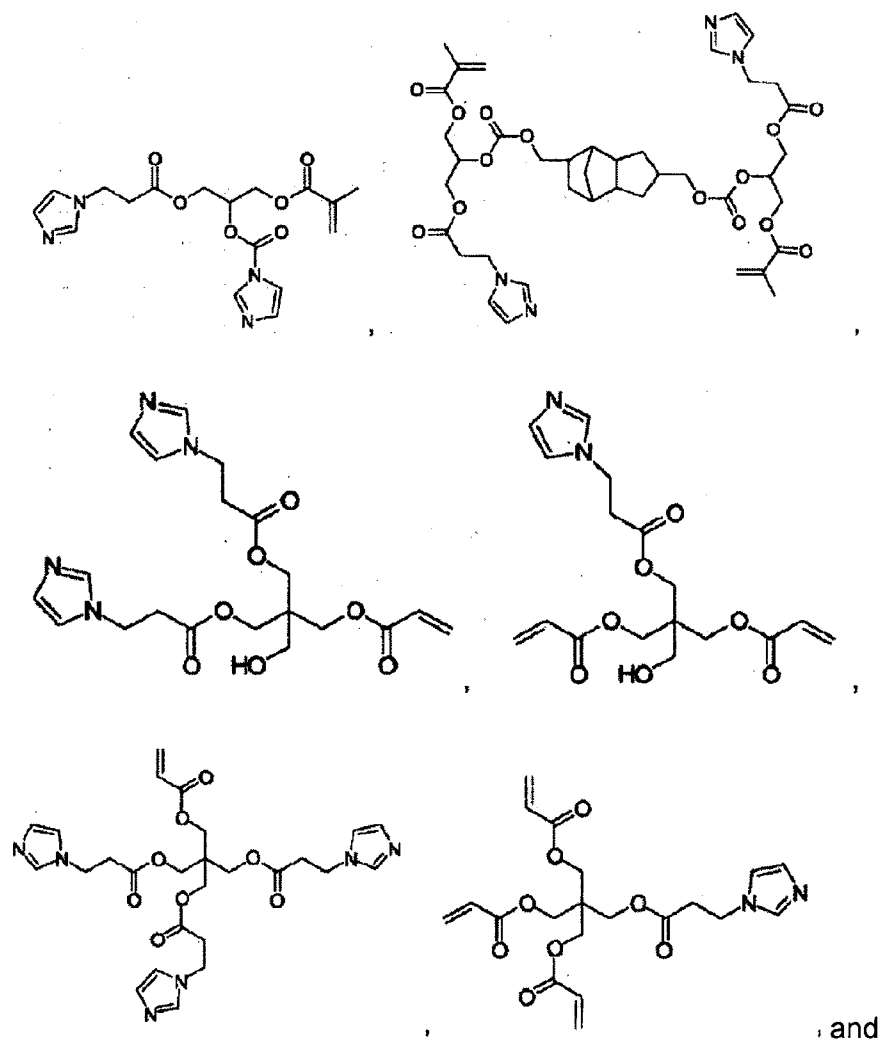
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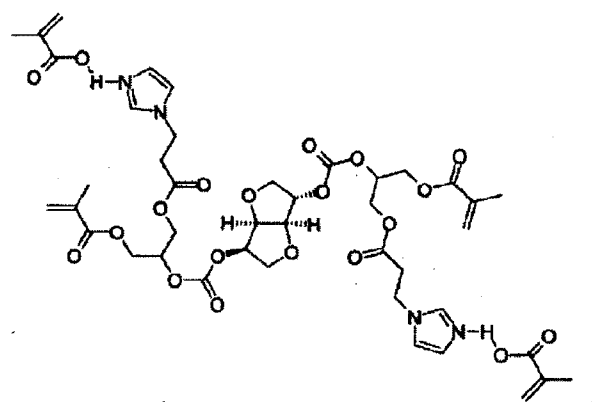
and wherein the polymerizable acid-neutralizing resin (II) is selected from the group consisting of



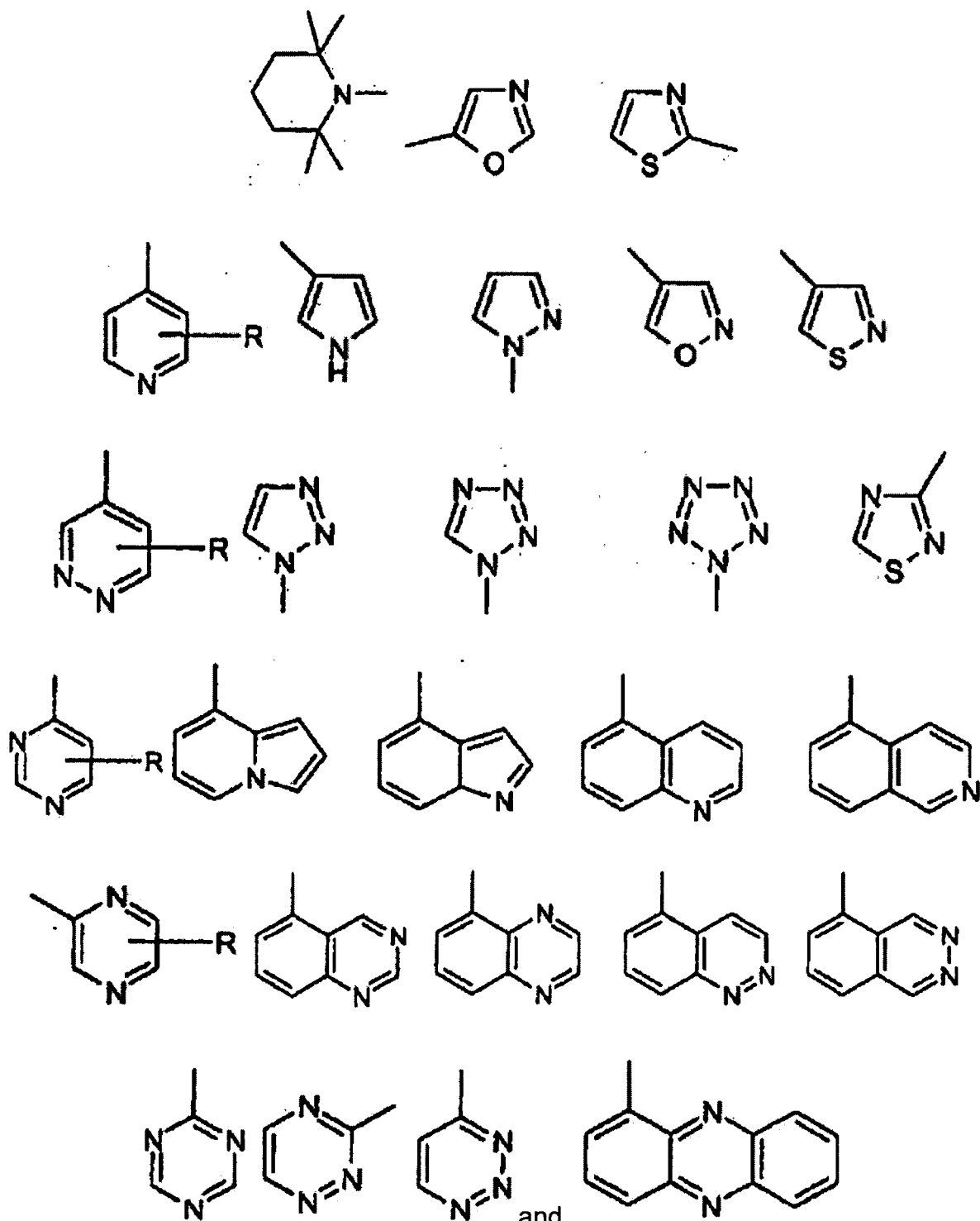




, and



wherein the imidazolyl moiety in the above non-polymerizable acid-neutralizing resins (I) and acid-neutralizing polymerizable resin (II) may be replaced by a moiety selected from the group consisting of



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BRIEF DESCRIPTION OF DRAWINGS

- [0009] Figure 1 depicts examples of acid neutralizing polymerizable resins.
- [0010] Figure 2 depicts more examples of acid neutralizing polymerizable resins.
- [0011] Figure 3 depicts yet more examples of acid neutralizing polymerizable resins.
- [0012] Figure 4 is a FTIR spectra of a complex of PENTA/bisimidazole dimethacrylate.
- [0013] Figure 5 is a FTIR spectra of a complex of polyacrylic acid/bisimidazole dimethacrylate.
- [0014] Figure 6 demonstrates one preparation of isosorbide passed polymerizable imidazole resin.
- [0015] Figure 7 demonstrates one preparation of AMAHP-based polymerizable imidazole resin via CDI process.
- [0016] Figure 8 depicts a TCDC-based bisimidazole dimethacrylate resin.
- [0017] Figure 9 depicts a HEMA based dimethacrylate imidazole resin.
- [0018] Figure 10 demonstrates one preparation of AMAHP based polymerizable imidazole resins via an imidazole process.
- [0019] Figure 11 demonstrates one preparation of an IEM based dimethacrylate imidazole resin.

[0020] Figure 12 depicts imidazole acrylate resins.

[0021] Figure 13 depicts further examples of imidazole acrylate resins.

[0022] Figure 14 depicts a complex of methacrylic acid and bisimidazole dimethacrylate resin.

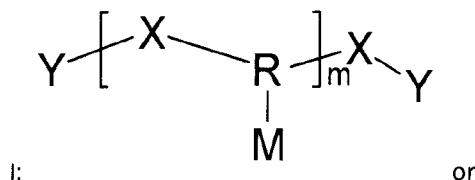
[0023] Figure 15 depicts two typical nonpolymerizable triimidazole resin and tetraimidazole resin.

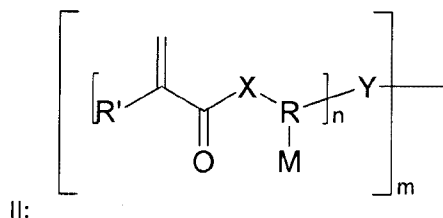
[0024] Figure 16 depicts further nonpolymerizable bisimidazole resins.

DETAILED DESCRIPTION

[0025] In this disclosure, identified are a class of novel additive, acid-neutralizing resins, which could be readily formulated in conventional restoratives and make them capable of neutralizing the acidic component from adhesive and consequently lead to pronounced enhancement in bonding strength due to improved polymerization of the restorative. In addition, as a natural extension of this disclosure, a self-neutralizable adhesive composition should be also formulated by incorporating such polymerizable base resins, which will work similarly towards self-etching primer and any other conventional, dual-cure, self-cure and/or light-cure restoratives. Pronounced improvement in bonding strength was true benefit from such simplified procedures due to incorporation of such polymerizable base resins.

[0026] The following formula illustrates the representative structure of such acid-neutralizing resins. It is expected further alteration from such formulate is possible based on basic knowledge in organic chemistry, which should fall in the scope of this disclosure.





R': H or Me;

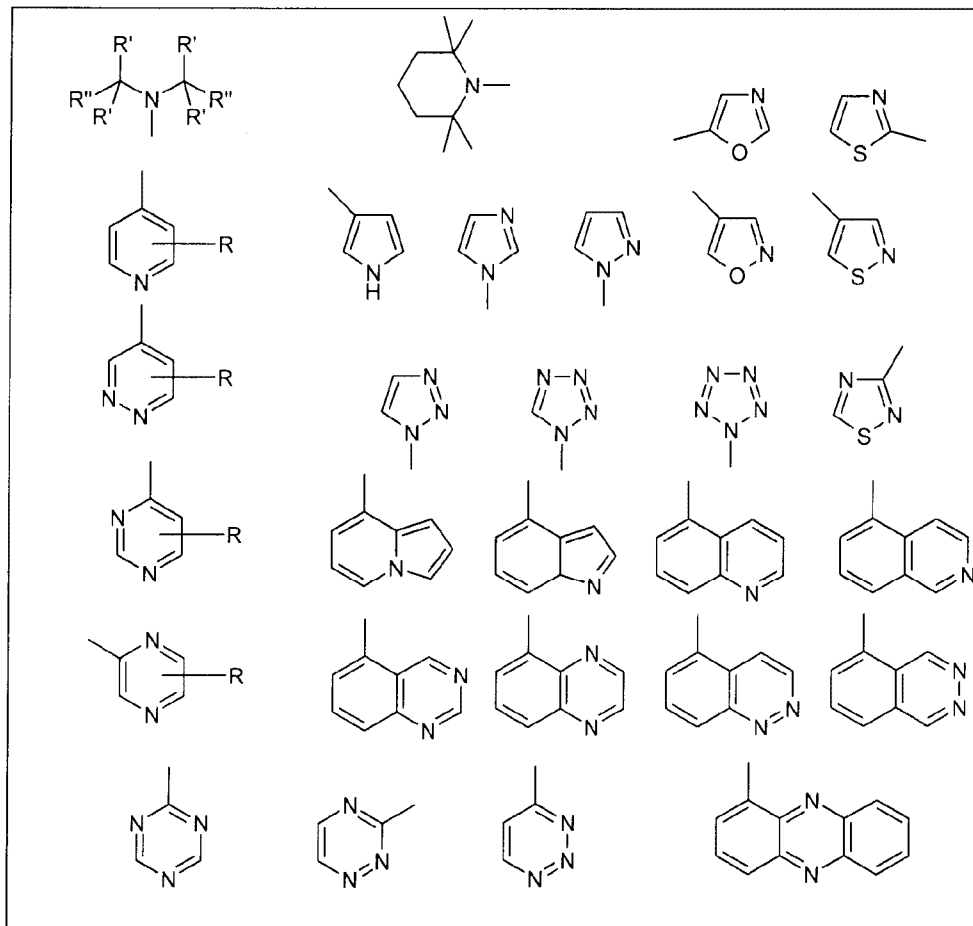
X: O, S, NH, NR1 (R1=CH3, C2H5)

R and Y: independently of each other, have C1-C24, linear and/or branched alkylene residue, or aromatic/substituted residue;

M: alpha-substituted tertiary amine, pyridine or substituted pyridine, imidazole and/or substituted imidazole, pyrrole and/or substituted pyrrole, piperidine and/or substituted piperidine, pyrazole and/or substituted pyrazole, oxazole and/or substituted oxazole, thiazole and/or substituted thiazole, isoxazole and/or substituted isoxazole, isothiazole and/or substituted isoxazole, thiadiazole indole and/or substituted thiadiazole indole, indolizine and/or substituted indolizine, triazole and/or substituted triazole, tetrazole and/or substituted tetrazole, pentazole and/or substituted pentazole, quinoline and/or substituted quinoline, isoquinoline and/or substituted isoquinoline, pyridazine and/or substituted pyridazine, pyrimidine and/or substituted, pyrazine and/or substituted pyrazine, cinnoline and/or substituted cinnoline, phthalazine pyrimidine and/or substituted phthalazine, quinazoline and/or substituted quinazoline, quinoxaline and/or substituted quinoxaline, phenazine and/or substituted triazines, triazines and/or substituted triazines or any combination of these residues;

$n=1-10$ and $m=1-10$.

[0027] In the following chart, the typical M is illustrated:



EXAMPLES

[0028] Example 1: Isosorbide-based bisimidazoledimethacrylate Resin (Figure 6) was prepared via a two-step process as described in the following: to a 1000ml 3-neck round flask, 98.88g of 1,1-carbonyldiimidazole(CDI), 550g of methylene dichloride and 43.9g of isosorbide were charged and soon the system turns clear at room temperature. Then the crystal was developed as resulted of imidazole

formation. After 2hrs reaction at RT, 131.1g of 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AMAHP), 40.0g of potassium carbonate and 4.0g of terabutylammoniumbromide were added. Keep the reaction proceeding at room temperature for additional 10-12hrs prior to 200ml of water was added to stop the reaction. The resulting solution was extraction several times with water to remove all of imidazole and catalysts. Then it was dried over magnesium sulfate overnight at RT prior to it was filtrated. Solvent was removed via Rotovapor at 35-40°C under vacuum. 240g of liquid resin was collected with yield of 89%.

[0029] Example 2: TCDC-based bisimidazole-dimethacrylate Resins (Figure 8) was prepared via a two-step process as described in the following: to a 1000ml 3-nech round flask, 74.45g of CDI, 400ml of methylene dichloride and 98.36g of AMAHP were charged and soon the system turns clear at room temperature. After 6hrs reaction at RT, a bisimidazole precursor was formed as shown in Figure 7, then 45.0g of 4,8-bis(hydroxymethyl)-tricyclo[5,2,1,0^{2,6}](TCDC) and 40.0g of potassium carbonate and 3.8g of terabutylammoniumbromide were added. Keep the reaction proceeding at room temperature for additional 10-12hrs prior to 250ml of DI water was added to stop the reaction. The resulting solution was extraction several times with water to remove all of imidazole and catalysts. Then it was dried over magnesium sulfate overnight at RT prior to it was filtrated. Solvent was removed via Rotovapor at 35-40°C under vacuum.

[0030] Example 3: HEMA-based Monoimidazole-dimethacrylate Resins (Figure 9) was also prepared via a two-step process as described in the following: to a 1000ml 3-nech round flask, 81.8g of CDI, 450ml of methylene dichloride and 107.5g of AMAHP were charged and soon the system turns clear at room temperature. After 6hrs reaction at RT, 66.5g of HEMA, 40.0g of potassium carbonate and 4.0g of terabutylammoniumbromide were added. Keep the reaction proceeding at room temperature for additional 10-12hrs prior to 200ml of water was added to stop the reaction. The resulting solution was extraction several times with DI water to remove all of imidazole and catalysts. Then it was dried over

magnesium sulfate overnight at RT prior to it was filtrated. Solvent was removed via Rotovapor at 35-40°C under vacuum.

[0031] Example 4: AMAHP-based monoimidazole-monomethacrylate Resins (Figure 10) was also prepared via a one-step process as described in the following: to a 1000ml 3-nech round flask, 102grams of imidazole, 700ml of methylene dichloride and 161grams of AMAHP were charged and soon the system turns clear at room temperature. After reaction over night at RT, the resulting solution was extracted several times by using aqueous solution of potassium carbonate. Then it was dried over night with magnesium sulphate prior to remove the solvent via Rotovapor at 35-40°C under vacuum. Liquid resin was collected.

[0032] Example 5: IEM-based monoimidazole-monomethacrylate Resins (Figure 11) was prepared via a two-step process as described in the following: to a 500ml 3-nech round flask, 237grams of AMAHP and 146.2grams of 2-isocynate ethoxylmethacrylate(IEM), and 0.53gam of DBTOL were charged at 35°C. Keep reaction for 6hrs. 339grams liquid resin was collected. Then 185.1 grams of the precursor resin and 800ml of methylene dichloride were charged into a 1000ml three neck round flask at room temperature. Then slowly it was added of 55.5 grams of imidazole crystalline powder. Keep reaction for overnight. The resulting solution was extracted several times by using aqueous solution of potassium carbonate. Then it was dried over night with magnesium sulphate prior to remove the solvent via Rotovapor at 35-40°C under vacuum. 214grams of liquid resin was collected.

Table 1: Compositions for Various Bisimidazole Dimethacrylate Resins

	Example 3	Example 1	Example 2
Resin Composition	AMAHP/HEMA	Isosorbide/AMAHP/TEGDMA	TCDC/AMAHP/TEGDMA
IMMA Resin, TEGDMA,	100 0	90 10	90 10

(wt/wt, %)			
Resin Form	Liquid	Liquid	liquid
Viscosity @ 20°C Pa.s	3	690	40
Solubility @ 37°C in water	partially soluble	partially soluble	partially soluble
Solubility @ 37°C in water/ethanol(50:50,w/w%)	soluble	soluble	soluble

Table 2: Physical Property for Various Imidazole-based Resin Complexes

	Example 1 Complex A	Example 1 Complex B	Example 1 Complex C
	50% Example 1/TEGDMA(80/20) 50% OEMA/TEGDMA(75/25)	50% Example1/TEGDMA(80/20) 50% PENTA/TEGDMA(75/25)	33% Example 1 67% PAA(50K, 25% in Water)
As-aged2dRT Viscosity@20°C Pa.s	23	85	N/A
As-aged2wksRT Viscosity@20°C Pa.s	20	1610	elastic gel

* TEGDMA = Triethylene glycol dimethacrylate

OEMA = 4,4'-oxydiphenylether 1,1',6,6'-tetracarboxylic acid-1,1'-(2-methacryloxy) dimethacrylate

PENTA = Dipentaerythritol penta-acrylate phosphate

Table 3: Physical Property for Various Formulated Imidazole Resins

	Formulated Imidazole Resin 1	Formulated Imidazole Resin 2	Formulated Imidazole Resin 3
	80% Example 1 20% TEGDMA 0.165% CQ 0.30% EDAB 0.015% BHT	100% Example 3 0.165% CQ 0.30% EDAB 0.015% BHT	100% BIDMA Resin 3 0.165% CQ 0.30% EDAB 0.015% BHT
Viscosity@20°C Pa.s	12	10	60
Shrinkage @ 24hrs %	NA	NA	NA
Stress @ 60 min MPa	1.10	2.30	0.45/0.30
ΔH_1 in N ₂ @ UV-Vis J/g	119	107	83
t_0 seconds	14	17	28
t_{max} seconds	42	40	58
ΔH_1 in N ₂ @ Vis J/g	121	103	83
t_0 seconds	15	16	30
t_{max} seconds	45	38	77

*BIDMA = Bisimidazole-dimethacrylate

Table 4: Physical Property for Various Formulated Imidazole Resins

	Formulated Imidazole Resin 4	Formulated Imidazole Resin 5	Formulated Imidazole Resin 6	Formulated Imidazole Resin 7
	80% Example 1 20% TEGDMA 0.165% CQ 0.30% EDAB 0.015% BHT	80% Example 1 20% BIDMA Resin 4 0.165% CQ 0.30% EDAB 0.015% BHT	80% Example 1 20% HEMASA 0.165% CQ 0.30% EDAB 0.015% BHT	67% Example 1 13% MA Acid 20% TEGDMA 0.13% CQ 0.012% BHT 0.32% LTPO
Viscosity@20°C Pa.s	15	160	280	12
Shrinkage @ 24hrs %	NA	NA	NA	NA
Stress @ 60 min MPa	1.70/1.00	1.15/0.50	0.45/0.32	3.50/2.40
ΔH_1 in N ₂ @ UV-Vis J/g	108	86	89	136
t_0 seconds	20	23	22	9
t_{max} seconds	48	47	50	28
ΔH_1 in N ₂ @ Vis J/g	101	81	79	131
t_0 seconds	21	24	25	8
t_{max} seconds	53	48	66	29

Table 5: Physical Property for Various Formulated Imidazole Composites

	Composite 1	Composite 2	Composite 3	Composite 4
Resins	19.42% IMMA Resin 67% Example 1 13% MA Acid 20% TEGDMA 0.13% CQ 0.012% BHT 0.32% LTPO	21.05% IMMA Resin 80% Example 1 20% TEGDMA 0.165% CQ 0.30% EDAB 0.015% BHT	20% Conventional 100% EsthetXflow Resin 0.10% CQ 1.30% EDAB 0.005% BHT	20% Conventional 100% EsthetXflow Resin 0.10% CQ 1.30% EDAB 0.005% BHT 1.2% Uvinol M-40 0.196% Flublau conc.
Fillers (wt/wt)	80.58%	78.95%	(80.0%)	80.0%
Stickiness@37°C mm	NA	NA	0.60	1.30
Stress @ 60 min MPa		2.30/1.92	1.81/2.58	
ΔH_1 in N ₂ @ UV-Vis J/g	29	25	25	
t ₀ seconds	2	9	36	
t _{max} seconds	23	46	117	
ΔH_1 in N ₂ @ Vis J/g	26	24	22	
t ₀ seconds	4	14	21	
t _{max} seconds	28	47	107	

[0033] One of typical acid-neutralizing polymerizable resins is polymerizable imidazole resin (Example 3) as shown in Figure 9, which structurally is a dimethacrylate resin containing imidazole moiety. Imidazole is well known for its rather basic property; in fact it is approximately sixty times more basic than pyridine. Thus it should indicate that imidazole is intrinsically capable to neutralize readily most of acidic compounds. In addition, unlike other organic basic compounds, such as tertiary amine, imidazole is stable towards oxidants and would not involve in any redox/H-abstraction reactions that occurred in self-cure and/or light-cure process.

[0034] There has been a compatibility issue between a simplified adhesive and a typical BPO/amine based resin cement in self-cure mode. It is believed that acid-base reaction between acid monomer in a simplified adhesive and amine in cement causes deactivation of amine as co-initiator. It was thought that a cement incorporating Resin Example 3 could neutralize acids in a simplified adhesive to mitigate or eliminate the issue of deactivation of amine in the cement. As a result, the incompatibility of a simplified adhesive and resin cement in self-cure mode may be reduced or eliminated.

Table 6. Base Resin Blend-1 with Imidazole-based Monomer

	% By Wt.
Nupol™	20.000
Example 3	65.980
TEGDMA	10.000
Camphorquinone (CQ)	0.150
EDAB	0.160
DHEPT	1.700
Uvinul™ M40	2.000
BHT	0.010
Total	100.000

Table 7. Catalyst Resin Blend-2 with Imidazole-based Monomer

	% By Wt.
Nupol	20.000
Example 3	67.700
TEGDMA	10.000
Benzoyl Peroxide (BPO)	2.200
BHT	0.100
Total	100.000

Table 8. Base Paste-1 with Imidazole-based Monomer

	% By Wt.
Blend-1	32.600
Filler	67.400
Total (paste)	100.000

Table 9. Catalyst Paste-2 with Imidazole-based Monomer

	% By Wt.
Blend-2	38.000
Filler	62.000
Total	100.000

[0035] When the catalyst Paste-2 was stored at RT for 72 hrs, a chunk of solid mass was seen on the bottom, most possibly due to some premature polymerization. It is assumed that some impurities in Resin Example 3 may act as self-cure co-initiators.

[0036] Comparative data results of the experimental cement and the control of Calibra are presented on Table 5 and 6. In summary, the experimental cement is compatible with Prime&Bond NT without the use of Self-cure Activator (SCA). The bond strength on dentin for Prime&Bond NT to bond the experimental cement in self-cure on dentin is similar to Prime&Bond NT in combination with a Self-cure Activator, whereas without a self-cure activator, Prime&Bond NT essentially does not bond Calibra in self-cure on dentin. The overall mechanical performance of experimental cement is similar to that of Calibra, except for somewhat lower flexural modulus.

Table 10. 24 hr shear bond strength (SBS) of Prime&Bond NT to Bond cements in Self-cure on Dentin

Bonding Agent	Prime&Bond NT	Prime&Bond NT/ SCA (1:1)	Prime&Bond NT	Prime&Bond NT
Cement	Calibra base/catalyst (1:1)	Calibra base/catalyst (1:1)	Paste-1/Paste-2 (1:1)	Paste-1/ Calibra catalyst (1:1)
SBS (MPa)	1.9 (2.2)	14.1 (2.7)	12.0 (2.5)	16.2 (3.4)

Table 11. Mechanical Properties Paste-1/Calibra Catalyst vs. Calibra base/catalyst in SC

	Paste-1/Calibra catalyst	Calibra base/catalyst
CS (MPa)	274 (11)	278 (8)
FS (MPa)	98 (9)	103 (14)
FM (MPa)	6173 (643)	7086 (297)

*FS = Flexural Strength; FM = Flexural Modulus

Table 12. Base Resin Blend-3 Containing DMEMA

	% By Wt.
Nupol	62.330
DMEMA	23.650
TEGDMA	10.000
Camphorquinone (CQ)	0.150
EDAB	0.160
DHEPT	1.700
Uvinul M40	2.000
BHT	0.010
Total	100.000

*DMEMA= 2-(Dimethylamino)ethyl methacrylate

EDAB = Ethyl-4-dimethylamino benzoate

DHEPT = N-N-bis(2-hydroxyethyl)-p-toluidine

Table 13. Base Paste Paste-3 with DMEMA

	% By Wt.
Blend-3	32.600
Filler	67.400
Total (paste)	100.000

[0037] When Paste-3 was mixed with Calibra catalyst paste (1:1), no curing into solid was observed even after 3 hrs.

Table 14. Base Resin Blend-4 with 4-VPy

	% By Wt.
Nupol	69.080
4-Vpy	15.820
TEGDMA	11.080
Camphorquinone (CQ)	0.150
EDAB	0.160
DHEPT	1.700
Uvinul M40	2.000
BHT	0.010
Total	100.000

*4-Vpy = 4-Vinylpyridine

Table 15. Base Paste-4 with 4-VPy

	% By Wt.
Blend-4	32.600
Filler	67.400
Total (paste)	100.000

Table 16. Base Resin Blend-5 with MEMA

	% By Wt.
Nupol	56.880
MEMA	29.980
TEGDMA	9.120
Camphorquinone (CQ)	0.150
EDAB	0.160
DHEPT	1.700
Uvinul M40	2.000
BHT	0.010
Total	100.000

*MEMA= 2-N-Morpholinoethyl methacrylate

Table 17. Base Paste Paste-5 with MEMA

	% By Wt.
Blend-5	32.600
Filler	67.400
Total (paste)	100.000

Table 18. 24 hr SBS of Prime&Bond NT to Bond Cements in Self-cure on Dentin

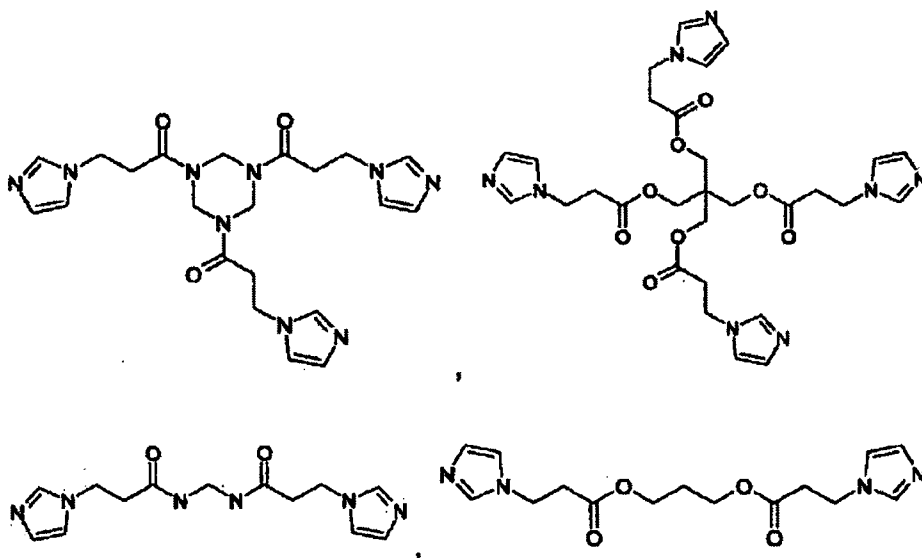
Bonding Agent	Prime&Bond NT	Prime&Bond NT/ SCA (1:1)	Prime&Bond NT	Prime&Bond NT
Cement	Calibra base/ catalyst (1:1)	Calibra base /catalyst (1:1)	Paste-4/ Calibra Catalyst (1:1)	Paste-5/ Calibra Catalyst (1:1)
SBS (MPa)	1.9 (2.2)	14.1 (2.7)	10.8 (3.4)	6.1 (2.2)

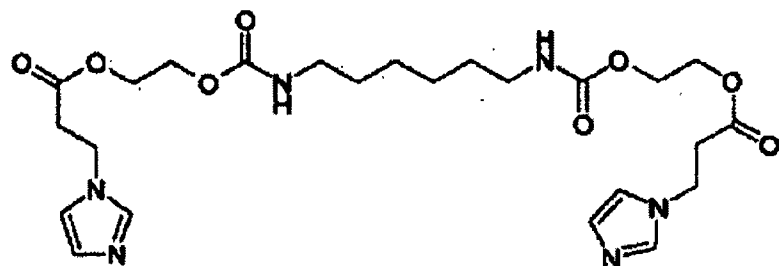
CLAIMS:

1. A dental composition comprising:

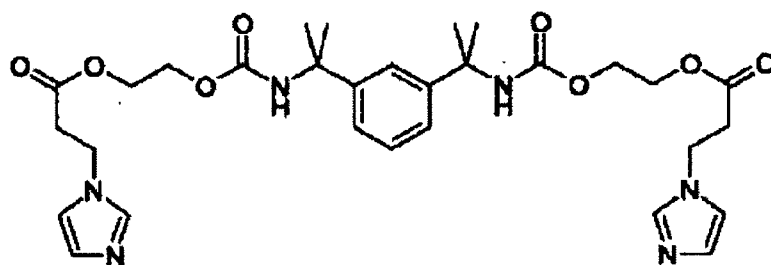
- a. 0.5-10% wt/wt of non-polymerizable acid-neutralizing resin (I) or 0.5-94.99% wt/wt of an acid-neutralizing polymerizable resin (II) or a mixture of (I) and (II), featuring a moiety that is capable to effectively neutralizing an acid group, where the neutralized acid group is a carboxylic acid, a sulphonic acid, a phosphonic acid or a phosphoric acid,
- b. 5-90% wt/wt of mixed conventional polymerizable resins;
- c. 0.01-5.00% of initiators and other additives;
- d. 0-90% wt/wt of a plurality of filler particles ranged from 10 nm-50 micron;

wherein the non-polymerizable acid-neutralizing resin (I) is selected from the group consisting of

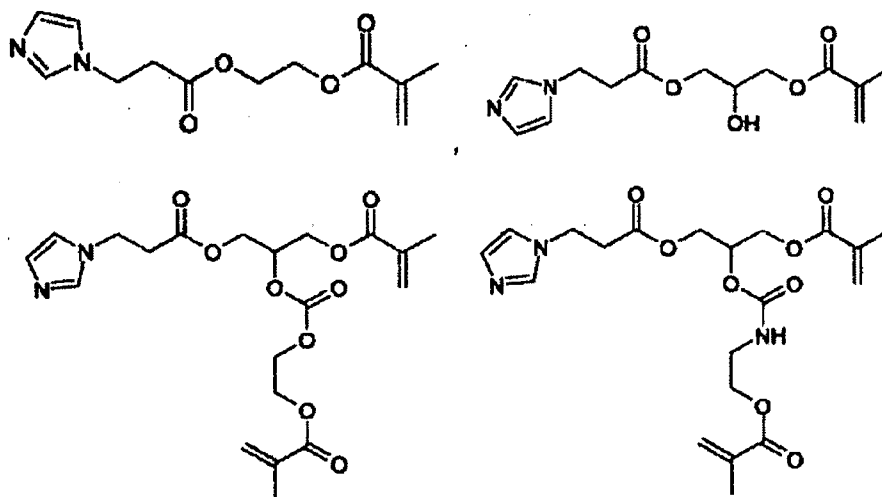


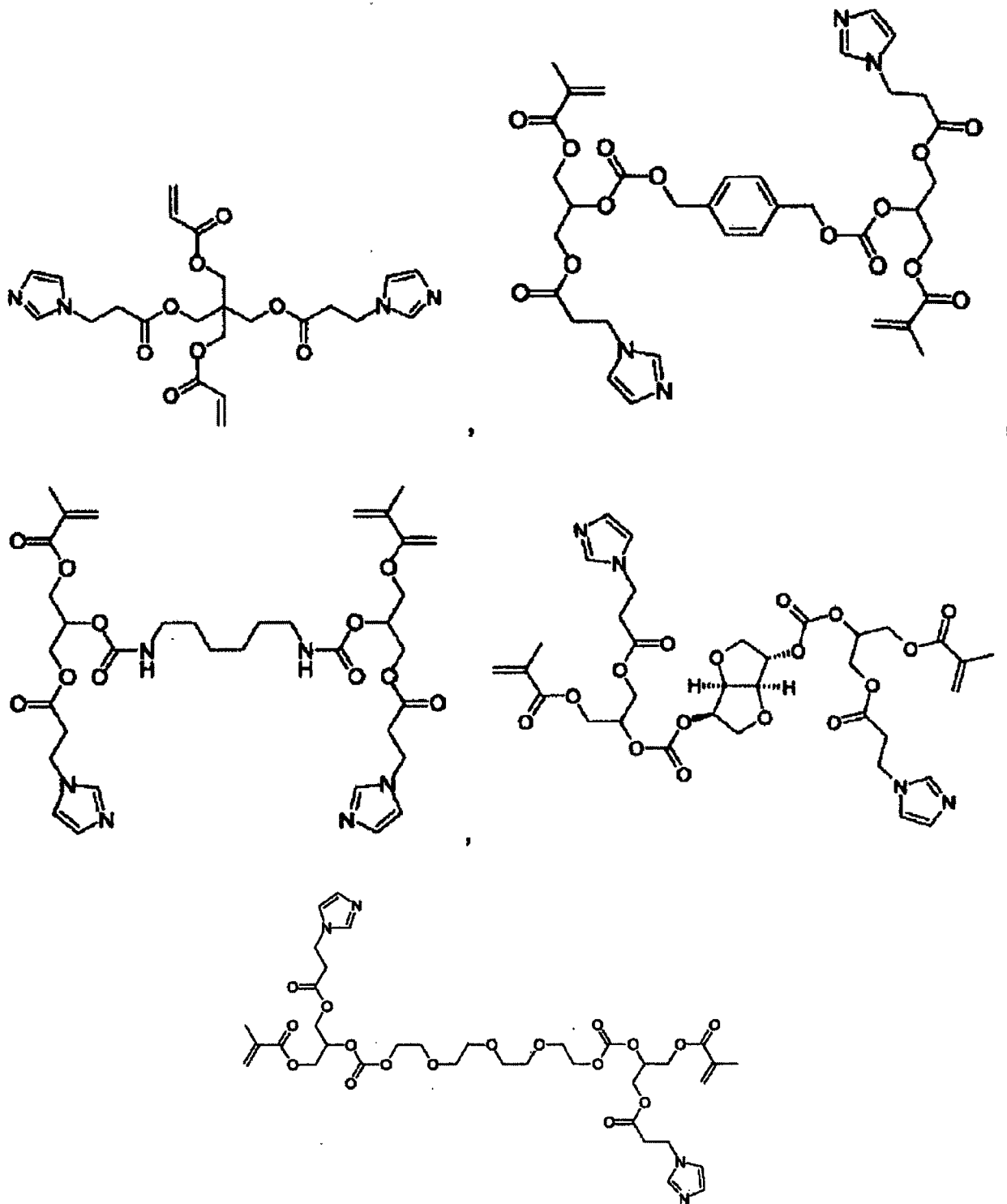


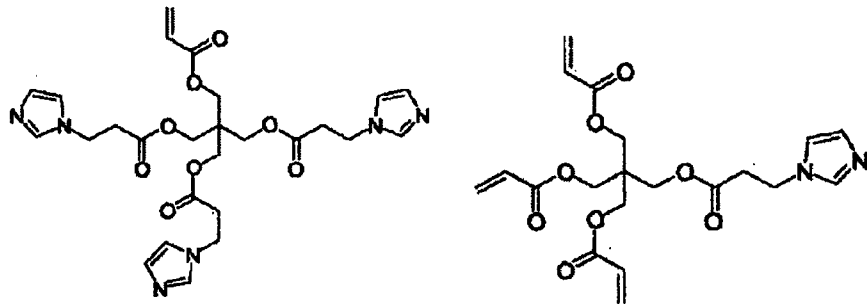
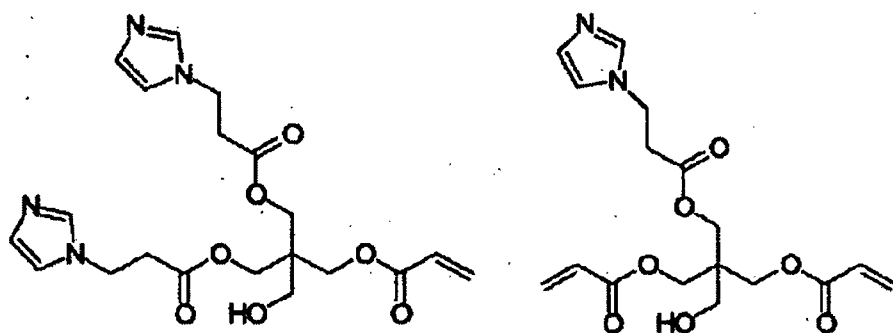
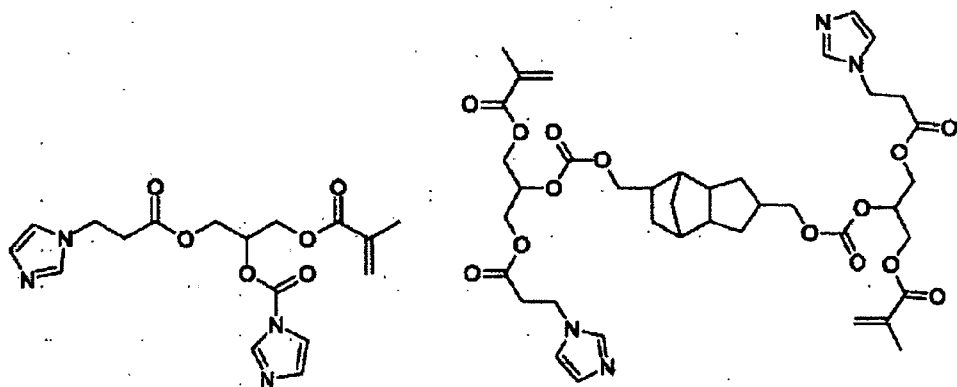
, and



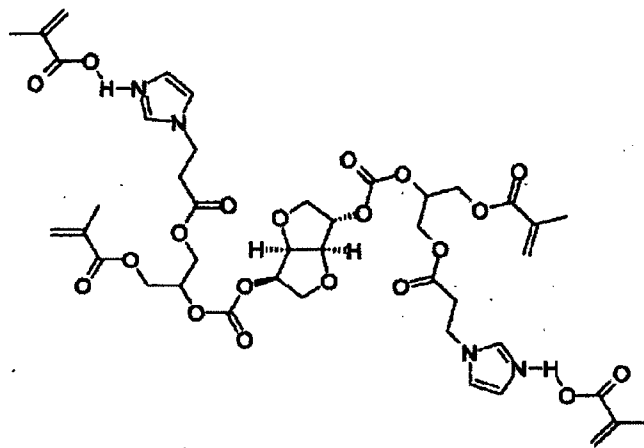
and wherein the polymerizable acid-neutralizing resin (II) is selected from the group consisting of



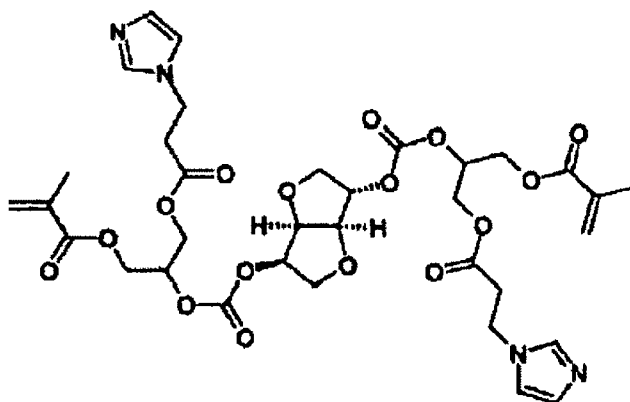




, and

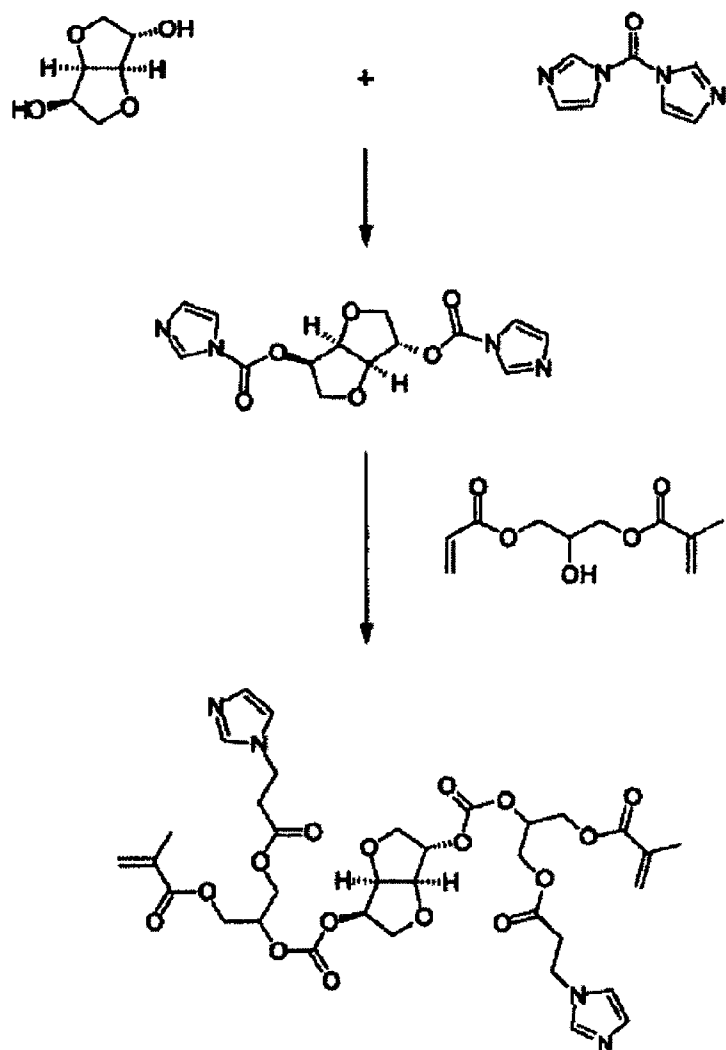


2. The dental composition of claim 1, for use with a dental adhesive without use of a self-cure activator.
3. The dental composition of claim 1, which has antibacterial capability.
4. The dental composition of claim 3, further comprising a salt of a weak acid.
5. An acid-neutralizing polymerizable resin (II) having the formula:



6. Process for preparing the acid-neutralizing polymerizable resin (II) of claim 5, which comprises subjecting the reaction product of 1,1-carbonyldiimidazole(CDI) and isosorbide to a reaction with 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AMAHP) according to the following:

81659470



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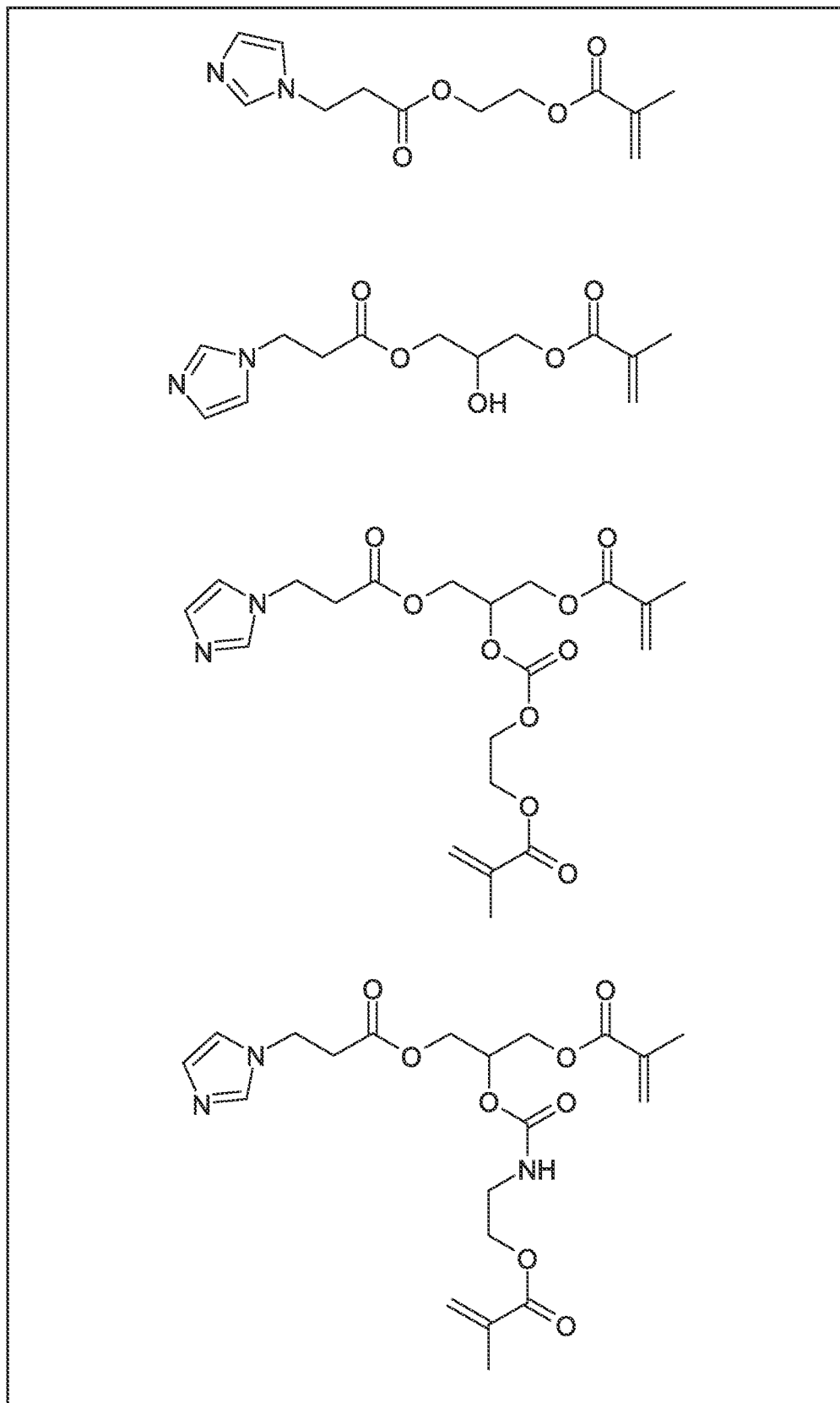


FIGURE 1

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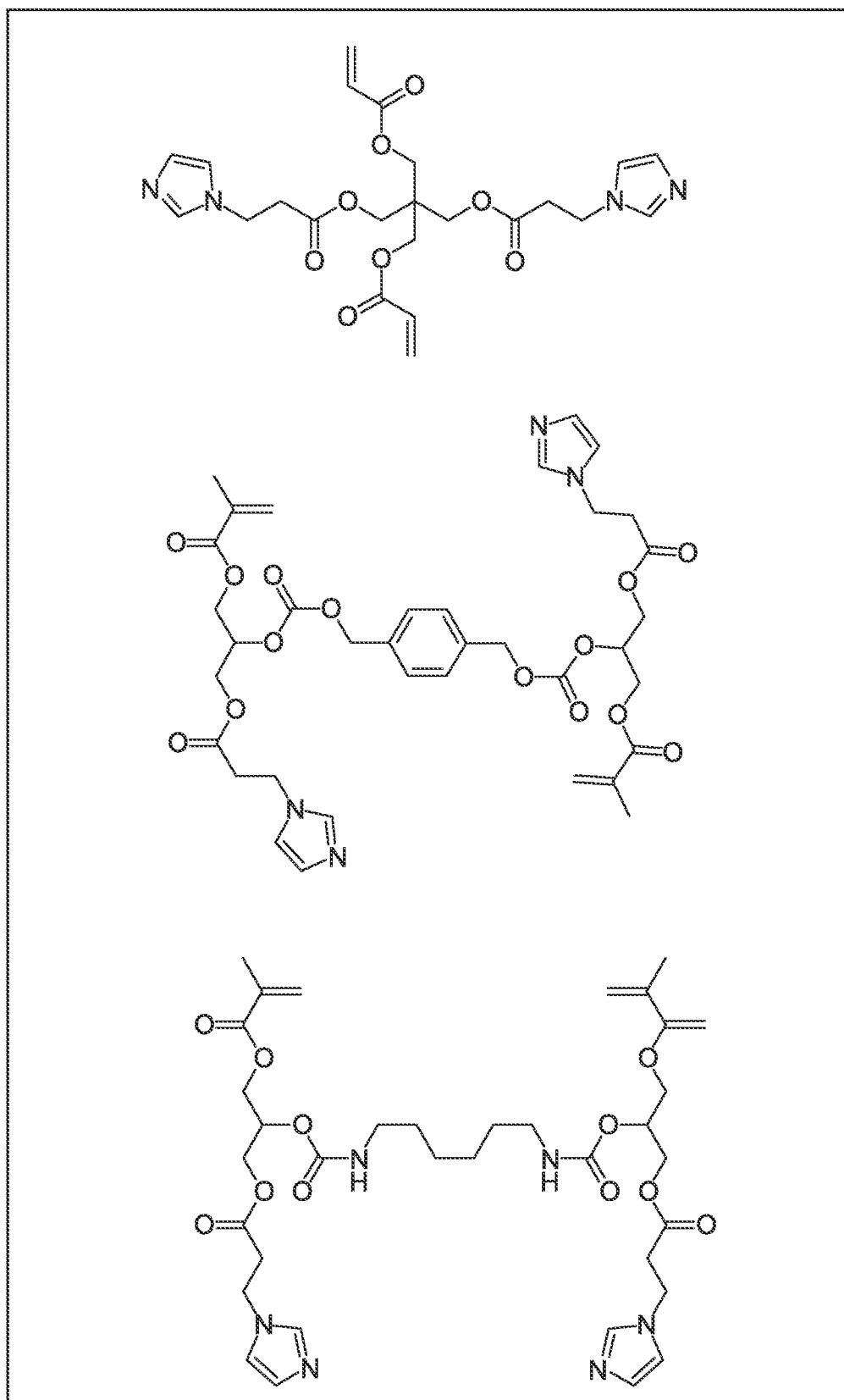


FIGURE 2

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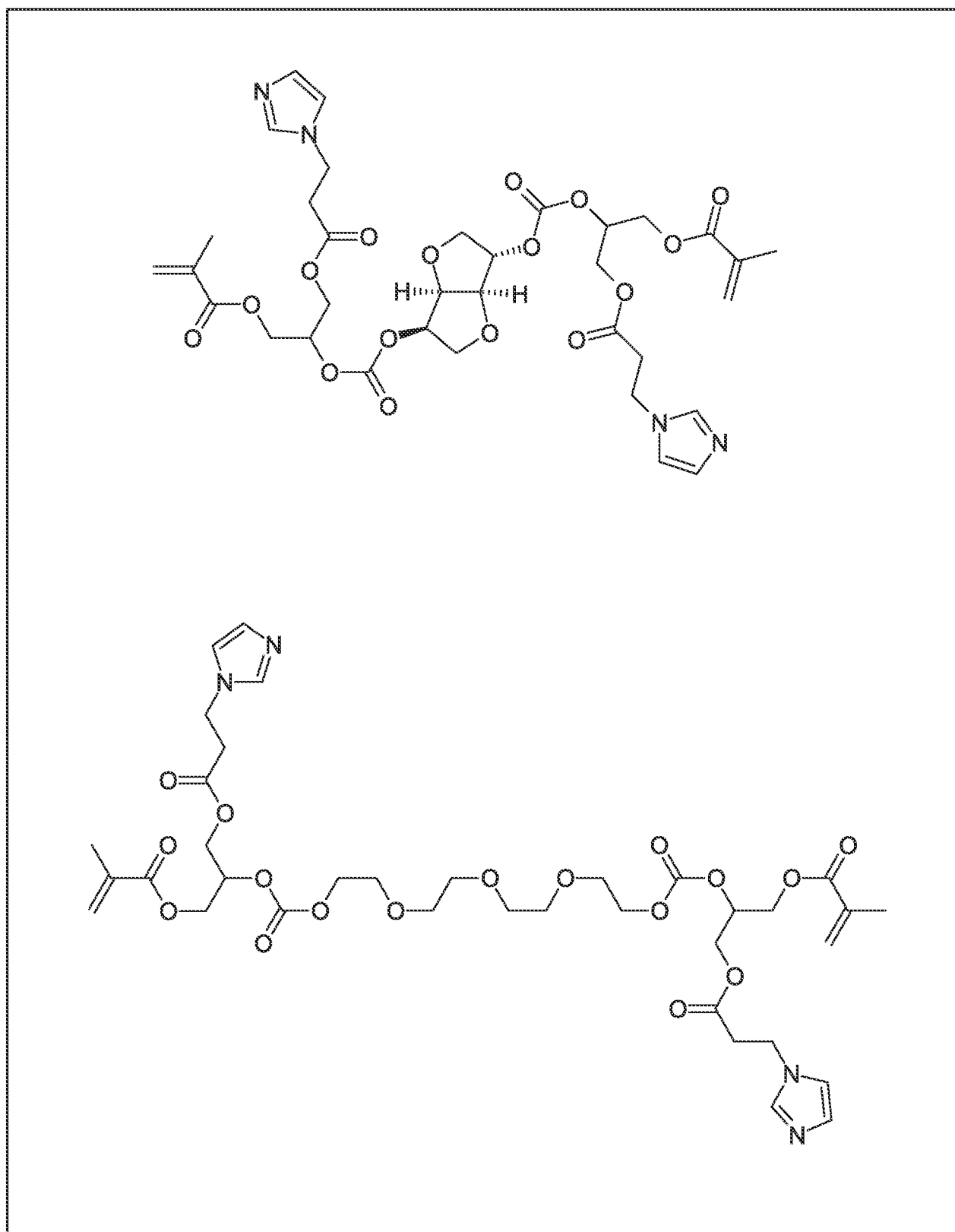
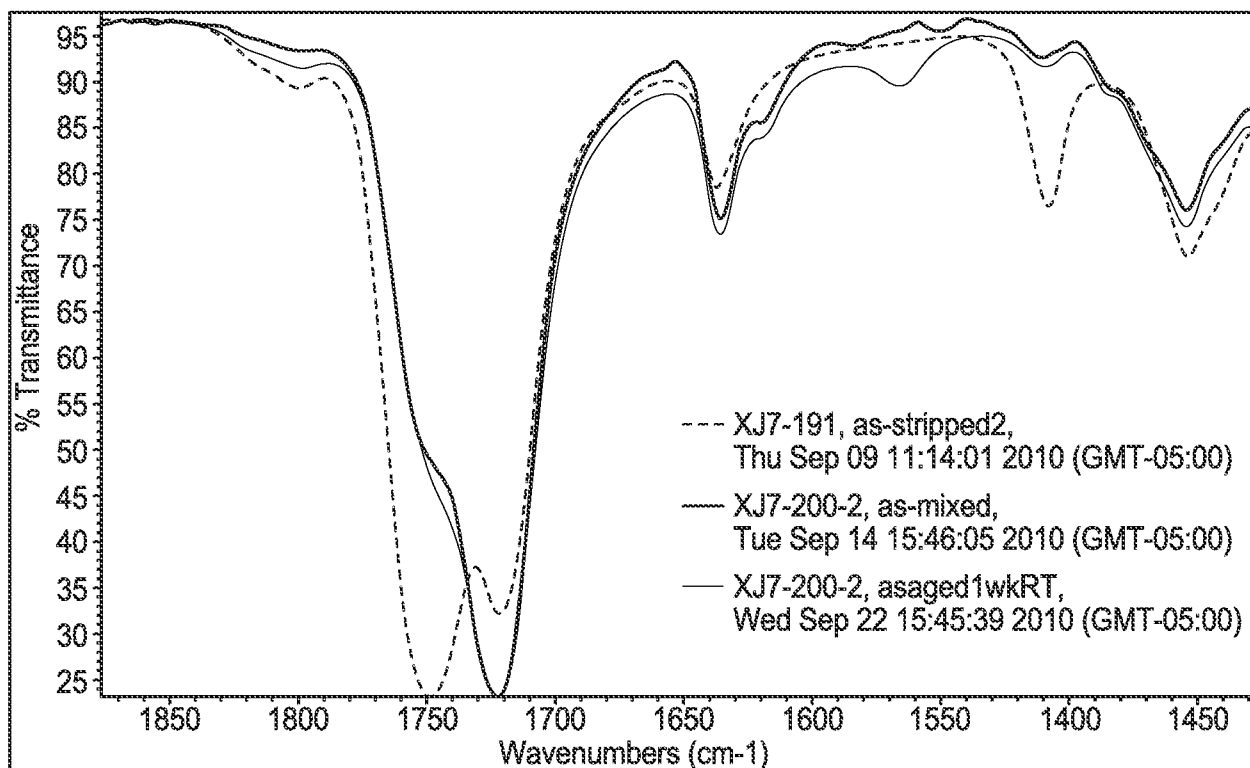
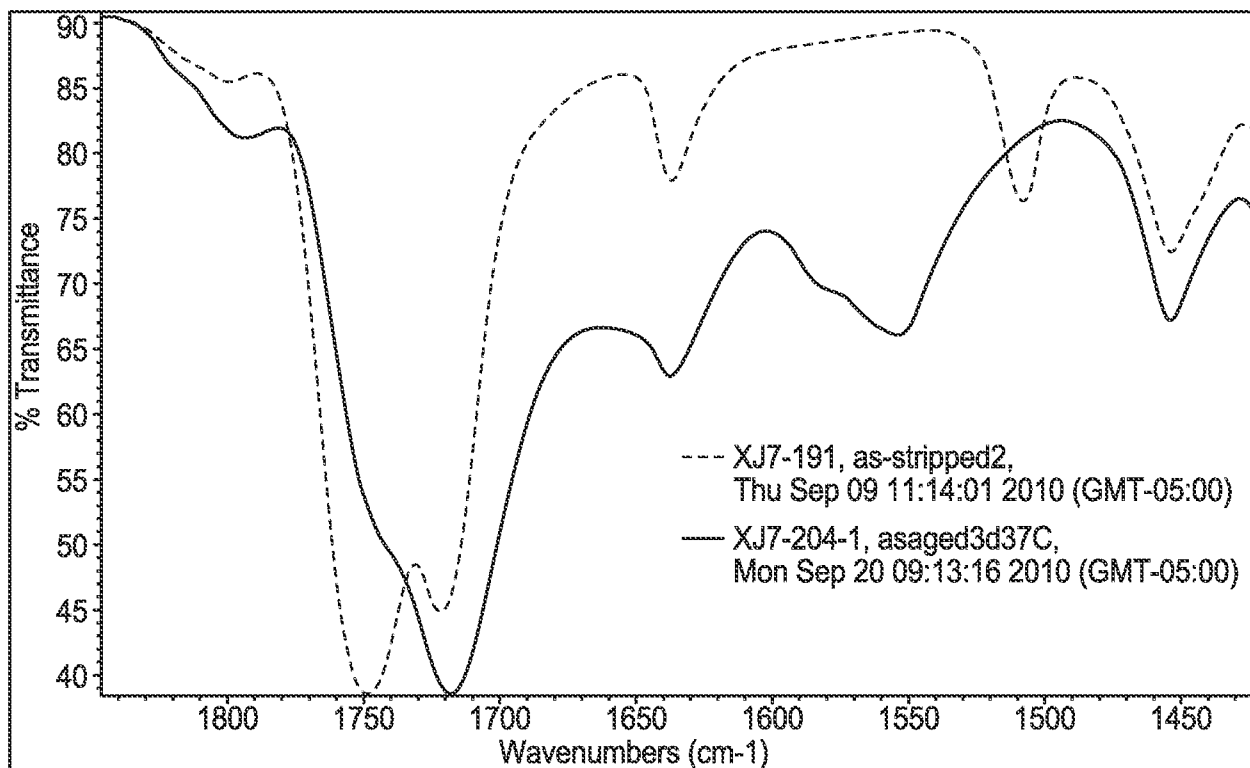


FIGURE 3

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**FIGURE 4****FIGURE 5**

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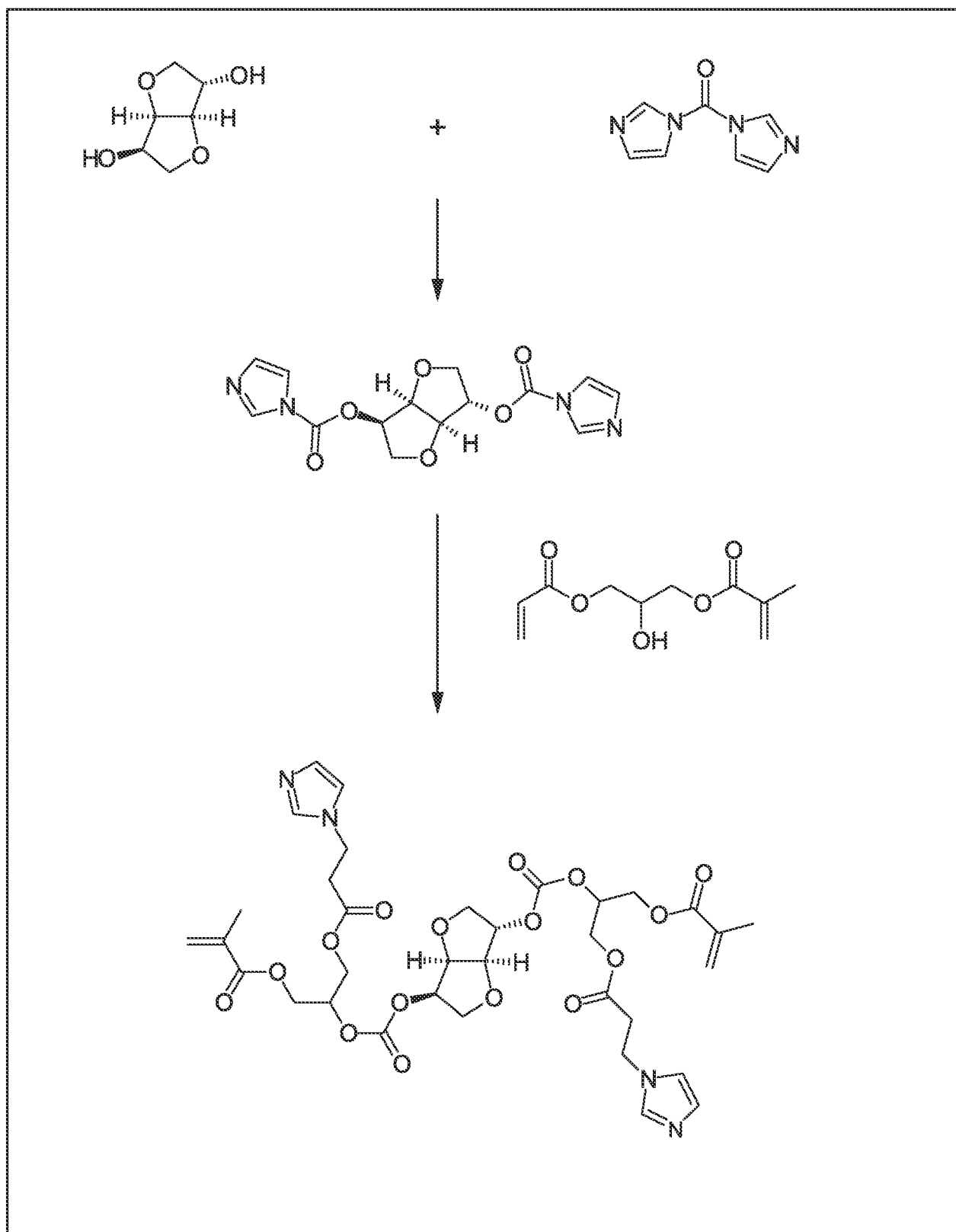


FIGURE 6

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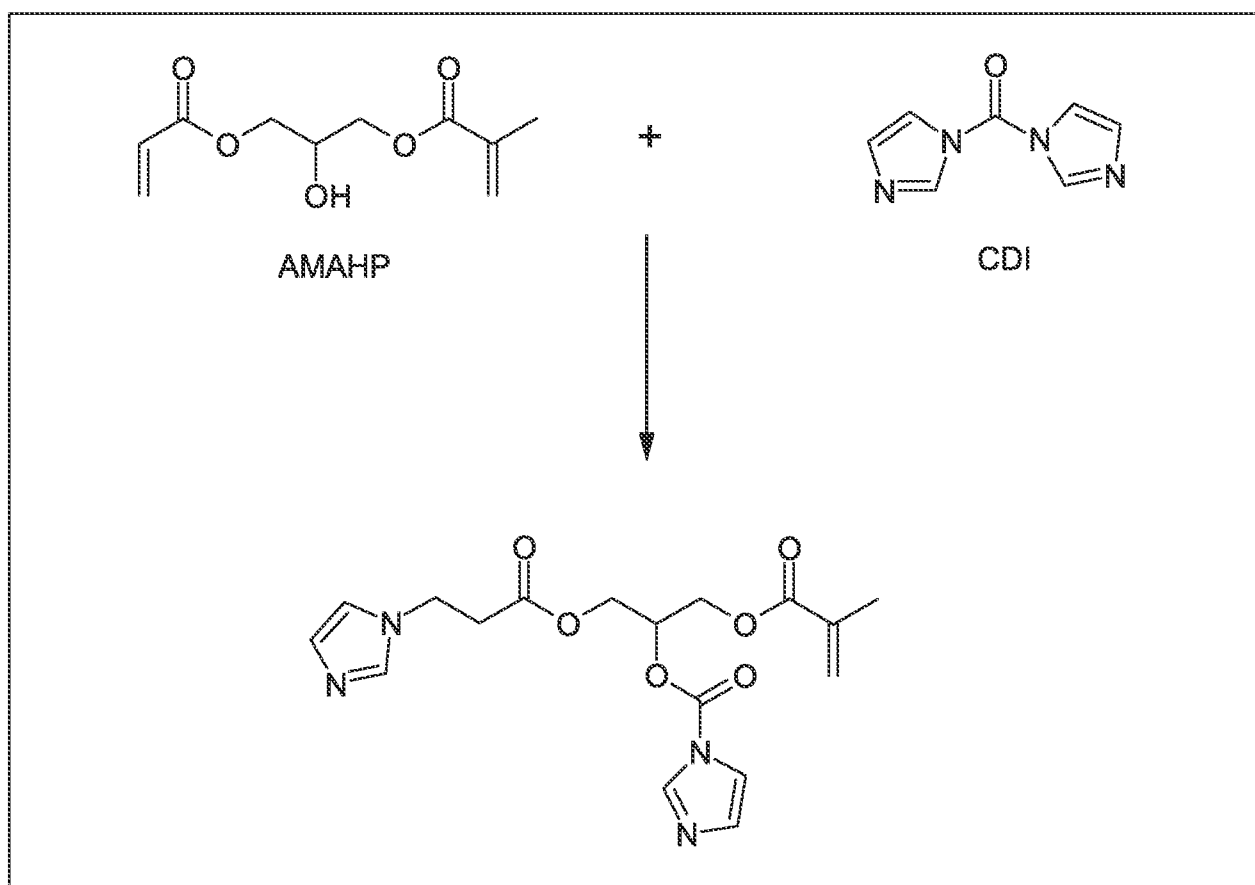
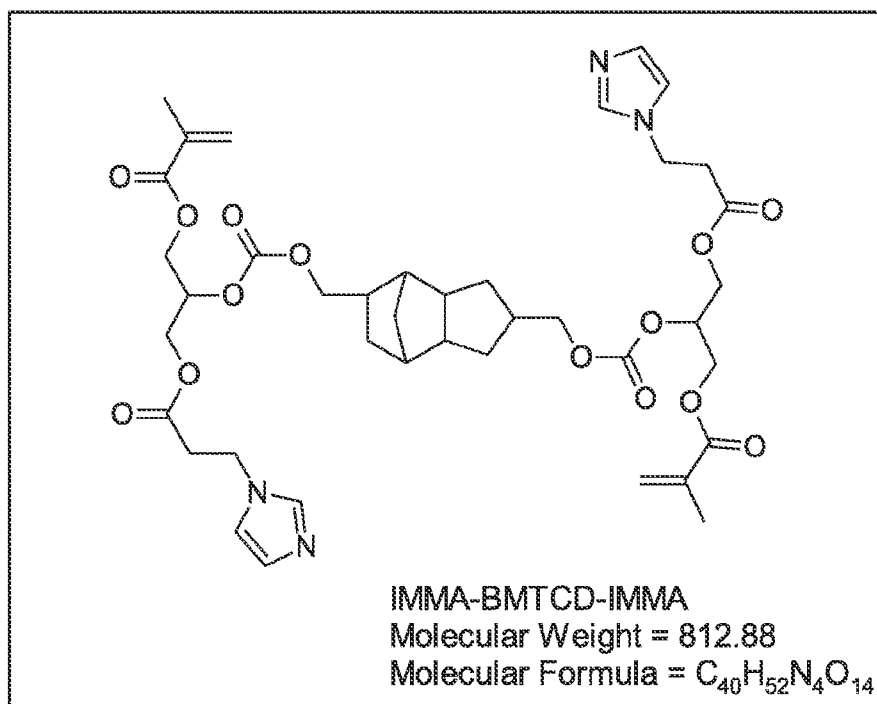
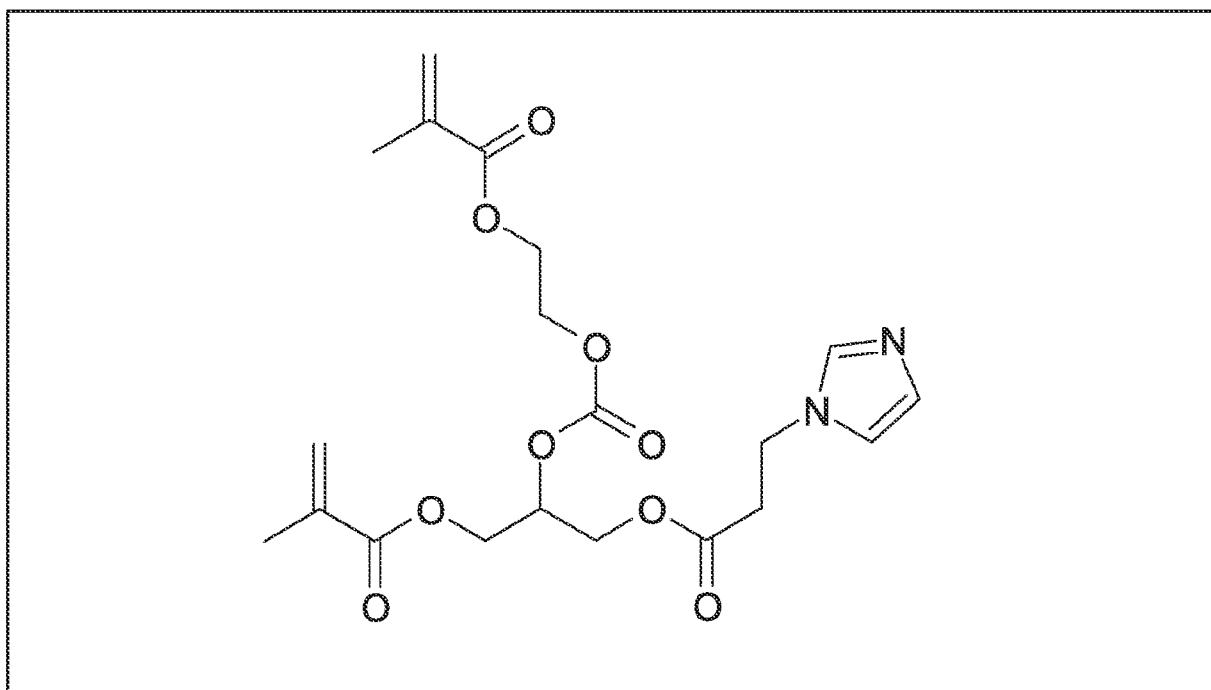


FIGURE 7

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**FIGURE 8****FIGURE 9**

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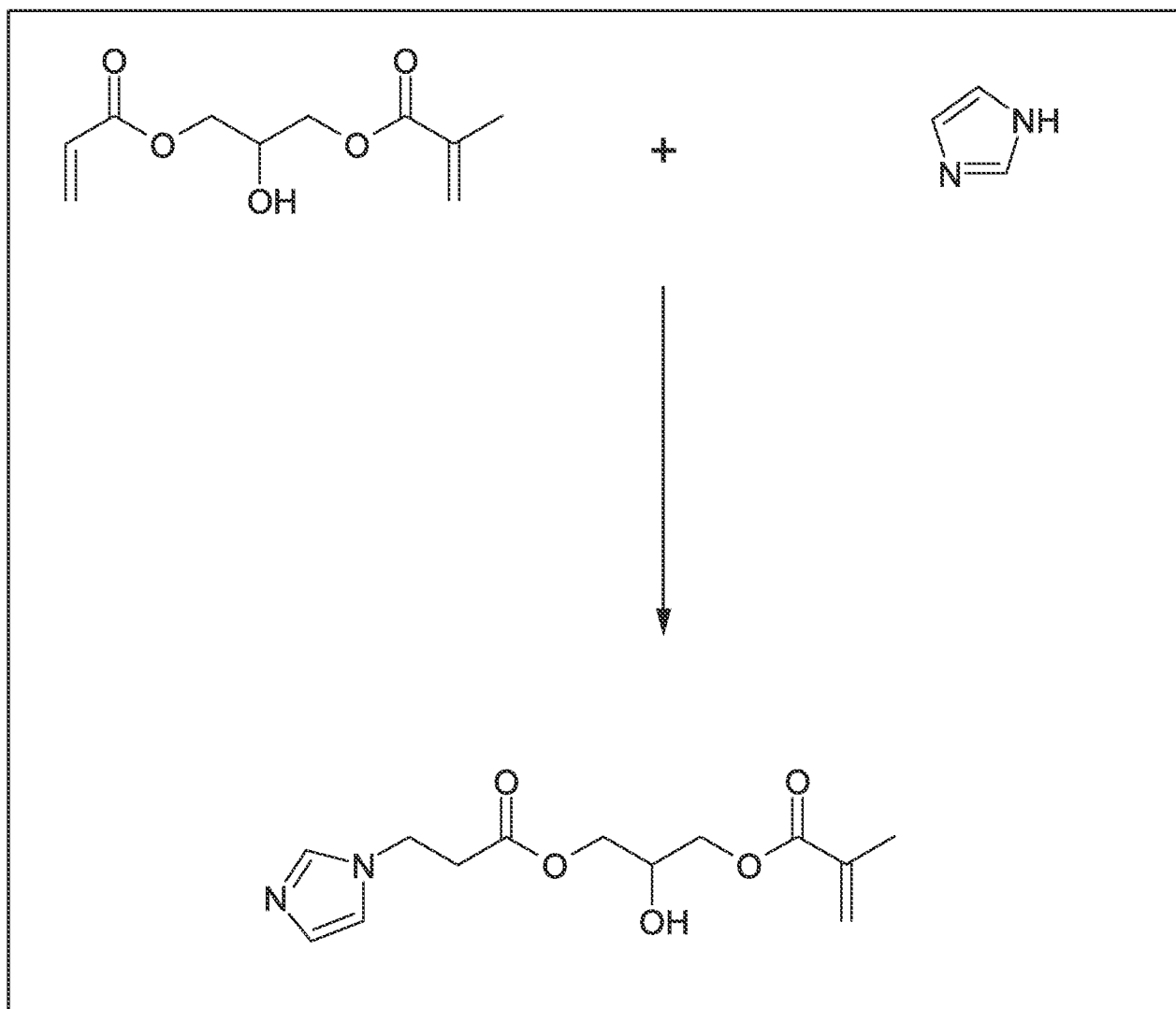


FIGURE 10

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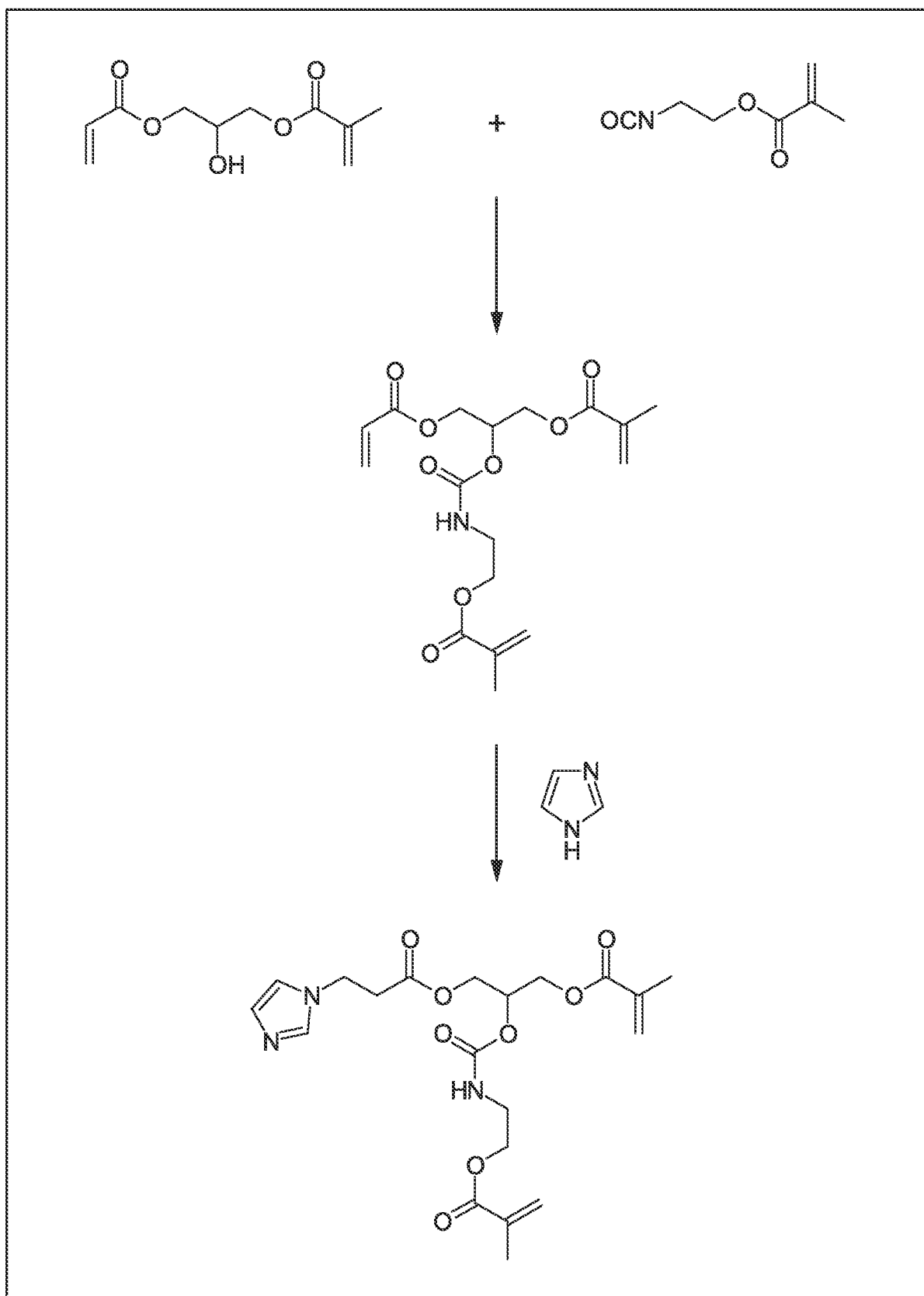


FIGURE 11

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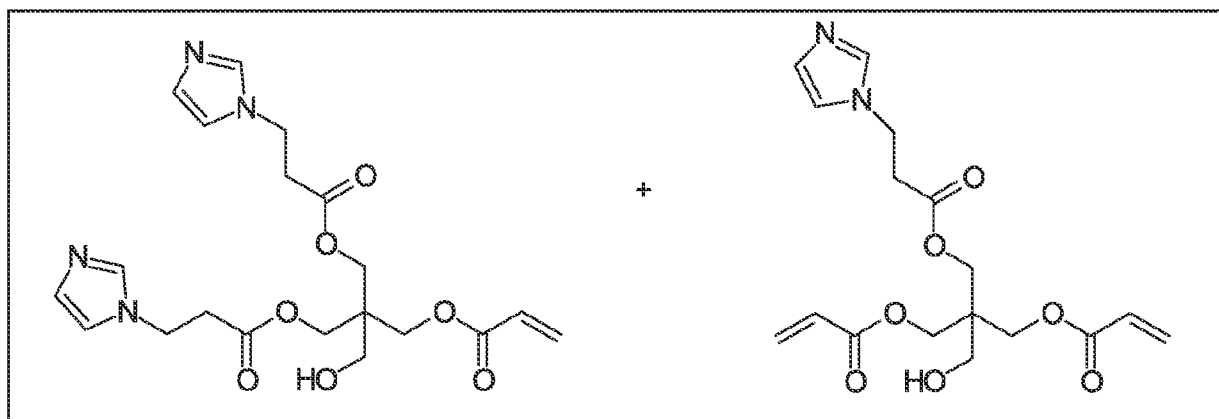


FIGURE 12

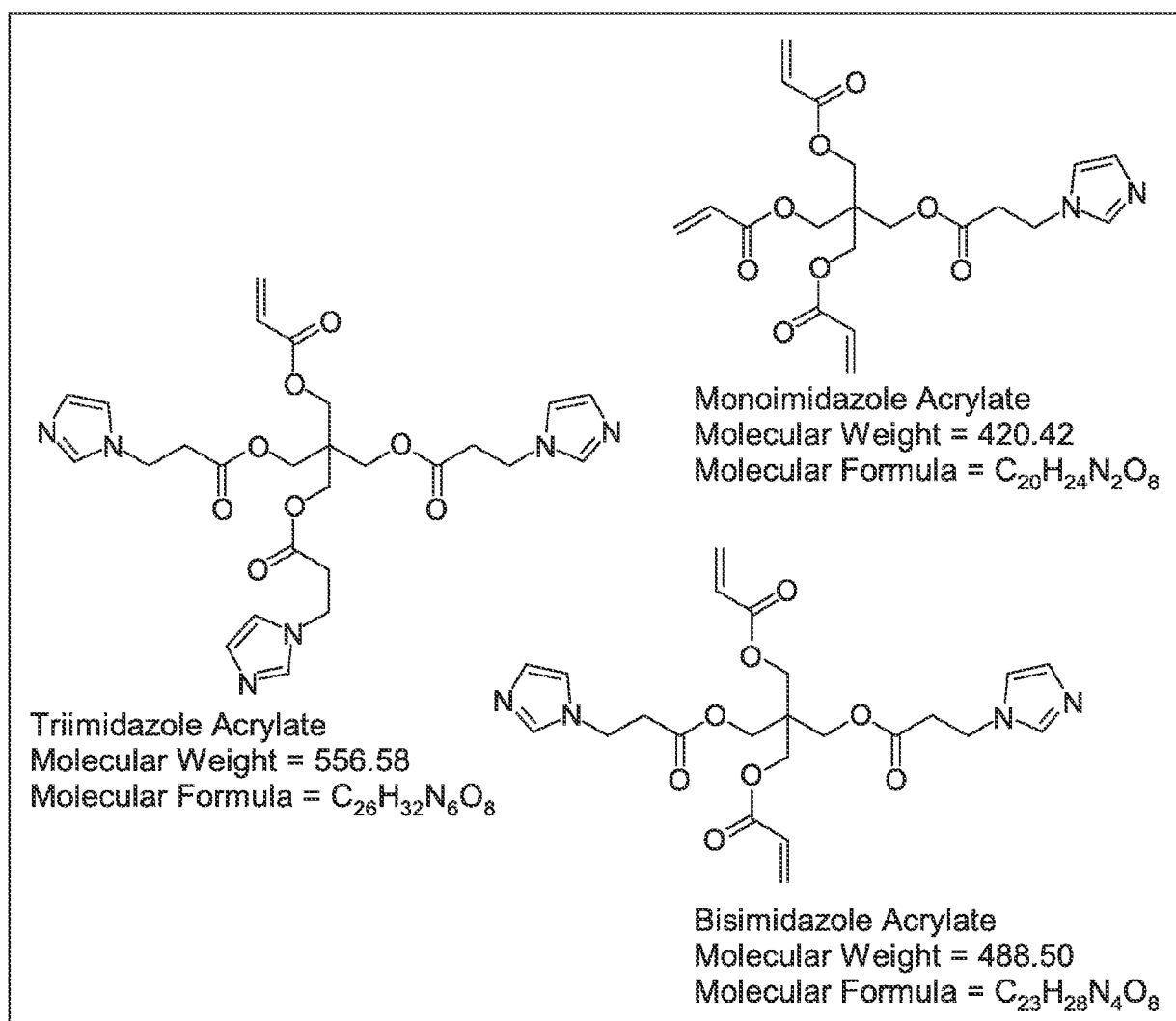


FIGURE 13

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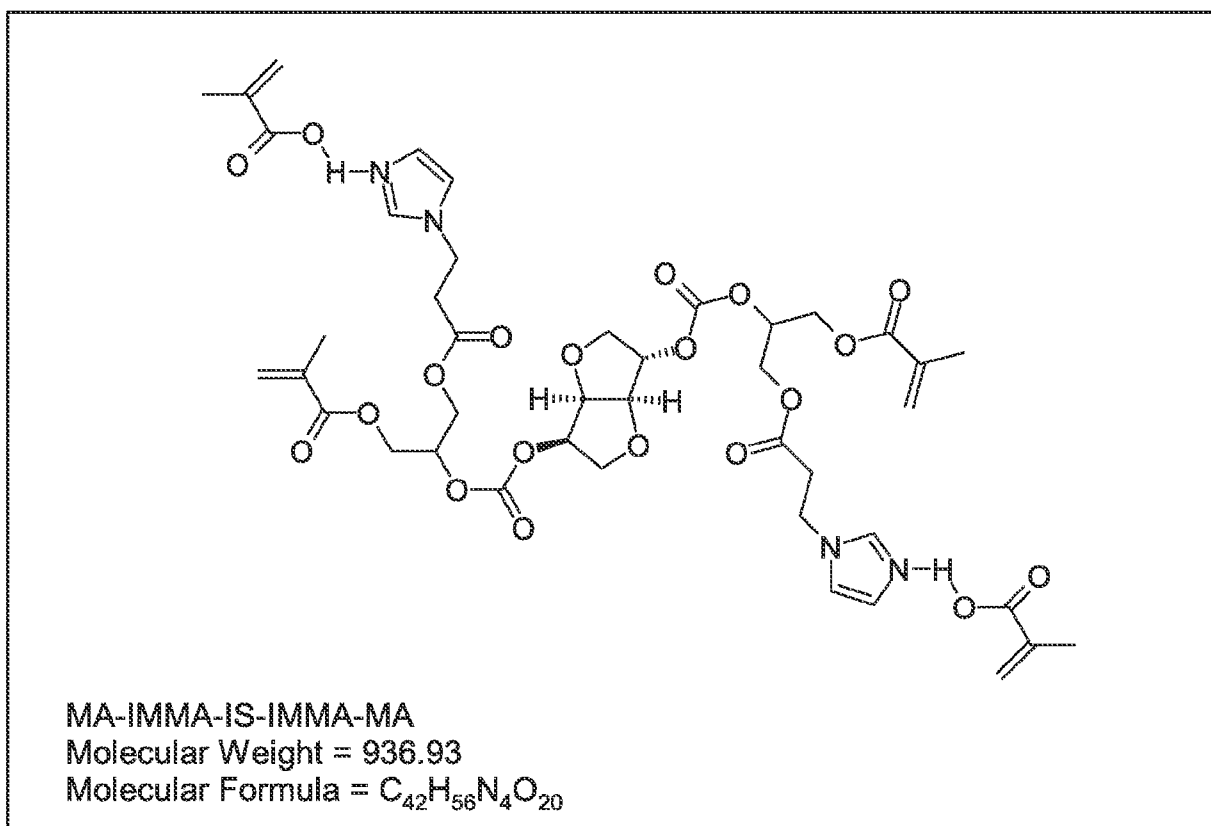
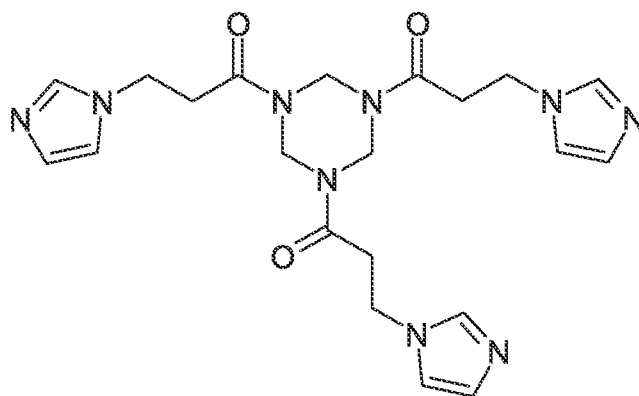


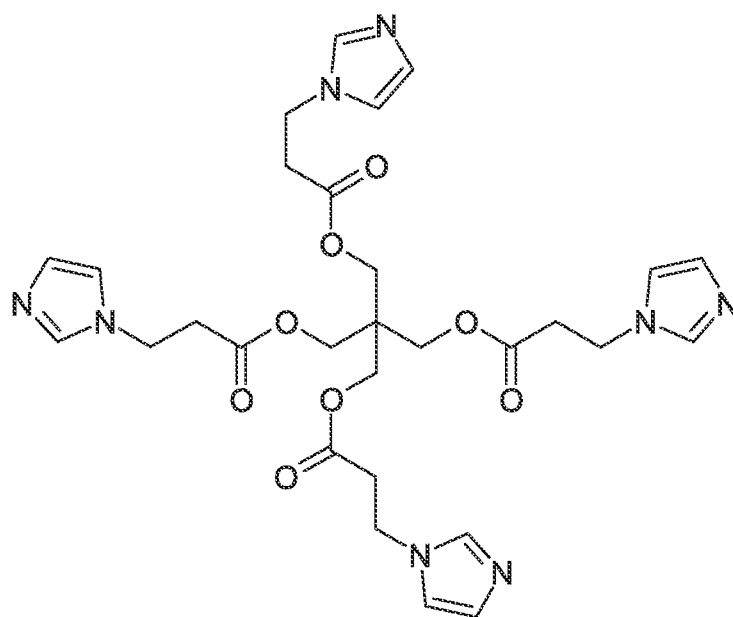
FIGURE 14

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TAT-Imidazoles

Molecular Weight = 453.51

Molecular Formula = $C_{21}H_{27}N_9O_3$ 

SR295-4-IM

Molecular Weight = 624.66

Molecular Formula = $C_{29}H_{36}N_8O_8$

FIGURE 15

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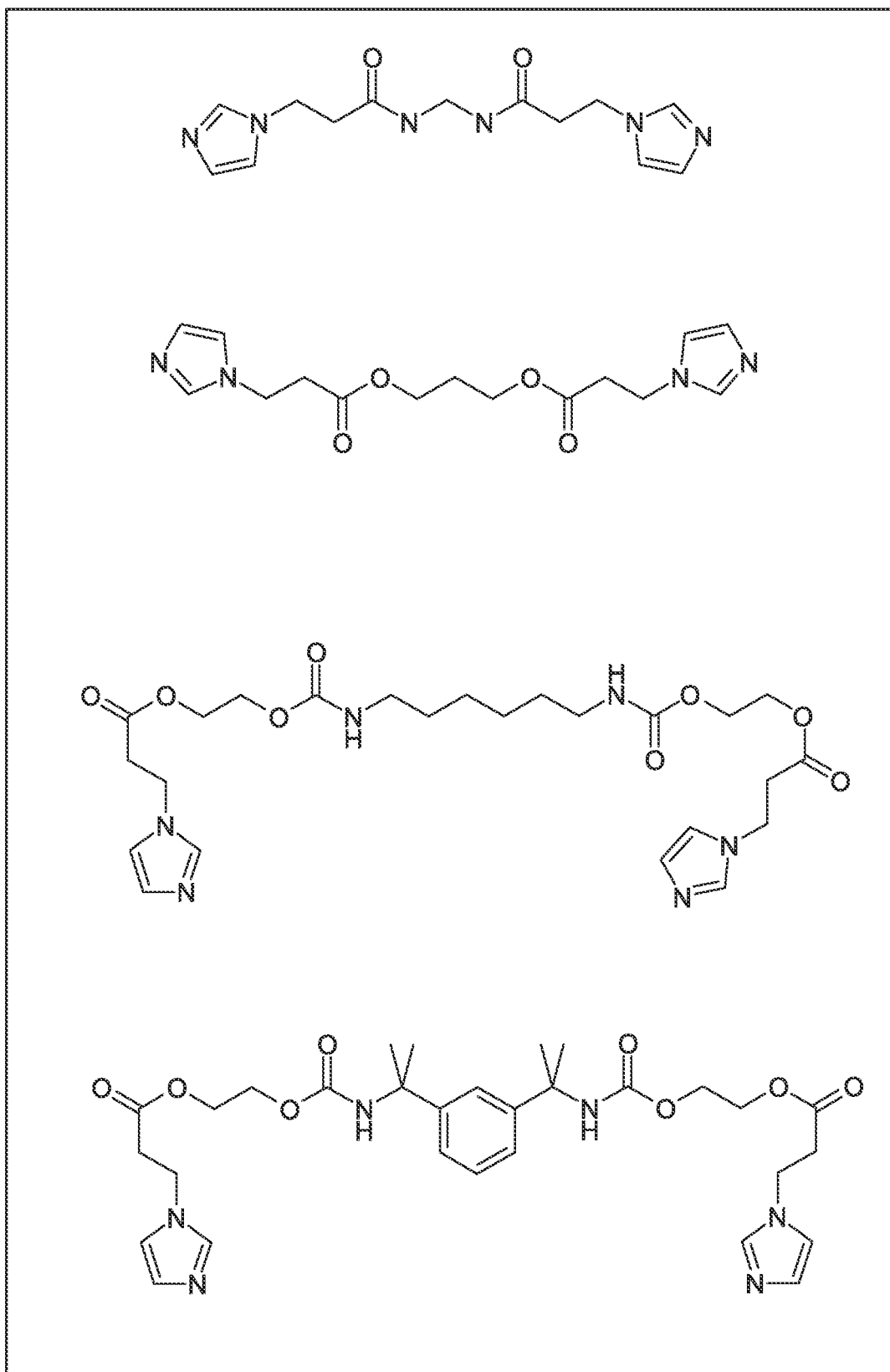


FIGURE 16