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(54) **IMIDAZOLE AND IMIDAZOLIUM RESINS AND METHODS FOR PREPARING CURABLE IMIDAZOLIUM ANTIMICROBIAL RESINS**

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Appl. No.: **13/530,248**
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A61K 31/74 (2006.01)
A61K 6/00 (2006.01)
A61K 6/083 (2006.01)

(52) **U.S. Cl.**
CPC *A61K 6/0067* (2013.01); *A61K 6/083* (2013.01)

(58) **Field of Classification Search**
CPC *A61K 6/0067*
USPC *424/78.08*
See application file for complete search history.

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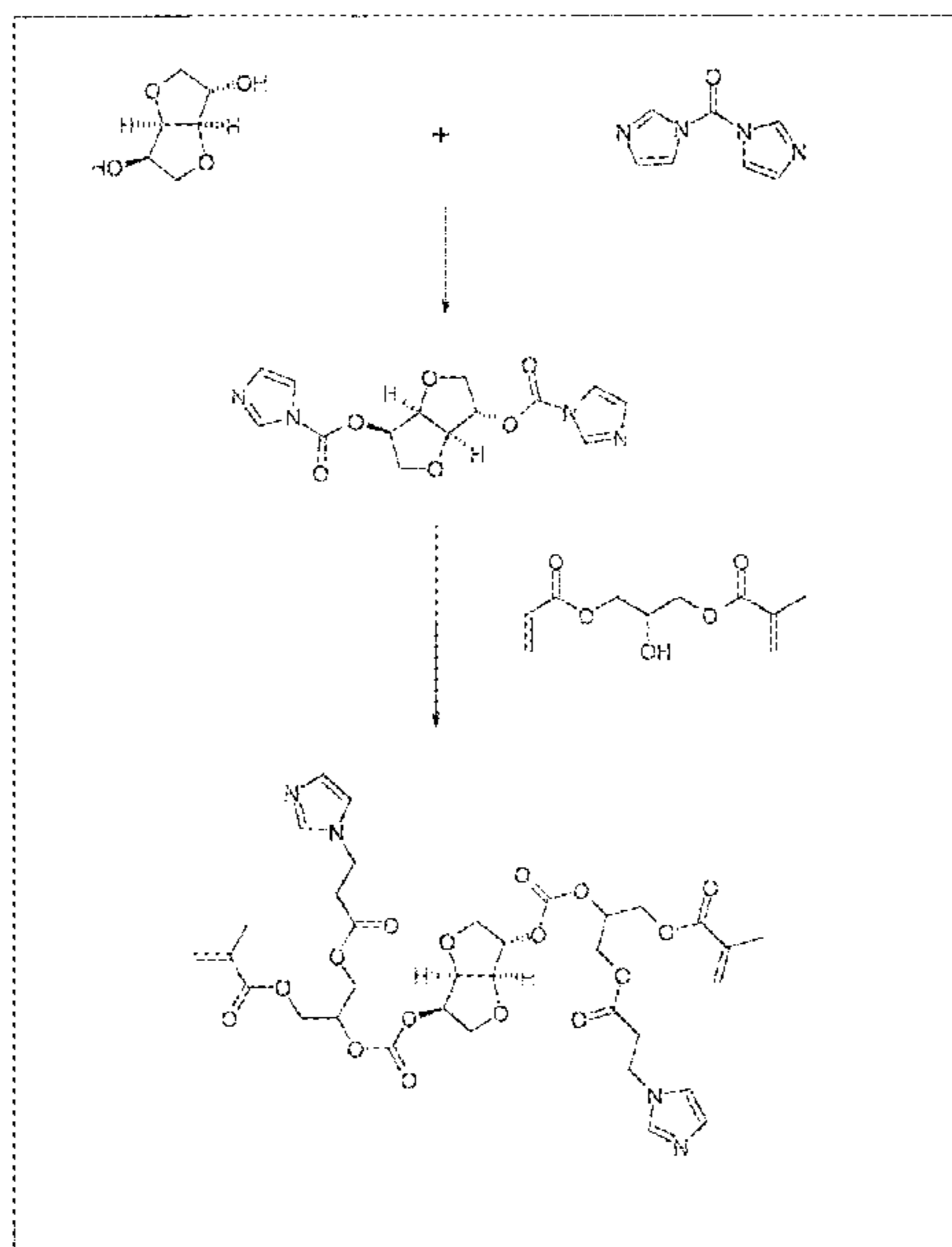
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(57) **ABSTRACT**

Disclosed herein is a composition and method of making a polymerizable antibacterial/antimicrobial resin and using such a bioactive resin in formulated dental compositions.

27 Claims, 14 Drawing Sheets



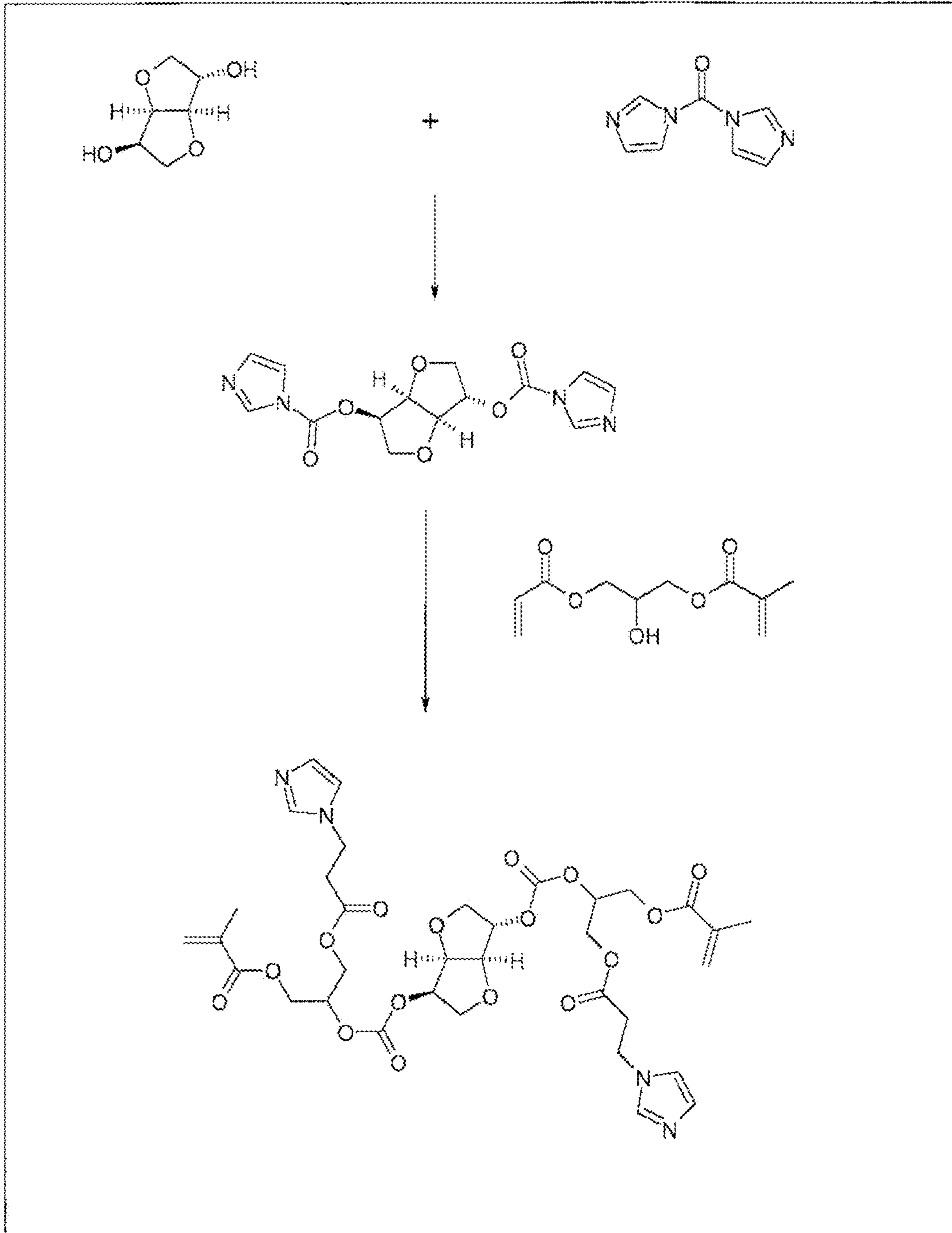


FIGURE 1

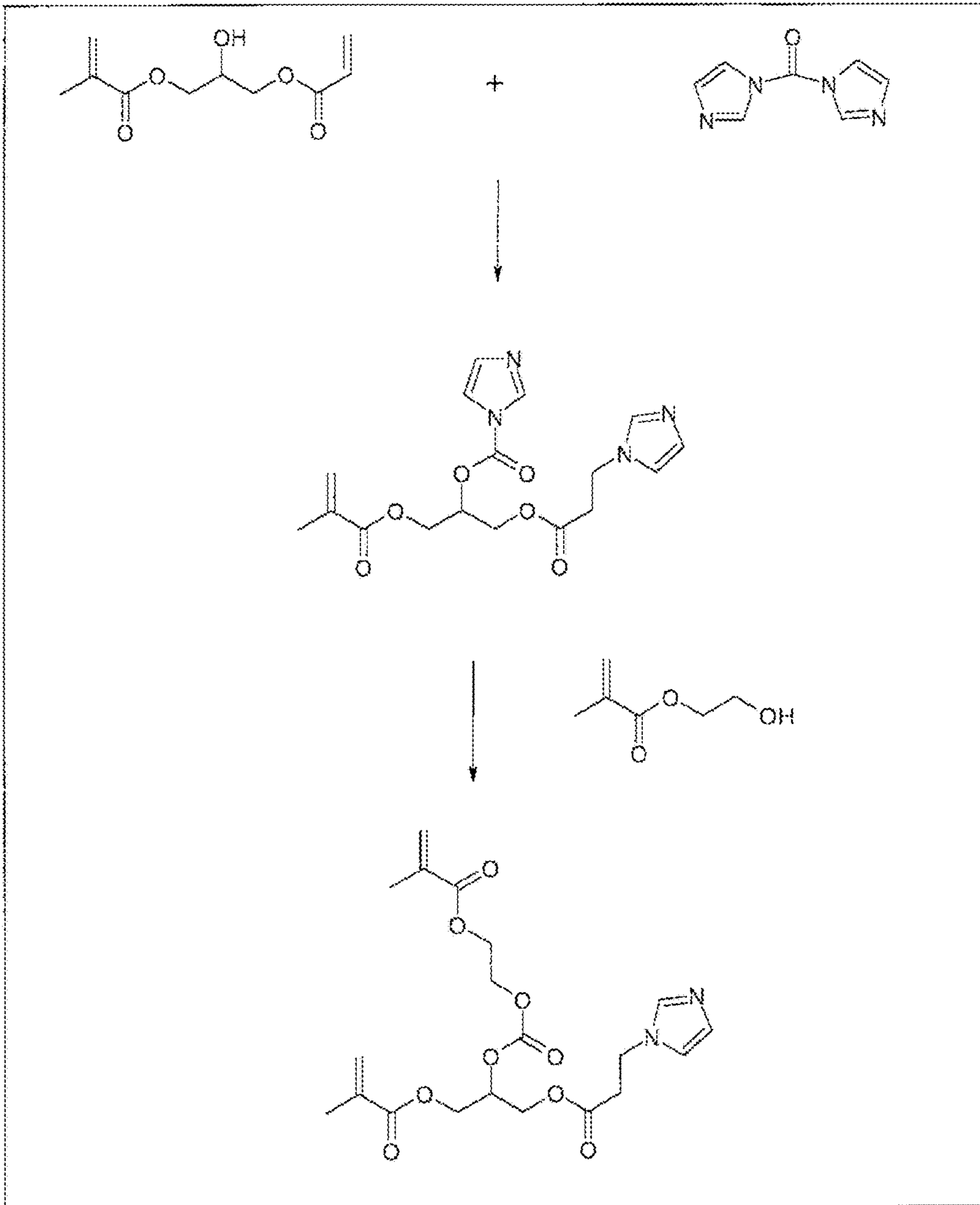


FIGURE 2

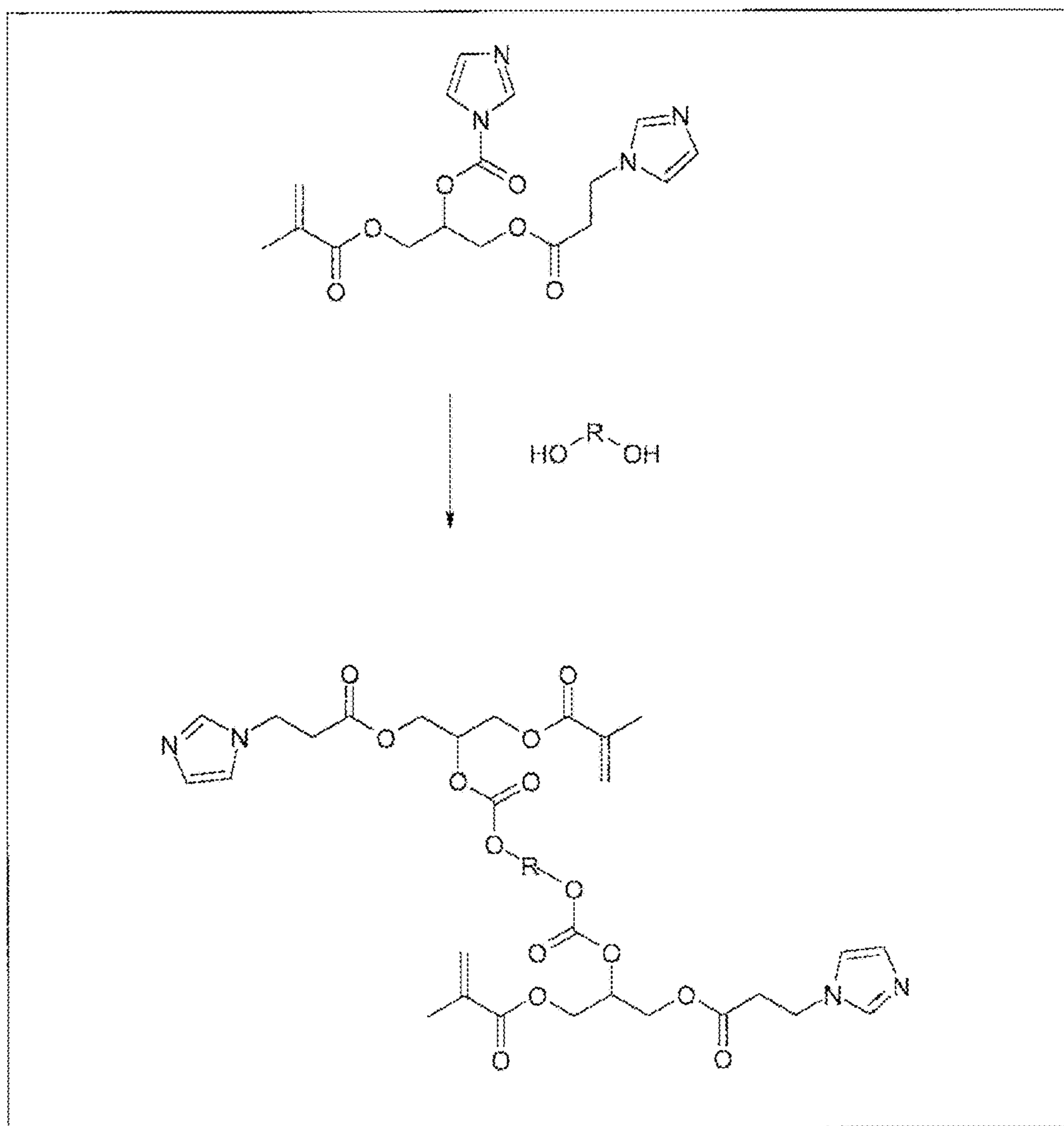


FIGURE 3

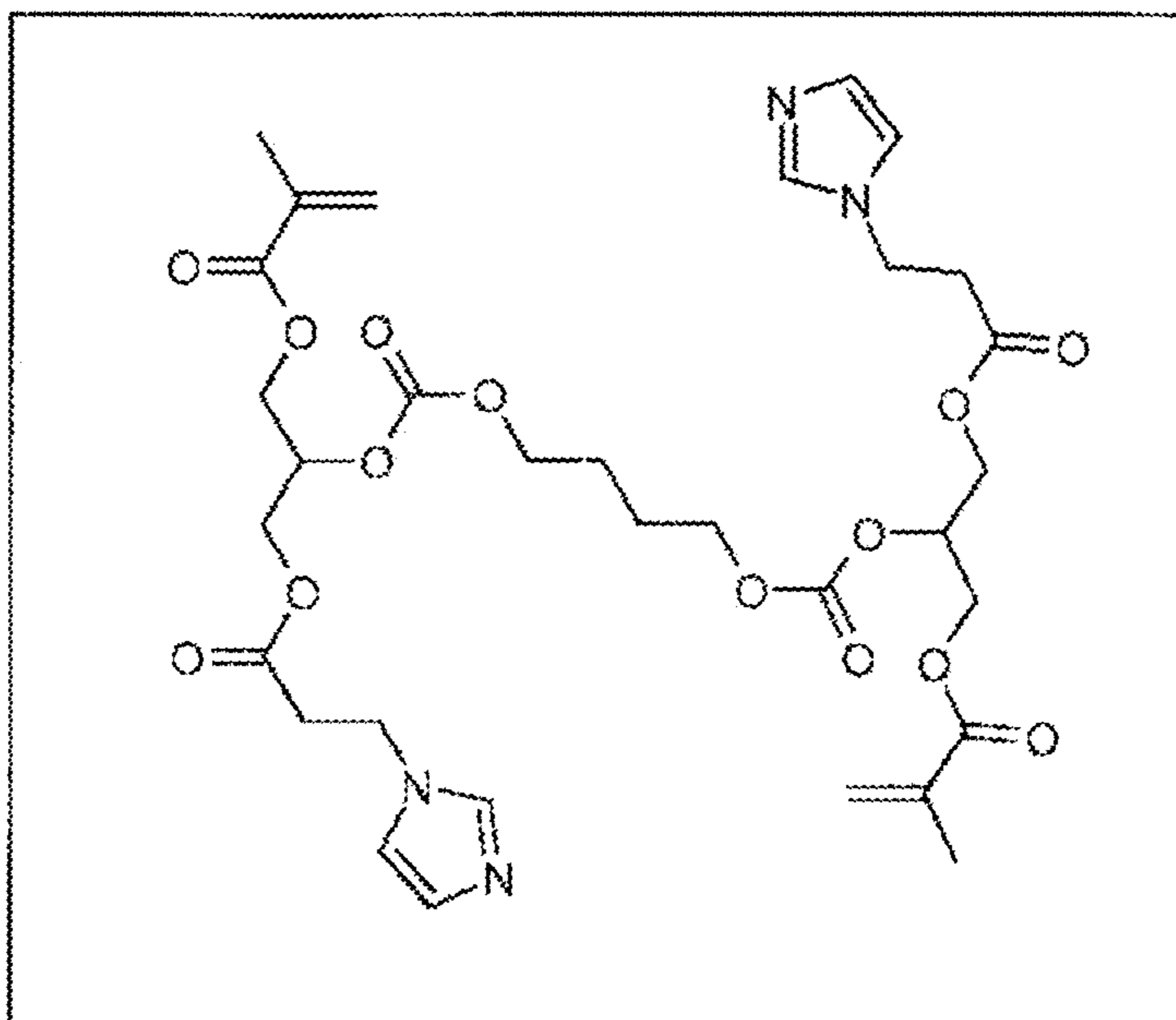


FIGURE 4

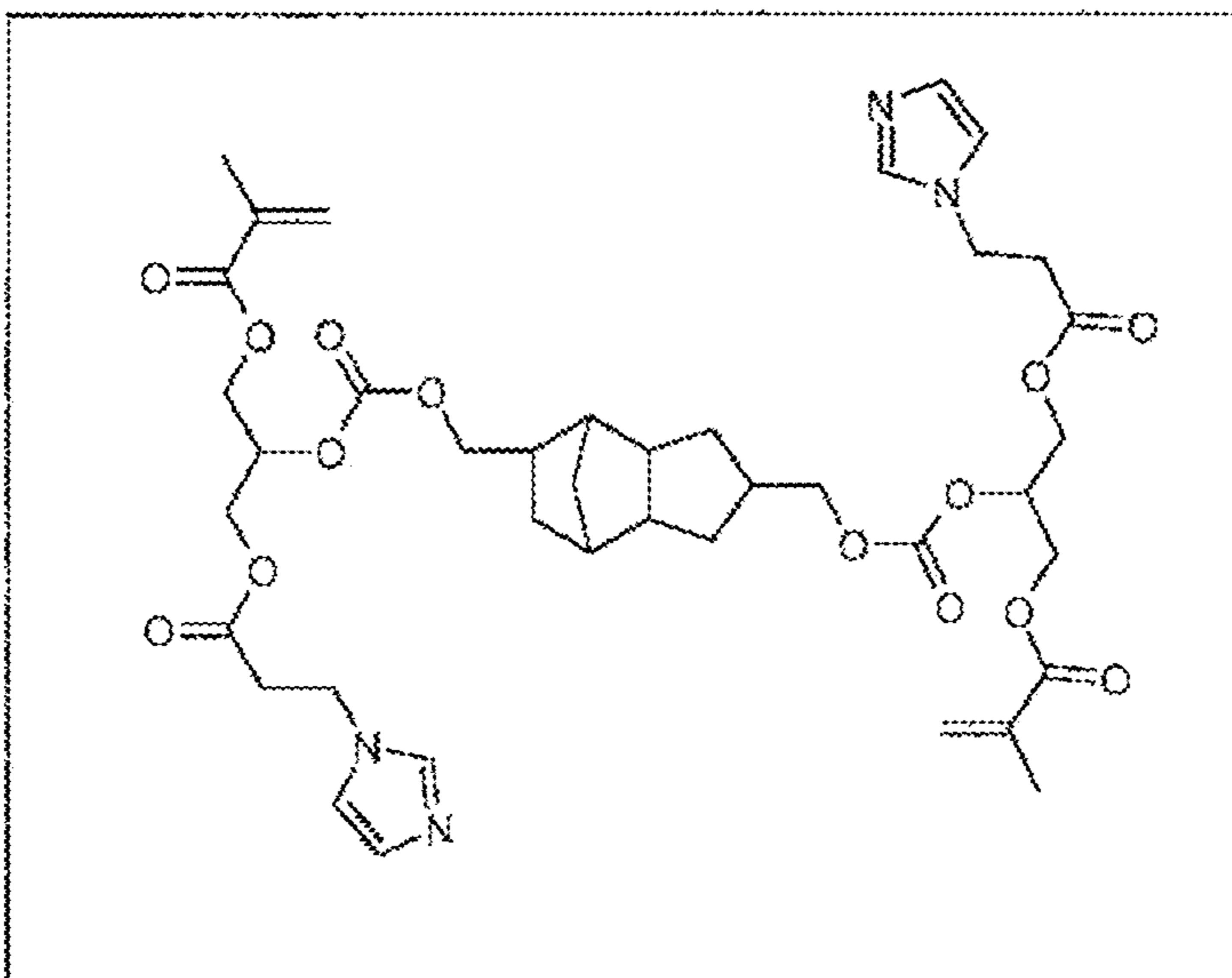


FIGURE 5a

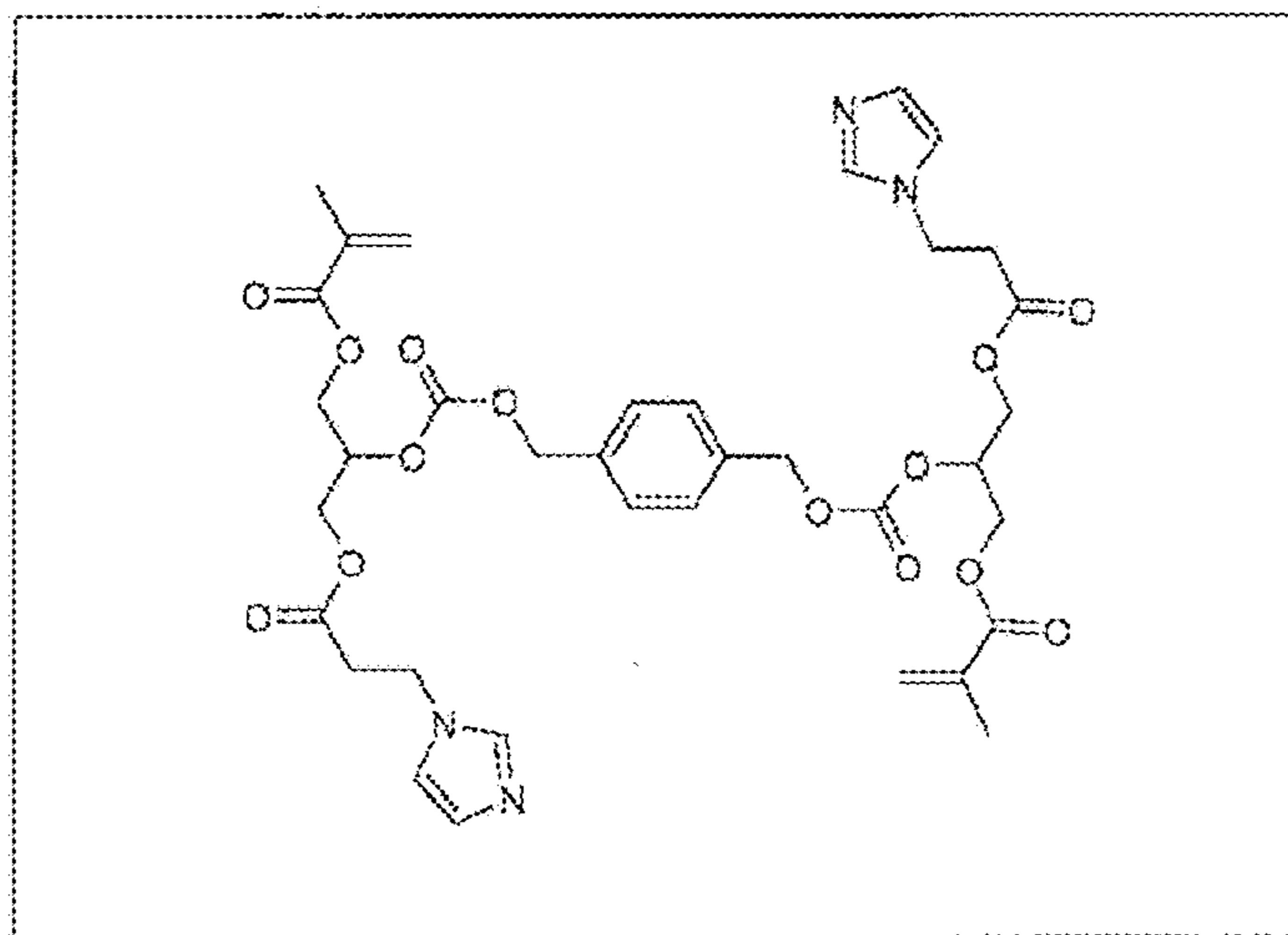


FIGURE 5b

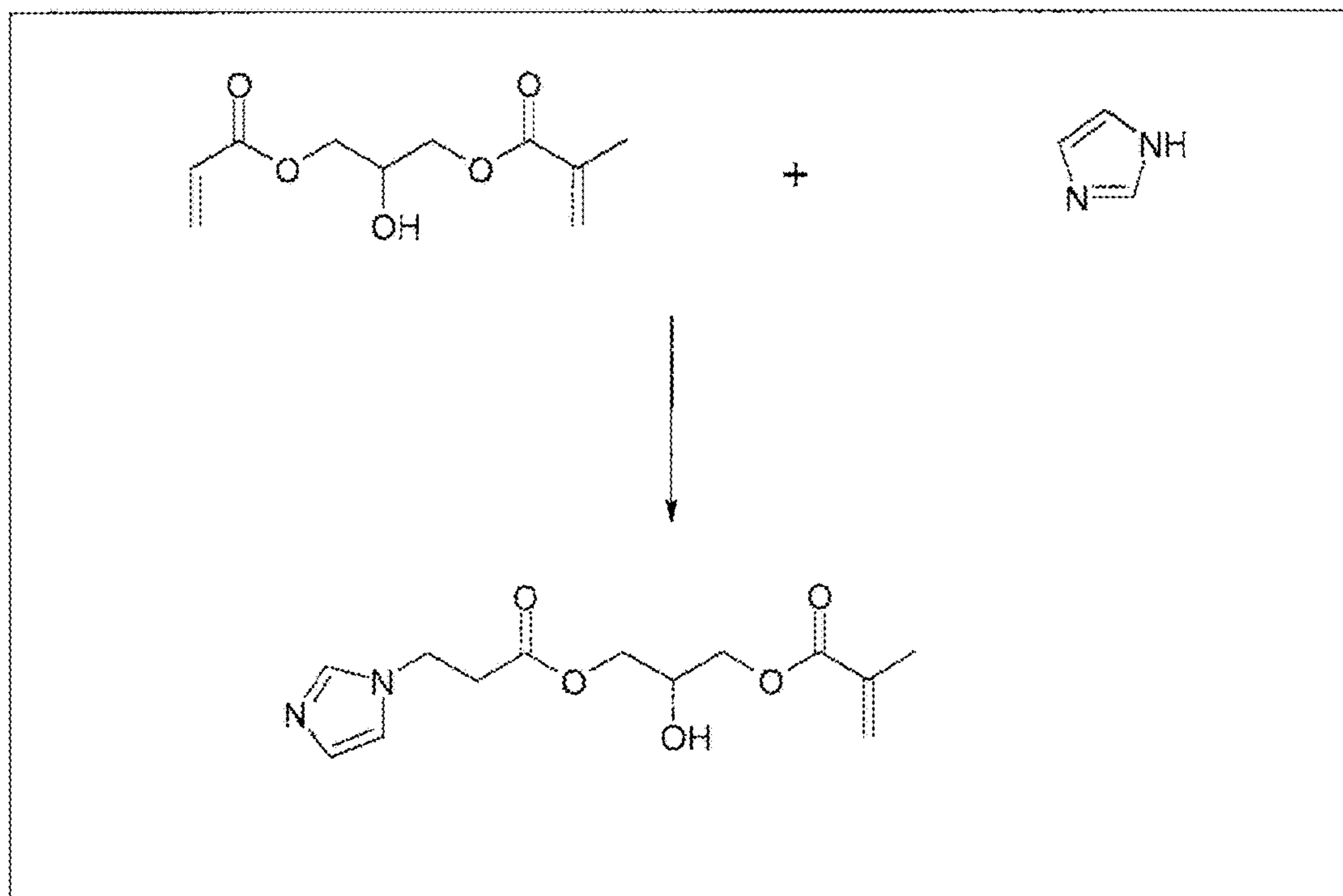


FIGURE 6

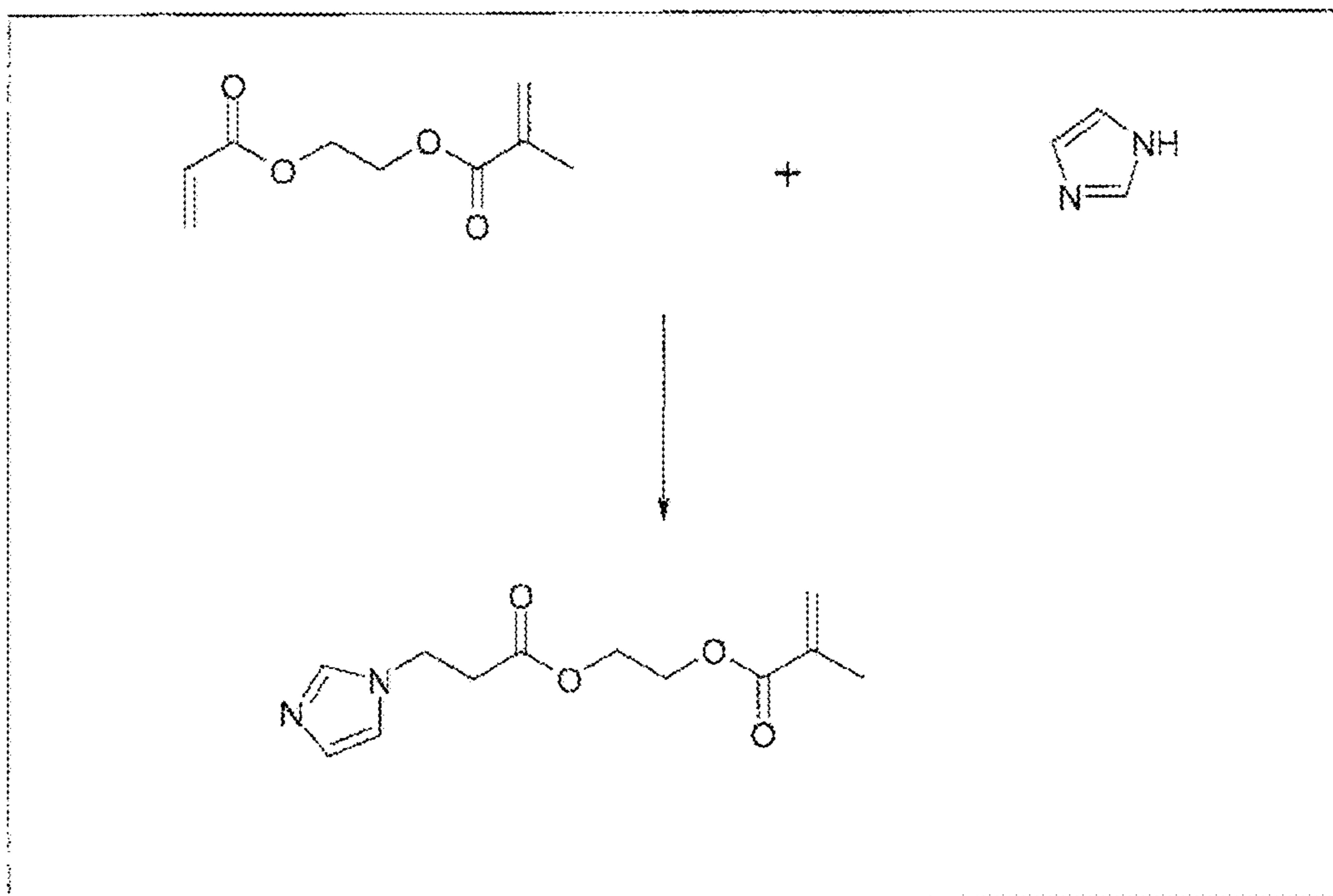


FIGURE 7

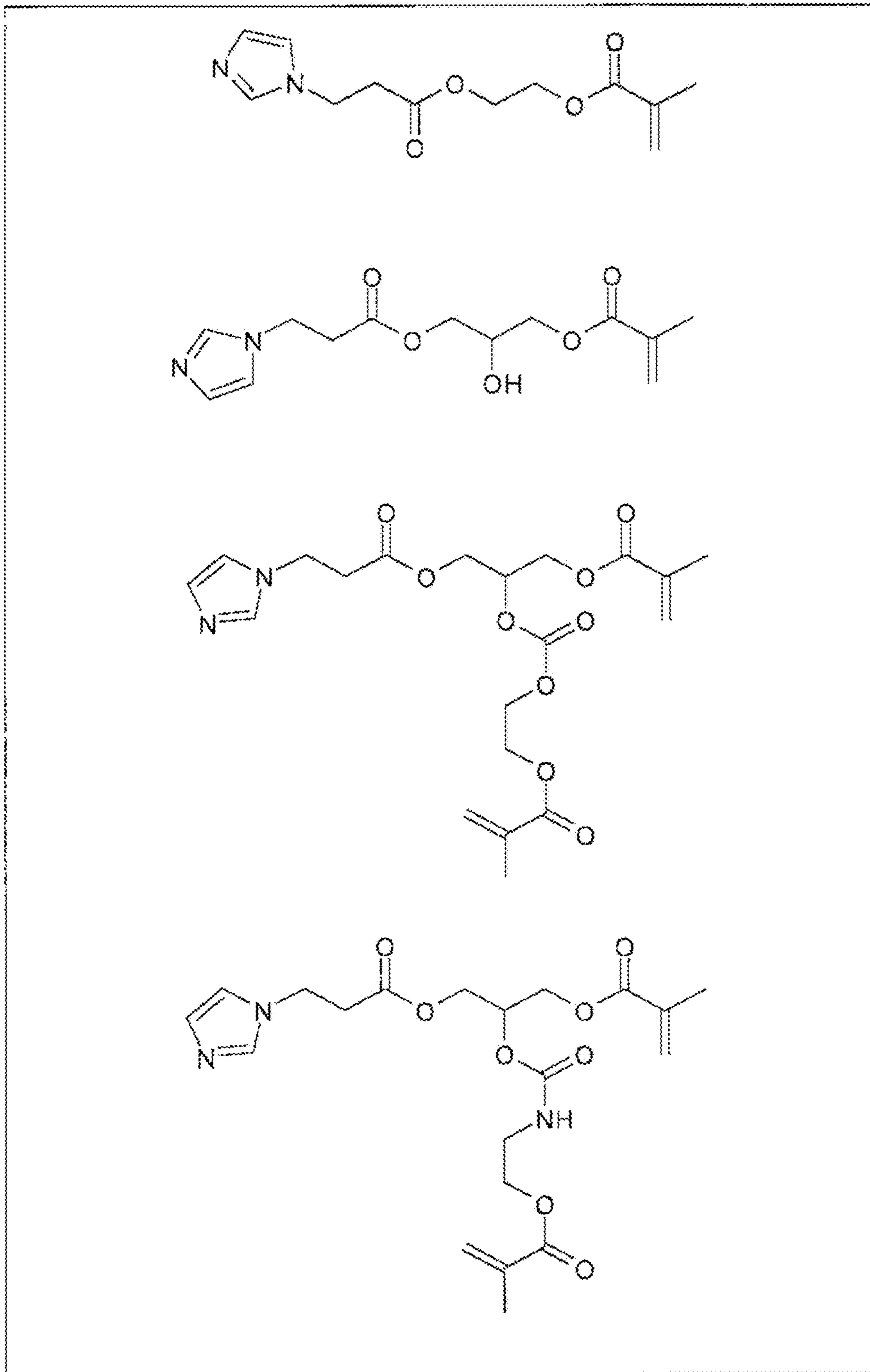


FIGURE 8

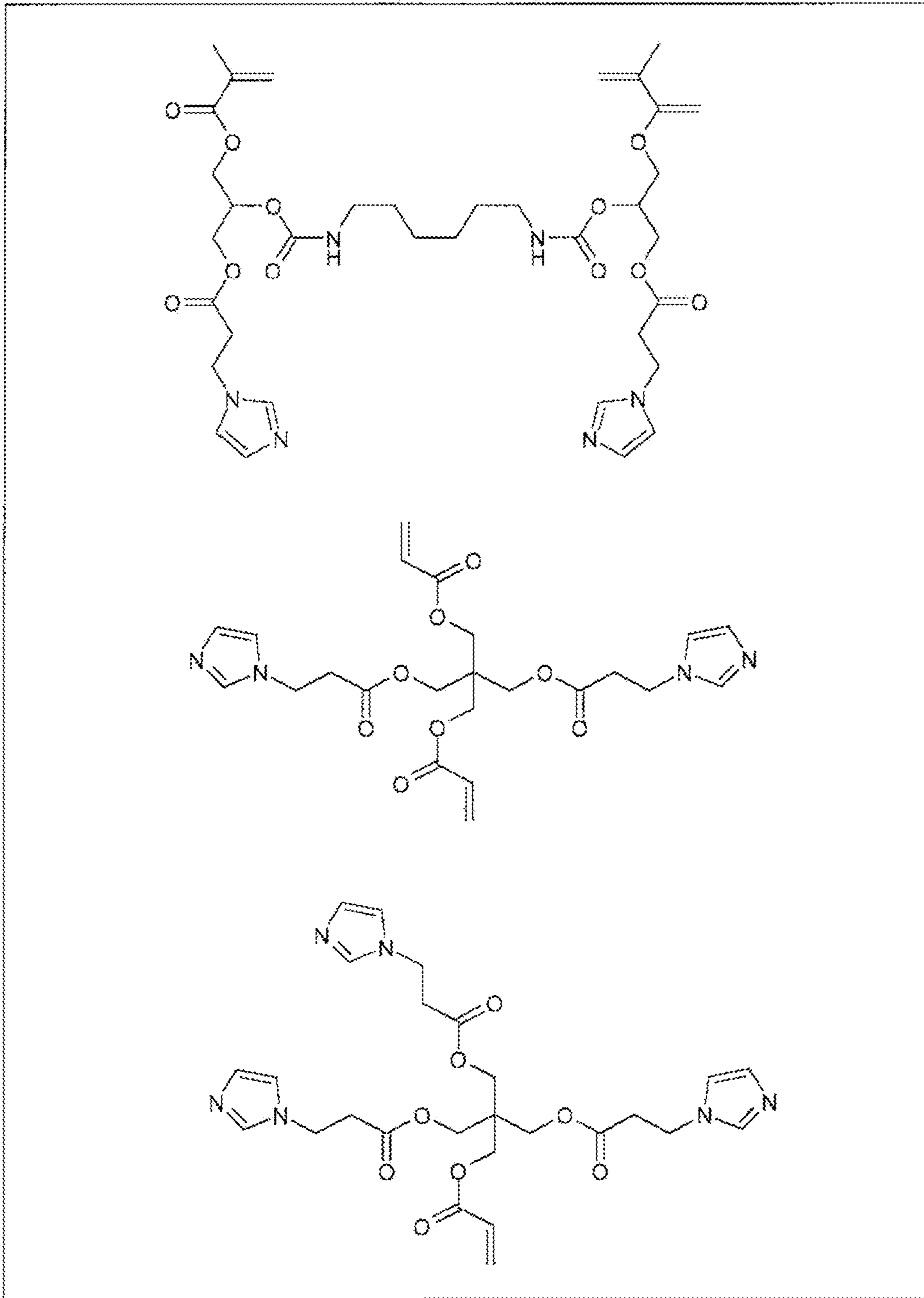


FIGURE 9

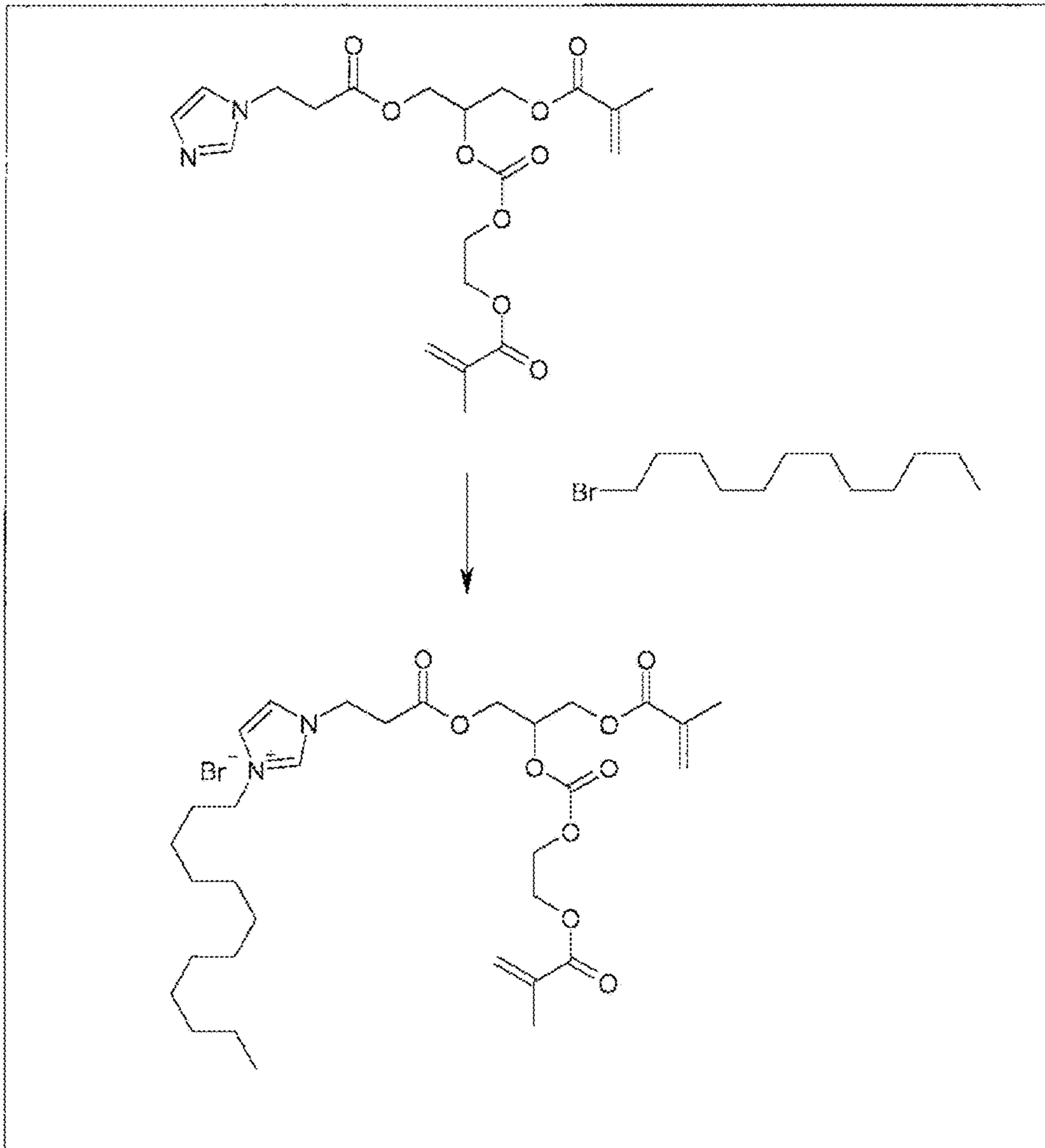


FIGURE 10

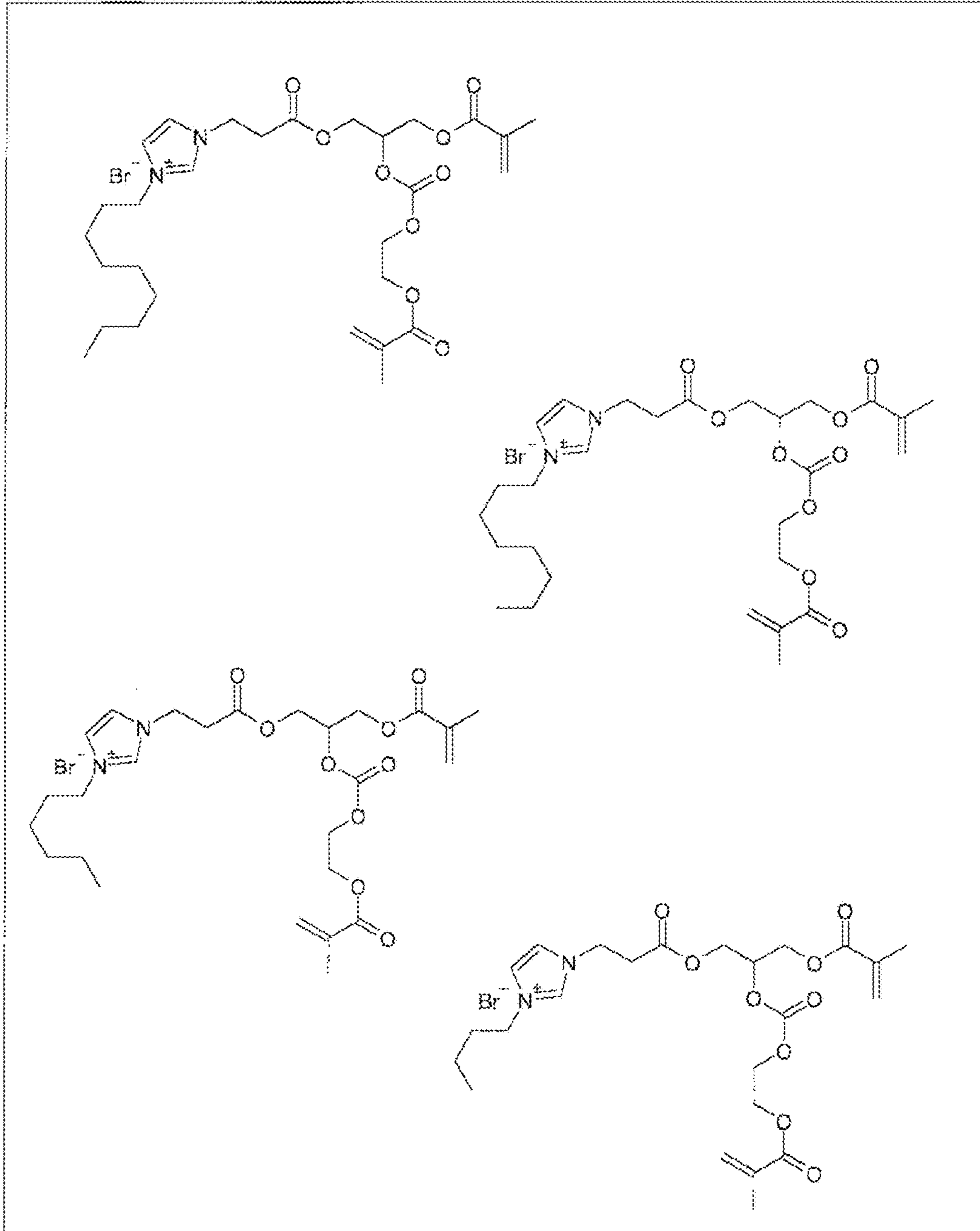


FIGURE 11

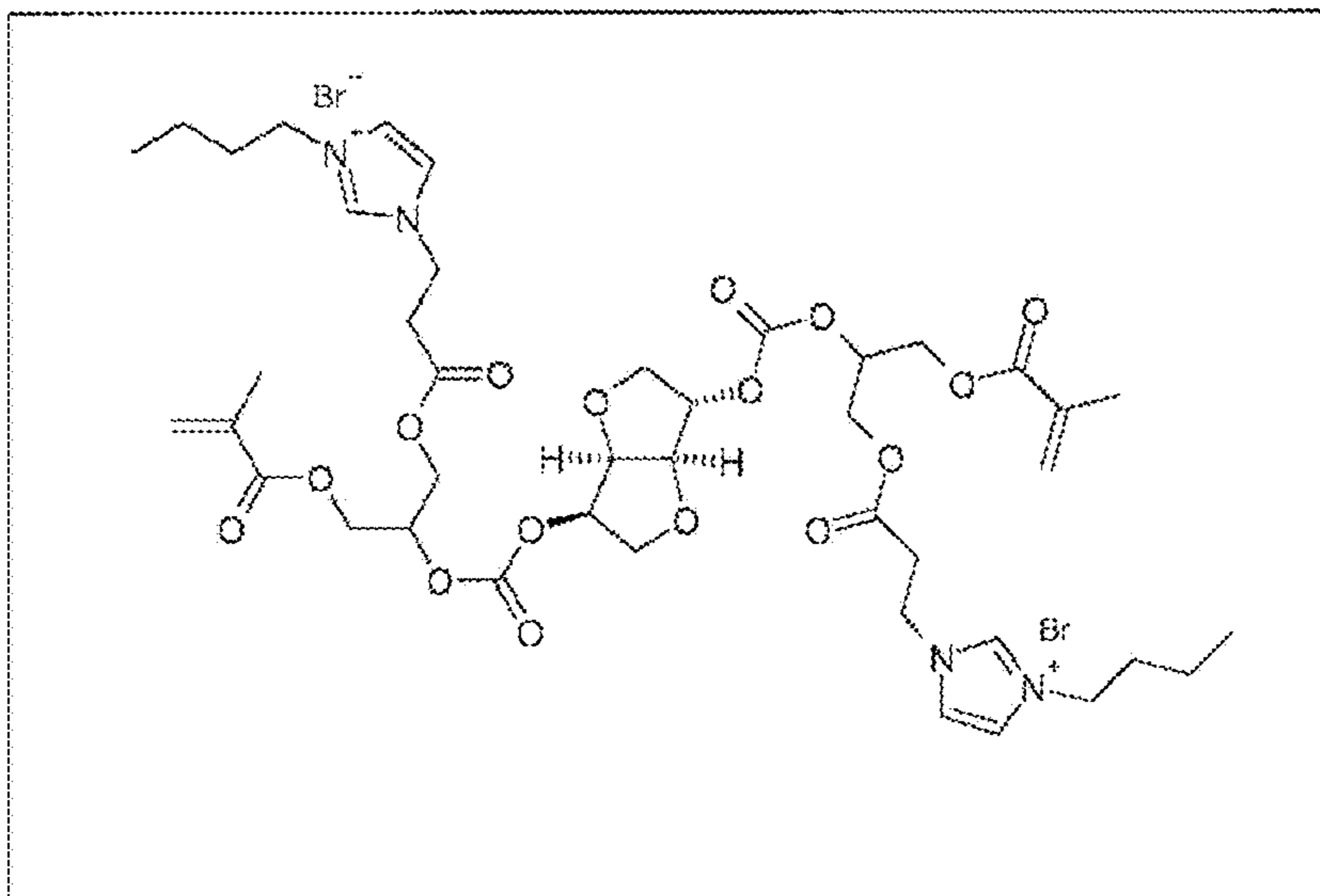


FIGURE 12

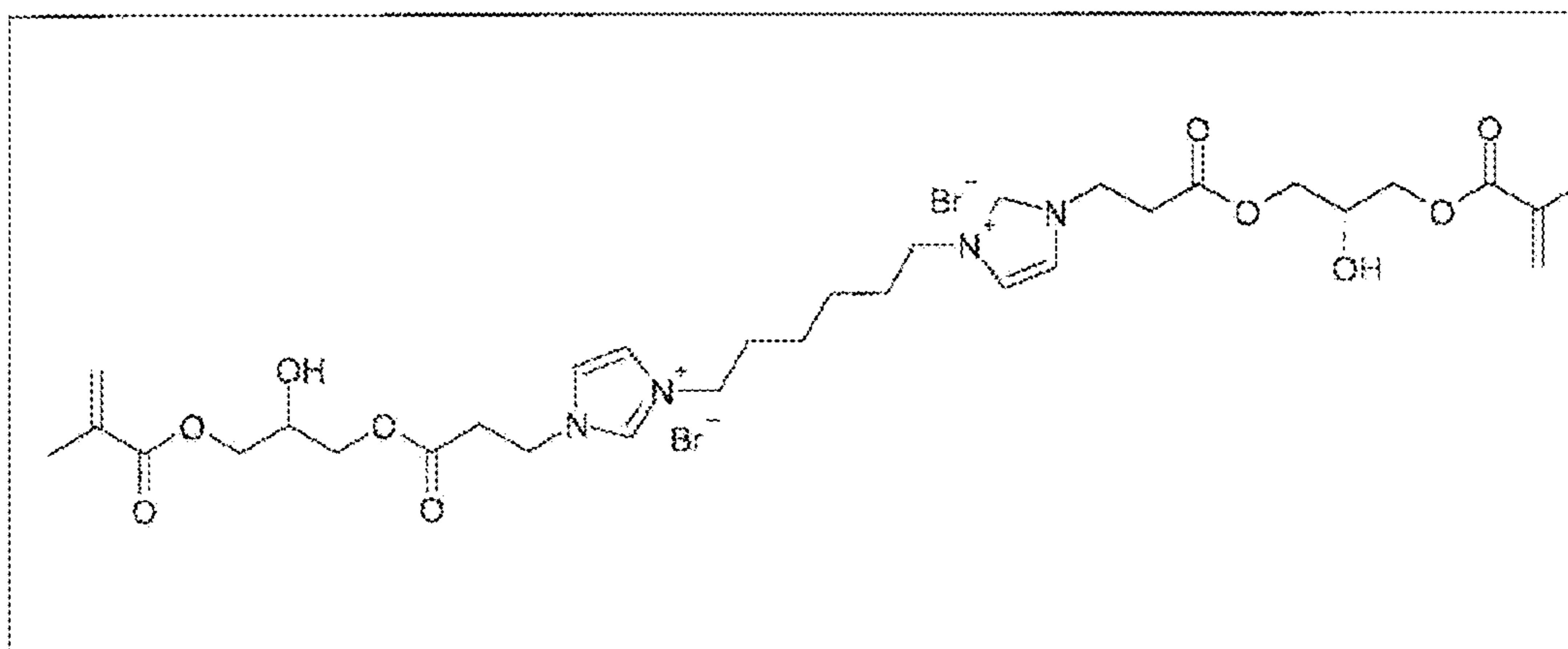


FIGURE 13

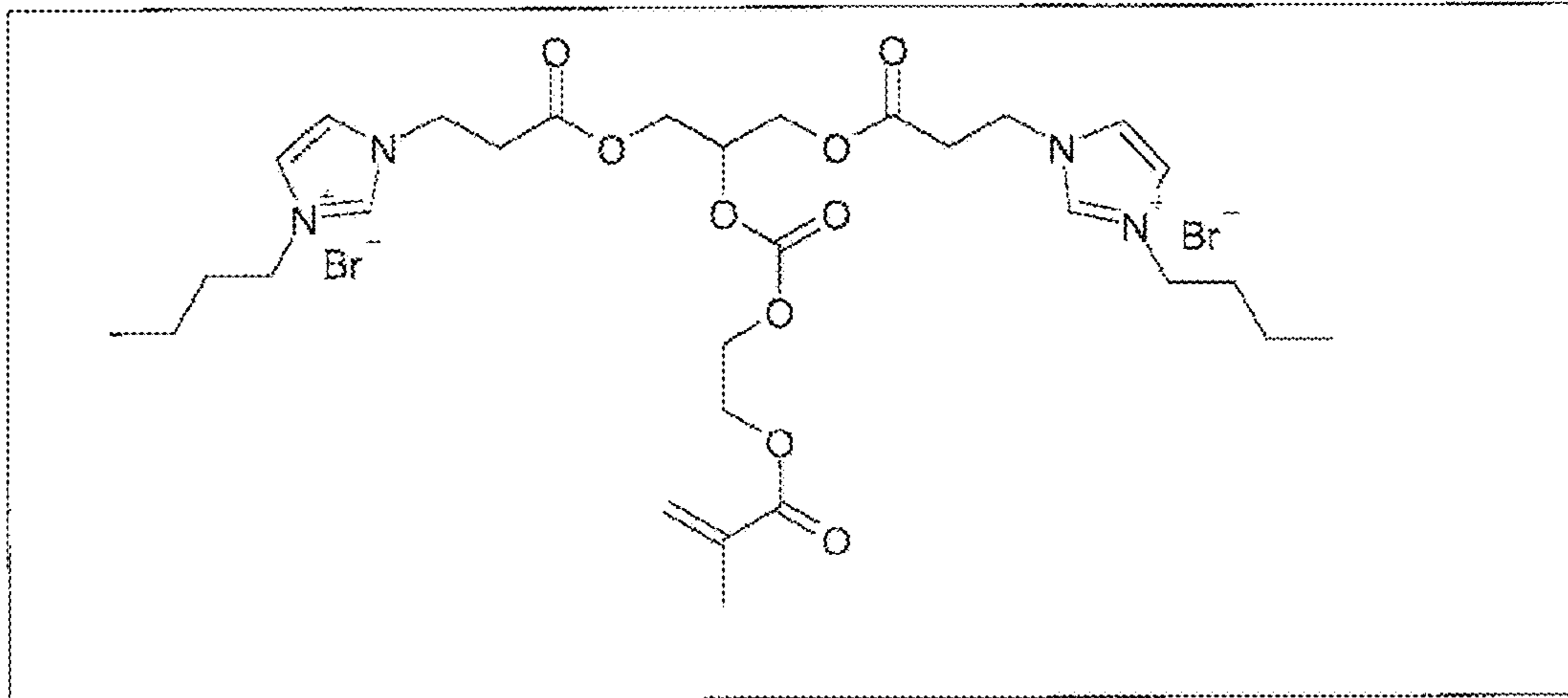


FIGURE 14

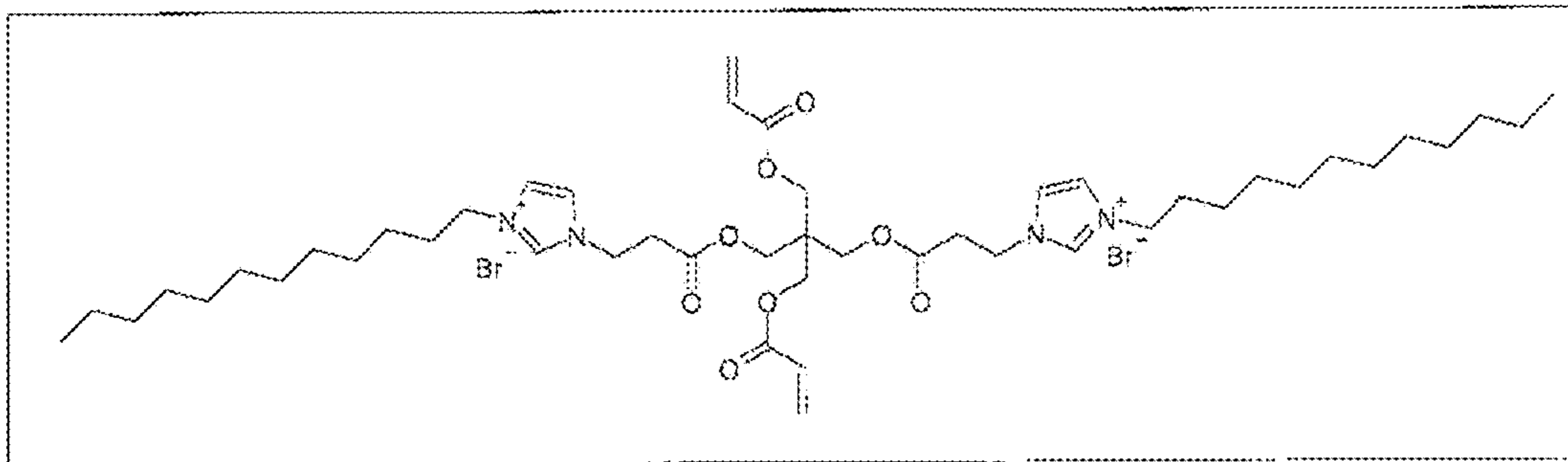


FIGURE 15

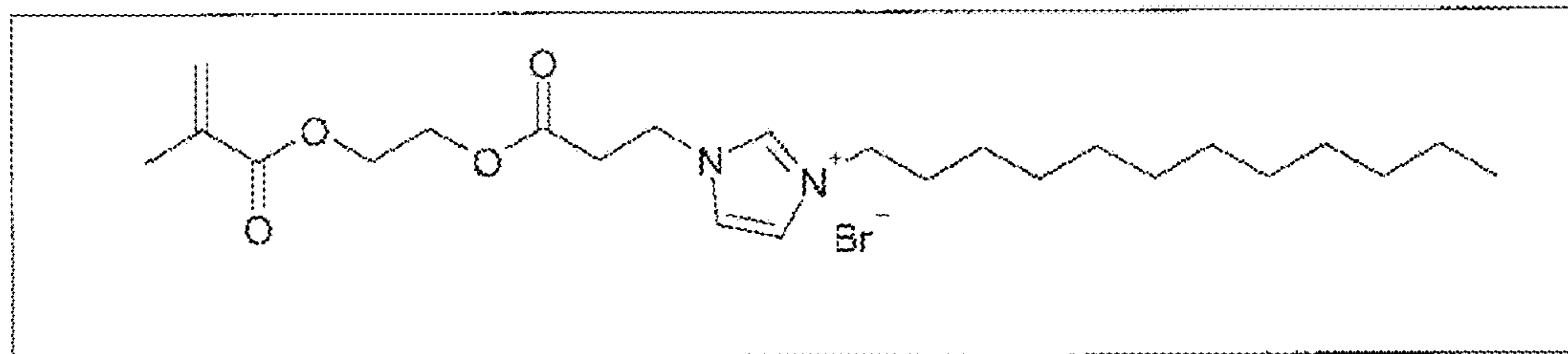


FIGURE 16

Modified JIS Z 2801 (Single Replicate) Study Report NG2664

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Results

Microorganism	Sample	Contact Time	CFU / Coupon	R Value
<i>S. mutans</i> ATCC 26175	Control	Time Zero	8.10E+05	N/A
		24 Hours	3.30E+03	
	Treated	Time Zero	7.60E+05	> 2.82
		24 Hours	< 5	

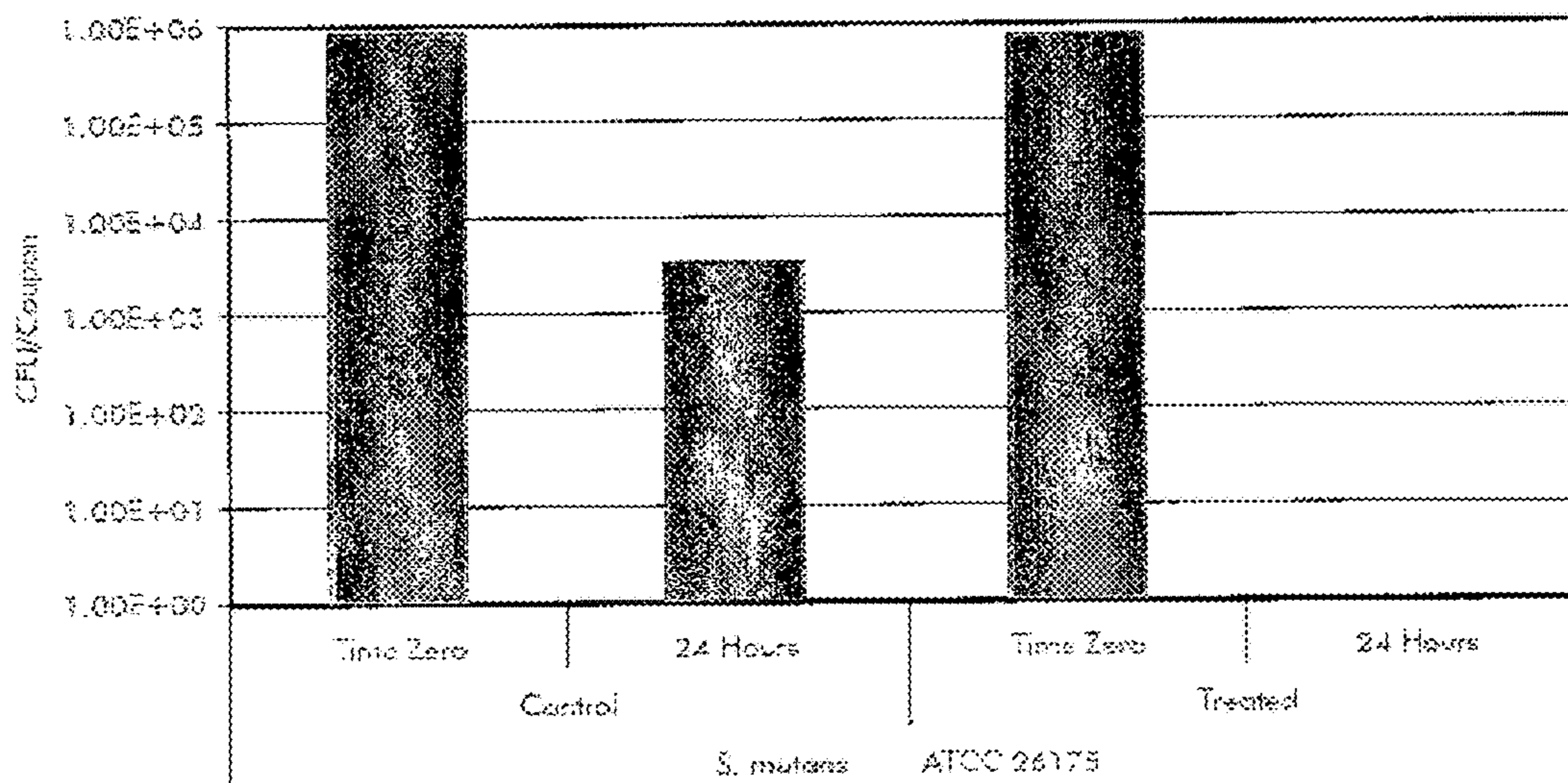


FIGURE 17

Microorganism	Sample	Contact Time	CFU / Coupon	R Value
<i>S. aureus</i> ATCC 6538	XJB-136	Time Zero	1.27E+05	4.44
		24 Hours	<5	
	XJB-137	Time Zero	1.27E+05	
		24 Hours	1.68E+05	

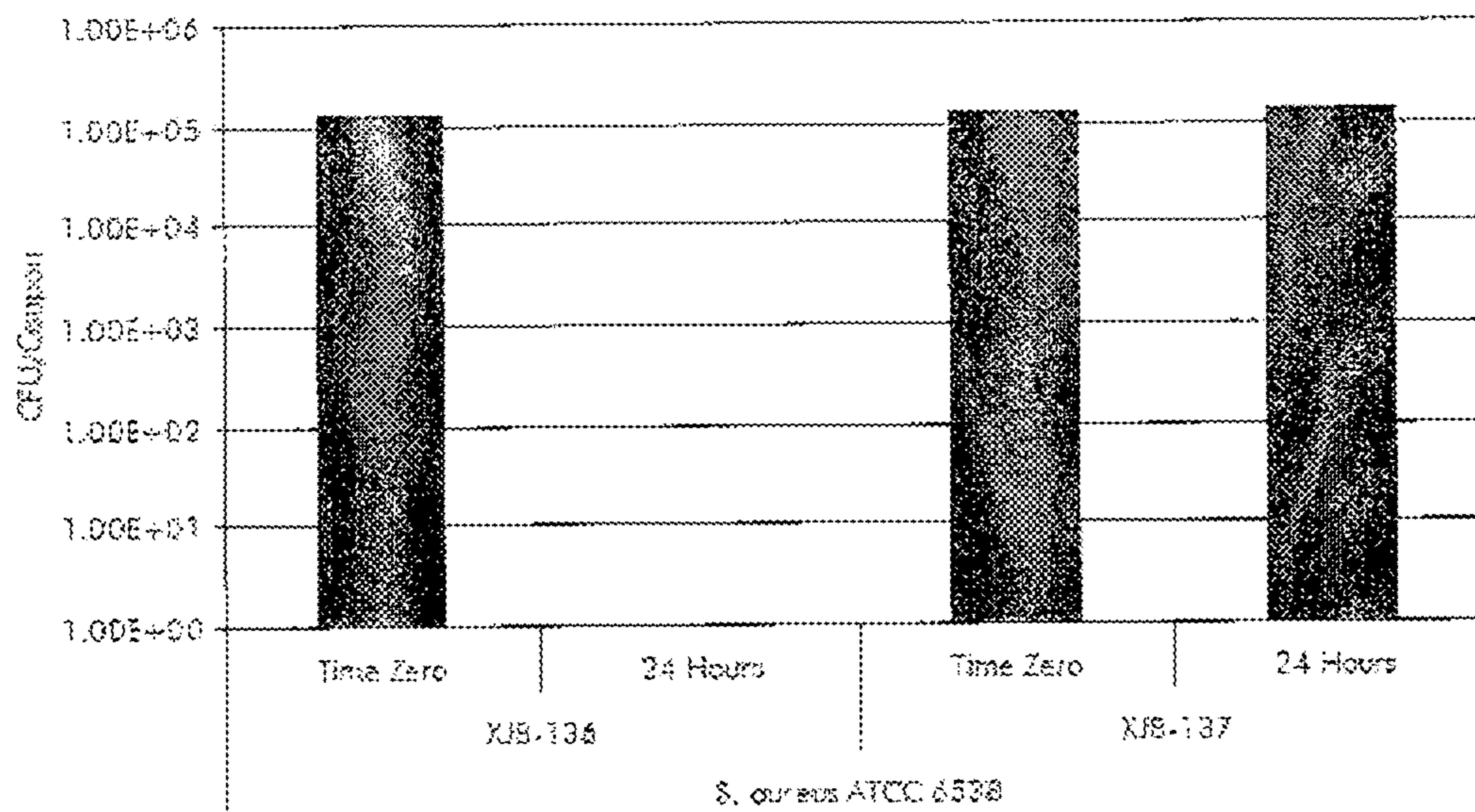


FIGURE 18

**IMIDAZOLE AND IMIDAZOLIUM RESINS
AND METHODS FOR PREPARING
CURABLE IMIDAZOLIUM ANTIMICROBIAL
RESINS**

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.

RELATED APPLICATIONS

This application is a reissue application of U.S. Pat. No. 8,747,831 issued on Jun. 10, 2014, which claims priority to U.S. Provisional Patent Application No. 61/499,910, [files] filed Jun. 22, 2011.

FIELD OF USE

Disclosed herein is a composition and method of making a polymerizable antibacterial/antimicrobial resin and using such a bioactive resin in formulated dental compositions.

BACKGROUND

Dental caries are associated with the bacterial contained in dental biofilm. Dental biofilm is complex, with a well-organized structure. Up to 500 bacterial species have been identified in dental biofilm. For oral and systemic health, the dental biofilm needs to be regularly and meticulously removed. Removal and reduction of biofilm can be by mechanical means or mechanical and chemical means. There have been increasing efforts to inhibit the development of biofilm. It is known prior to the development of dental biofilm, the salivary or acquired pellicle forms. This occurs through the adsorption of protein from saliva onto the clean tooth surface. Acquired pellicle formation provides oral bacterial with binding sites, resulting in bacterial adhesion, the first step in the formation of dental biofilm. Therefore, surface modification should inhibit the development of the acquired pellicle and dental biofilm.

In restorative dentistry, secondary caries are well known, which often occurs at the interface between the restoration and the cavity preparation as a result of demineralization of tooth structure due to the dental plaque formation by acid-producing bacteria such as *Streptococcus mutans* (*S. mutans*) in presence of fermentable carbohydrates. Thus dental compositions with antibacterial/antimicrobial effect were formulated by incorporation of a variety of antibacterial/antimicrobial agents, such as chlorhexidine, silver ions, and fluoride. Although such low molecular organic compounds demonstrated immediate effectiveness, there are issues related to their long-term effectiveness, potential toxicity and impact to the mechanical strength of the formulated dental composition due to the leachability. On the other hand, solid antibacterial/antimicrobial agents such as silver nanoparticles and polymeric QAS nanoparticles were also developed to address those issues associated with the low molecular weight of antibacterial/antimicrobial agents. There are issues like color stability and optical opacity and mechanical strength. Recently polymerizable antibacterial/antimicrobial resins were developed but their effectiveness varied and most of them demonstrated negative impact on mechanical property of the formulated dental composition.

U.S. Pat. No. 5,494,987 disclosed antimicrobial polymerizable compositions having an ethylenically unsaturated monomer with antimicrobial activity for dental application composed of quaternary ammonium dodecylpyridinium (MDPB).

U.S. Publication No. 2010/0256242 disclosed a polymerizable biomedical composition that includes a quaternary ammonium group bonded at its quaternary sites.

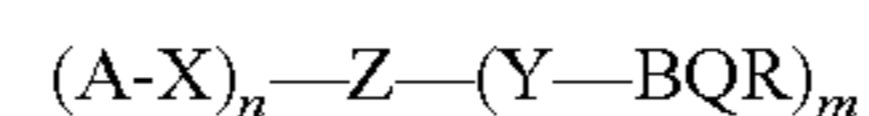
U.S. Pat. Nos. 6,710,181 and 7,094,845 disclosed an imidazole-based silane and monocarboxylic acid salt for improving adhesion between resins and metal or glass.

U.S. Pat. No. 7,553,881 disclosed dental compositions based on polymerizable macromers based on quaternary ammonium salts for antimicrobial effect.

Thus there is strong need to highly effective polymerizable antibacterial resin that is capable to offer a balanced antibacterial effectiveness and excellent mechanical property without severe cytotoxicity. In this invention, a method and composition of polymerizable antibacterial/antimicrobial resins is disclosed and high performance dental compositions are formulated from such novel bioactive resins.

SUMMARY

Disclosed herein is a composition and method of making and using such a composition in dental restorations. The composition disclosed herein includes novel polymerizable resins. More specifically, the composition disclosed herein is related to a method of preparing such polymerizable resins that contains multiple *imidazole and imidazolium* groups and multiple radically polymerizable groups as shown in the following formula:



A: polymerizable moiety like methacrylate, acrylate, epoxy, vinyl ether, etc; n=1, 2, 3, 4

B: substituted imidazole moiety like imidazole, methyl-imidazole, etc, m=1, 2, 3, 4,

R: a hydrogen atom or an alkyl group having 1-22 carbon atoms

Q: counter ion groups such as halogen atom, chlorine, bromine, iodine, etc

X, Y: equal or different, ether, ester, amide, imide, direct link, alkyl, aromatic, etc,

Z: alkyl, aromatic, etc.

Furthermore, formulated dental compositions, including composite or cements, from this invented polyimidazolium resin are able to offer balanced antibacterial effectiveness and mechanical property without causing any severe cytotoxicity. Such resins may be formulated with conventional resins to provide an improved adhesive to hard tissues in a prepared tooth cavity.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts isosorbide-based bisimidazole-dimethacrylate resins.

FIG. 2 depicts a CDI-based reaction pathway to monoimidazole-dimethacrylate resin.

FIG. 3 depicts CDI-based reaction pathways to bisimidazole-dimethacrylate resins.

FIG. 4 depicts a butanediol-based bisimidazole-dimethacrylate resin.

FIG. 5a depicts a TCDC-based bisimidazole-dimethacrylate resin.

FIG. 5b depicts a paraXylenediol-based bisimidazole-dimethacrylate resin.

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FIG. 6 depicts an imidazole-based reaction pathway to monoimidazole-monomethacrylate resin.

FIG. 7 depicts an imidazole-based reaction pathway to monoimidazole-monomethacrylate resin.

FIG. 8 depicts typical monoimidazole resins.

FIG. 9 depicts other polyimidazole(meth)acrylate resins.

FIG. 10 depicts a reaction of 3-dodecanylimidazolium-bromide-dimethacrylate resin.

FIG. 11 depicts typical alkylimidazoliumbromide-dimethacrylate resins.

FIG. 12 depicts an isosorbide-based bis(3-butyylimidazoliumbromide)-dimethacrylate resin.

FIG. 13 depicts a 1,6-hexane-bisimidazoliumbromide-dimethacrylate resin.

FIG. 14 depicts a bis(3-butyylimidazoliumbromide)bisacrylate resin.

FIG. 15 depicts a bis(3-dodecanylimidazoliumbromide)bisacrylate resin.

FIG. 16 depicts a 3-dodecanylimidazoliumbromide-monomethacrylate resin.

FIG. 17 depicts the antibacterial effectiveness of polymerizable antibacterial resin against *S. mutans*.

FIG. 18 depicts the antibacterial effectiveness of cured composite containing antibacterial resin against *S. aureus*.

DETAILED DESCRIPTION

During the attempt to prepare a carbonate-based polymerizable resin (FIG. 1) by using an acrylate-methacrylate resin (AMAHP) and 1,1-carbonyl-diimidazole (CDI), it was surprisingly discovered that a chemically bonded imidazole resin was formed exclusively in the resulting resin. It has been elucidated that the formation of the imidazole resin was the result of a Michael adduct between the acrylate group in AMAHP and the CDI in-situ generated by-product (imidazole) in the absence of any catalysts. The imidazole was found to react exclusively toward the acrylate group. Thus a variety of polymethacrylated resins containing at least one polyimidazole moiety could be readily prepared by proper hybrid acrylate-methacrylate resins or even polyacrylate resins with proper control of the conversion of the imidazole addition. Therefore, this is an effective method to incorporate an imidazole moiety into a polymerizable resin as novel functional resins for acid-free adhesive resins. Furthermore, such polymerizable imidazole-containing resins may be further chemically modified by reaction with a variety of halogenated alkyls to form polymerizable resins with ionic moiety of imidazolium, which may be new class of polymerizable ionic liquid resins.

Accordingly from such a reaction platform, other derivatives may be readily prepared as illustrated in FIGS. 2 through 5: a variety of polymethacrylate resins with polyimidazoles are able to be prepared via the precursor as showed in FIGS. 2 and 3 by coupling with different mono, di, tri, or polyols or polyamines.

Further, in order to streamline the process of making such imidazole-based polymerizable resins for use in making imidazolium-based polymerizable resins, a facile process based on imidazole and acrylated resins were investigated as illustrated in FIGS. 6 and 7. Thus a variety of imidazole-based polymerizable resins are able to be prepared, as shown in FIGS. 8 and 9.

Furthermore, as illustrated in FIGS. 10 through 15, a variety of imidazolium-based polymerizable resins may be prepared from a wide range of imidazole-based polymerizable resins as discussed previously. The preferred imidazolium-based polymerizable resin contains at least one polym-

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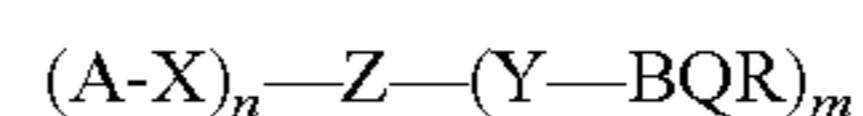
erizable group such as methacrylate or acrylate and at least one imidazolium moiety bearing linear long alkyl chain of C8-C14. The most preferred resin contains two methacrylate group and at least one imidazolium moiety bearing a C12 linear alkyl chain.

Such imidazolium-based polymerizable resin was found highly effective in killing bacteria such as *S. mutans* as showed in FIG. 17. It was also demonstrated that such imidazolium-based polymerizable resins are also very effective in inhibiting MMP even at low concentration. Matrix metalloproteinases (MMP) bond to dentin and are thought to contribute to the progressive degradation of collagen fibrils in hybrid layers formed during dentin bonding. The dentin matrix contains MMP-2, MMP-8, MMP-9, and MMP-20. It is known that chlorhexidine (CHX) has broad anti-MMP activity in addition to antimicrobial activity. However, the long term anti-MMP activity for CHX is not effective, which has been attributed to possible leaching out of the CHX. It has been shown that cationic quaternary ammonium methacrylates (QAS) may exhibit dentin MMP inhibition comparable with that of CHX, but require higher concentrations.

Such effectiveness in killing bacteria for the imidazolium-based polymerizable resins were further demonstrated by the formulated dental composites as showed in Table V and FIG. 18. More importantly it was discovered that a low level loading (less than 1%, wt/wt) of such an imidazolium-based polymerizable resin may remain effective in killing bacteria as showed in Table VI. Furthermore, with optimized compositions not only highly effective antibacterial activity is achieved but also excellent mechanical properties were yielded as shown in Tables VII through XIV. The effectiveness in antibacterial properties of this novel polymerizable imidazolium resin offers another crucial benefit without causing severe cytotoxicity. Conventional QAS-based polymerizable resins, on the other hand, are less effective and high dose loading (up to 30%) is needed, which usually leads to decreases in mechanical property and increases cytotoxicity.

Obviously from the resin disclosed herein a variety of applications could be found as photopolymerizable dental products. Certainly, it can also be polymerized by heat, and/or redox initiation process. In addition, due to the nature of the imidazole moiety, it is also expected that the disclosed polymerizable resin can also find application in forming a complex with acidic resins or polymers, including PENTA, OEMA, methacrylic acid, polyacrylic acid or reactive acidic glass powders to form a soluble liquid resin, soft gel or hard gel structures or highly-crosslinked solids.

Disclosed herein is a composition and method of making and using such compositions in dental restorations. The composition disclosed herein includes novel polymerizable resins. More specifically, the composition disclosed herein is related to a method of preparing such polymerizable resins that contains multiple imidazole groups and multiple radically polymerizable groups as shown in the following formula:



A: polymerizable moiety like methacrylate, acrylate, epoxy, vinyl ether, etc; n=1, 2, 3, 4

B: substituted imidazole moiety like imidazole, methylimidazole, etc, m=1, 2, 3, 4,

R: a hydrogen atom or an alkyl group having 1-22 carbon atoms

Q: counter ion groups such as halogen atom, chlorine, bromine, iodine, etc

X, Y: equal or different, ether, ester, amide, imide, direct link, alkyl, aromatic, etc,

Z: alkyl, aromatic, etc.

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Dental composition disclosed herein may be composed of (1) the functional polymerizable resins contains imidazole group or imidazolium groups described herein in amount of from about 0.5 weight percent to about 99 weight percent of the dental composition, (2) conventional polymerizable resin in amounts of from about 10 weight percent to about 99 weight percent of the dental composition, (3) initiators and other additives in amounts of from about 0.001 weight percent to about 5.0 weight percent of the dental composition, (4) a plurality of filler particles having a size of from about 10 nm to about 100 micron of the dental composition, and (5) an optional inert solvent in amounts not to exceed 1 weight percent of the dental composition.

HEMA and HPMA are typical monomethacrylate resins; BisGMA, TEGDMA, UDMA are typical conventional dimethacrylate resins, which are polymerizable/curable by heat, light and redox initiation processes. CQ and LTPO are typical photoinitiators. Tertiary aromatic amines, such as EDAB, may be included as an accelerator for CQ-based photoinitiator. Other additives such as inhibitors, UV stabilizers or fluorescent agents may also be used. In addition, a variety of particles, polymeric, inorganic, organic particles may be incorporated to reinforce the mechanical properties, rheological properties and sometime biological functionalities.

The following abbreviations may be used:

BisGMA: 2,2-bis(4-(3-methacryloyloxy-2-hydroxypropoxy)-phenyl)propane

HEMA: 2-hydroxyethyl methacrylate

HPMA: 2-hydroxypropyl methacrylate

TEGDMA: triethylene glycol dimethacrylate

UDMA: di(methacryloxyethyl)trimethyl-1,6-hexaethylene-diurethane

BHT: butylhydroxytoluene

CQ; camphorquinone

LTPO: lucirin TPO/2,4,6-trimethylbenzoyldiphenylphosphine oxide

EDAB: 4-Ethyl dimethylaminobenzonate

AMAHP: 3-(acryloyloxy)-2-hydroxypropyl methacrylate

EGAMA: ethyleneglycol acrylate methacrylate

TCDC: 4,8-bis(hydroxymethyl)-tricyclo[5,2,1,0^{2,6}]

CDI: 1,1-carbonyl-diimidazole

SR295: pentaerythritol tetraacrylate

EXAMPLES

Example 1

Isosorbide-based Bisimidazole-dimethacrylate Resin (XJ8-9/FIG. 1) was prepared via a two-step process as described in the following: to a 1000 ml 3-neck round flask, 98.88 g of 1,1-carbonyl-diimidazole (CDI), 550 g of methylene dichloride and 43.9 g of isosorbide was charged and soon the system turned clear at room temperature. Then the crystal was developed as a result of imidazole formation. After 2 hrs reacting at RT, 131.1 g of 3-(acryloyloxy)-2-hydroxypropyl methacrylate (AMAHP), 40.0 g of potassium carbonate and 4.0 g of terabutylammoniumbromide was added. The reaction proceeded at room temperature for an additional 10-12 hrs prior to 200 ml of DI water being added to stop the reaction. The resulting solution was extracted several times with DI water to remove all of imidazole and catalysts. Then it was dried over magnesium sulfate overnight at RT prior to being filtrated. Solvent was removed via Rotovapor at 35-40° C. under vacuum. 240 g of liquid resin was collected with a yield of 89%.

Example 2

TCDC-based Bisimidazole-dimethacrylate Resin (XJ8-13/FIG. 5a) was prepared via a two-step process as

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described in the following: to a 1000 ml 3-neck round flask, 74.45 g of CDI, 400 ml of methylene dichloride and 98.36 g of AMAHP was charged and soon the system turned clear at room temperature. After 6 hrs reacting at RT, 45.0 g of 4,8-bis(hydroxymethyl)-tricyclo[5,2,1,0^{2,6}](TCDC) and 40.0 g of potassium carbonate and 3.8 g of terabutylammoniumbromide was added. The reaction continued at room temperature for an additional 10-12 hrs prior to 250 ml of DI water being added to stop the reaction. The resulting solution was extracted 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 being filtrated. The solvent was removed via Rotovapor at 35-40° C. under vacuum.

Example 3a

HEMA-based Monoimidazole-dimethacrylate Resin (XJ8-6/FIG. 2) was prepared via a two-step process as described in the following: to a 1000 ml 3-neck round flask, 81.8 g of CDI, 450 ml of methylene dichloride and 107.5 g of AMAHP was charged and soon the system turned clear at room temperature. After a 6 hrs reaction at RT, 66.5 g of 2-hydroxyethyl methacrylate (HEMA), 40.0 g of potassium carbonate and 4.0 g of terabutylammoniumbromide was added. The reaction continued at room temperature for an additional 10-12 hrs prior to 200 ml of DI water being added to stop the reaction. The resulting solution was extracted several times with DI water to remove all of the imidazole and catalysts. Then the solution was dried over magnesium sulfate overnight at RT prior to being filtrated. The solvent was removed via Rotovapor at 35-40° C. under vacuum.

Example 3b

HEMA-based Monoimidazole-dimethacrylate Resin (XJ8-48/FIG. 2) was prepared via a two-step process as described in the following: to a 1000 ml 3-neck round flask, 120.3 g of CDI and 200 ml of methylene dichloride were added. Then 159.3 g of AMAHP in 150 ml of methylene dichloride was charged and soon the system turned clear at room temperature. After an overnight reaction at RT, 100.1 g of HEMA, 40.0 g of potassium carbonate and 4.0 g of terabutylammoniumbromide were added. The reaction continued at room temperature for an additional 4 hrs prior to 200 ml of DI water being added to stop the reaction. The resulting solution was extracted several times with DI water to remove all of the imidazole and catalysts. Then the solution was dried over magnesium sulfate overnight at RT prior to being filtrated. The solvent was removed via Rotovapor at 35-40° C. under vacuum. 301 g of low viscosity liquid resin was collected.

Example 3c

AMAHP-based monosimidazole-methacrylate Resin (XJ8-111/FIG. 6) was prepared via a one-step solution process as described in the following: to a 2000 ml 3-neck flask, 800 ml of methylene dichloride, 161.1 g of AMAHP and 102.2 g of imidazole were charged. Soon the imidazole got dissolved and the clear solution was mixed at room temperature overnight prior to 200 ml of DI water being added to stop the reaction. The resulting solution was extracted several times with DI water to remove all of the excess imidazole and catalysts. Then the solution was dried over magnesium sulfate overnight at RT prior to being filtrated. The solvent was removed via Rotovapor at 35-40°

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C. under vacuum. 200 g of low viscosity liquid resin was collected, from which a reversible gel-like resin is formed once the temperature down to RT.

Example 3d

EGAMA-based monosimidazolium-bromide-dimethacrylate Resin (XJ8-157/FIG. 7) was prepared via a one-step bulk process as described in the following: to a 500 ml 3-neck round flask, 184.5 g of ethyleneglycol acrylate methacrylate (EGAMA) and 69.3 g of imidazole were charged. This slurry was mixed at room temperature for 60 hrs. 250 g of low viscosity liquid resin was collected.

Example 4

HEMA-based Monoimidazolium-bromide-dimethacrylate Resin (XJ8-45/FIG. 10) was prepared by a one-step condensation reaction from the imidazole precursor prepared as described in Example 3b. To a 250 ml 3-neck round flask, 61.7 g of HEMA-based monoimidazole-dimethacrylate resins (XJ8-38) and 40.2 g of 1-bromododecane and 200 ml of methylene dichloride was charged. The reaction continued at 40° C. for 7 days. Added 135 grams of hexane to the system and it is immiscible. After separated the hexane solution part, the resin was dissolved in methylene dichloride and extracted with water for several times. The solvent was removed via Rotovapor at 35-40° C. under vacuum. 80 grams of clear liquid resin was collected, which had a viscosity of 140 Pa·s at 20° C.

Example 5

Isosorbide-based Bisimidazolium-bromide-dimethacrylate Resin (XJ8-31/FIG. 12) was prepared by a one-step solution reaction from the imidazole precursor prepared as described in Example 1. To a 500 ml 3-neck round flask, 42.4 g of Isosorbide-based bisimidazole-dimethacrylate resins (XJ8-9), 13.7 g of 1-bromobutane, 200 ml of methylene dichloride and 8.65 g of triethylene glycol dimethacrylate (TEGDMA) were charged. The reaction continued at 40° C. for 2 days. Finally 65 g of highly viscose liquid resin was collected. The RI of this resin is 1.5130.

Example 6

HEMA-based Monoimidazolium-bromide-dimethacrylate Resin (XJ8-40/FIG. 11) was prepared by a one-step condensation reaction from the imidazole precursor prepared as described in Example 3b. To a 250 ml 3-neck round flask, 21.92 g of HEMA-based monoimidazole-dimethacrylate resins (XJ8-38) and 8.22 g of 1-bromobutane and 200 ml of methylene dichloride was charged. The reaction continued at 40° C. for 2 days. 25.6 grams of viscose liquid resin was collected, which had a RI of 1.5098.

Example 7

HEMA-based Monoimidazolium-bromide-dimethacrylate Resin (XJ8-54/FIG. 11) was prepared by a one-step condensation reaction from the imidazole precursor prepared as described in Example 3b. To a 250 ml 3-neck round flask, 60.2 g of HEMA-based monoimidazole-dimethacrylate resins (XJ8-48), 26.5 g of 1-bromooctane, 150 ml of methylene dichloride was charged. The reaction continued at 40° C. for

8

6 days. Finally 79 g of liquid resin was collected, which had a viscosity of 245 Pa·s at 20° C.

Example 8

HEMA-based Monoimidazolium-bromide-dimethacrylate Resin (XJ8-80/FIG. 10) was prepared by a one-step condensation reaction from the imidazole precursor prepared as described in Example 3b. To a 250 ml 3-neck round flask, 65.9 g of HEMA-based monoimidazole-dimethacrylate resins (XJ8-48) and 37.4 g of 1-bromododecane and 200 ml of methylene dichloride was charged. The reaction continued at 40° C. for 7 days. 99.5 grams of liquid resin was collected, which had a viscosity of 175 Pa·s at 20° C.

Example 9

Bis(3-dodecanylimidazolium-bromide)-Bisacrylate Resin (XJ8-152-1/FIG. 15) was prepared via a two-step one-pot process as described in the following: to a 250 ml 3-neck round flask, 72.5 g of pentaerythritol tetraacrylate (SR295) and 9.5 grams of imidazole, mixed at RT for 1 hr, then 9.4 grams of imidazole was added for addition 1 hr reaction prior to addition of another 9.6 grams of imidazole. It was mixed overnight at RT. Then set the flask into an oil-bath of 40° C. with addition of 95.2 grams of 1-bromododecane and continued for 7 days at 40° C. 221 grams of highly viscose resin was collected.

Example 10

EGAMA-based monoimidazolium-bromide-monomethacrylate Resins (XJ8-160/FIG. 16) was prepared by a one-step condensation reaction from the imidazole precursor prepared as described in Example 3d. To a 250 ml 3-neck round flask, 127 grams of EGAMA-based monoimidazole-monomethacrylate resins (XJ8-157) and 124.0 grams of 1-bromododecane were charged. The reaction continued at 40° C. for 10 days. Finally 245 g of liquid resin was collected, which had a viscosity of 50 Pa·s at 20° C.

Example 11

AMAHP-based monosimidazolium-methacrylate Resin (XJ8-88/FIG. 11) was prepared via a one-step solution process as described in the following: to a 500 ml 3-neck round flask, 65.9 g of AMAHP-based monoimidazole-methacrylate resins (XJ8-81) and 28.8 of 1-bromooctane and 200 ml of methylene dichloride were charged. The reaction continued at 40° C. for 6 days. 61.3 grams of liquid resin was collected, which had a viscosity of 170 Pa·s at 20° C.

Example 12

AMAHP-based monosimidazolium-methacrylate Resin (XJ8-94/FIG. 11) was prepared via a one-step solution process as described in the following: to a 500 ml 3-neck round flask, 56.5 g of AMAHP-based monoimidazole-methacrylate resins (XJ8-85) and 33.1 of 1-bromooctane and 200 ml of methylene dichloride were charged. The reaction continued at 40° C. for 7 days. 80 grams of viscose liquid resin was collected, which had a viscosity of 410 Pa·s at 20° C.

Example 13

AMAHP-based monosimidazolium-methacrylate Resin (XJ8-88/FIG. 11) was prepared via a one-step solution

process as described in the following: to a 500 ml 3-neck round flask, 43.0 of AMAHP-based monoimidazole-methacrylate resins (XJ8-111) and 25.0 of 1,12-dibromododecane and 150 ml of methylene dichloride were charged. The reaction continued at 40° C. for 3 days. 60 grams of highly viscose liquid resin was collected.

Example 14-15

Light curable flowable dental composites (IJ1-84-2 and IJ1-85-2) containing polymerizable imidazlium resin (XJ8-80 at 2-4% wt/wt) were formulated with 60% of filler, which demonstrated effective antibacterial activities as showed in Table VI.

Example 16-17

Light curable universal dental composites (XJ8-136 and XJ8-137) containing polymerizable imidazlium resin (XJ8-80 at 20.9-1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities and excellent mechanical properties without causing severe cytotoxicity as showed in Table VI.

Example 18-21

Light curable universal dental composites (IJ1-115, 117, 118, and 137) containing polymerizable imidazlium resin (XJ8-80 at 0.9-1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities and excellent mechanical properties without causing severe cytotoxicity as showed in Table VIII.

Example 22-25

Light curable universal dental composites (IJ2-39, 40, 41, and 42) containing polymerizable imidazlium resin (XJ8-152 at 0.9-1.8% wt/wt) were formulated with 82% of filler, which demonstrated excellent mechanical properties as showed in Table X.

Example 26-29

Light curable universal dental composites (IJ2-189, 190, 191, and 192) containing polymerizable imidazlium resin (XJ8-160 at 0.9-1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities and excellent mechanical properties as showed in Table XII.

Example 30

Light curable universal dental composites (IJ2-205) containing polymerizable imidazlium resin (XJ8-88 at 1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities as showed in Table XIV.

Example 31

Light curable universal dental composites (IJ2-206) containing polymerizable imidazlium resin (XJ8-94 at 1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities as showed in Table XIV.

Example 32

Light curable universal dental composites (IJ2-207) containing polymerizable imidazlium resin (XJ8-54 at 1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities as showed in Table XIV.

Example 33

Light curable universal dental composites (IJ2-208) containing polymerizable imidazlium resin (XJ8-114 at 1.8% wt/wt) were formulated with 82% of filler, which demonstrated effective antibacterial activities as showed in Table XIV.

Comparative Example 1-2

Light curable universal dental composites (IJ1-138 and 139) were formulated with 82% of filler, which demonstrated excellent mechanical properties as showed in Table VIII.

Comparative Example 3

Light curable universal dental composites (IJ1-171) were formulated with 82% of filler, which demonstrated excellent mechanical properties as showed in Table XIV.

TABLE I

Compositions for Various Bisimidazole Dimethacrylate Resins

	Example 1 (XJ8-9)	Example 2 (XJ8-13)	Example 3a (XJ8-6)	Example 3b (XJ8-48)
Resin Composition	Isosorbide/ AMAHP/ TEGDMA	TCDC/ AMAHP/ TEGDMA	AMAHP/ HEMA	AMAHP/ HEMA
BIDMA Resin, TEGDMA, (wt/wt, %)	90 10	90 10	100 0	100 0
Resin Form	Liquid	liquid	Liquid	liquid
Viscosity @ 20° C. Pa · s	690	40	3	40
Solubility @ 37° C. in water	partially soluble	partially soluble	partially soluble	partially soluble
Solubility @ 37° C. in water/ethanol (50:50, w/w %)	soluble	soluble	soluble	soluble

TABLE II

Compositions for Polymerizable Imidazolium-based Resins

	Example 4 (XJ8-45)	Example 5 (XJ8-31)	Example 6 (XJ8-40)	Example 7 (XJ8-54)
Imidazole-based Resin	XJ8-9	XJ8-9	XJ8-9	XJ8-88
Alkyl Bromide	C12	C4	C4	C8
Imidazolium-based	100	80	100	100

TABLE II-continued

Compositions for Polymerizable Imidazolium-based Resins				
	Example 4 (XJ8-45)	Example 5 (XJ8-31)	Example 6 (XJ8-40)	Example 7 (XJ8-54)
Resin/ TEGDMA, (Wt/wt, %)	0	20	0	0
Resin Form	Liquid	Wax-like	Liquid	Liquid
Viscosity @ 20° C. Pa · s	140	N/A	740	250
Solubility @ 37° C. in EtOH	soluble	soluble	soluble	soluble
Solubility @ 37° C. in water/ethanol (50:50, w/w %)	soluble	soluble	soluble	soluble
Refractive Index @ 25° C.	N/A	1.5130 ± 0.0007	1.5098 ± 0.0019	N/A

TABLE III

Compositions for Polymerizable Imidazolium-based Resins			
	Example 8 (XJ8-80)	Example 9 (XJ8-152)	Example 10 (XJ8-160)
Imidazole-based Resin	XJ8-48	XJ8-152-1	XJ8-157
Alkyl Bromide	C12	C12	C12
Imidazolium-based Resin/ HEMA (Wt/wt, %)	100	79 21	100
Resin Form	Liquid	Liquid	Liquid
Viscosity @ 20° C. Pa · s	175	50	50

TABLE IV

Compositions for Polymerizable Imidazolium-based Resins			
	Example 11 (XJ8-88)	Example 12 (XJ8-94)	Example 14 (XJ8-114)
Imidazole-based Resin	XJ8-81	XJ8-9	XJ8-48
Alkyl Bromide	C8	C6	1,12-C12
Imidazolium-based Resin/ TEGDMA, (Wt/wt, %)	80 20	100 0	100 0

TABLE IV-continued

Compositions for Polymerizable Imidazolium-based Resins			
	Example 11 (XJ8-88)	Example 12 (XJ8-94)	Example 14 (XJ8-114)
Resin Form	Liquid	Liquid	Liquid
Viscosity @ 20° C. Pa · s	170	410	N/A

TABLE V

Compositions of Formulated Resins and Composites				
Composition	XJ8-134	XJ8-135	XJ8-136	XJ8-137
Isosorbide-based Urethane Resin (999993/EBR10224)	63%	90%	25.2%	36.0%
TEGDMA (487170/110207)	7%	10%	2.8%	4.0%
Antibacterial Resin (XJ8-80)	30%	0%	12.0%	0%
Filler Blend (DP3-34)	0%	0%	60.0%	60.0%
CFU at Time zero			1.27 × 10 ⁵	1.27 × 10 ⁵
CFU at 24 hrs			<5	1.38 × 10 ⁵
Reduction, %			>99.999	none

TABLE VI

Compositions of Formulated Resins and Composites					
Composition	IJ1-138	IJ1-84-2	IJ1-85-2	IJ1-118	IJ1-137
Isosorbide-based Urethane Resin (999993/EBR10224)	90%	32.4%	34.2%	14.6%	15.4%
TEGDMA (487170/110207)	10%	3.6%	3.8%	1.6%	1.7%
Antibacterial Resin (XJ8-80)	0%	4.0%	2.0%	1.8%	0.9%
Filler Blend	0%	60.0%	60.0%	82.0%	82.0%
Cytotoxicity (ISO Agarose Overlay)	Zone of Lysis(mm) Grade	0 N/A	N/A N/A	0 2	0 1
Reactivity	0	N/A	N/A	mild	slight
Antibacterial/ <i>S. aureus</i> (ISO 22196)	CFU at 0 hr	1.75 × 10 ⁵	1.75 × 10 ⁵	1.75 × 10 ⁵	1.75 × 10 ⁵
	CFU at 24 hrs	2.10 × 10 ⁶	<5	<5	5
	(Reduction, %)	>99.999	>99.999	>99.999	>99.999

TABLE VII

Cytotoxicity of Formulated Resins Containing Antibacterial Resin						
Resin Compositions	IJ1-107	IJ1-109	IJ1-108	IJ1-110	IJ1-112 (XJ8-135)	IJ1-111
Isosorbide-based Urethane Resin (999993/EBR10224)	81%	81%	85.5%	85.5%	90%	90%
TEGDMA (487170/110207)	9%	9%	9.5%	9.5%	10%	10%
Antibacterial Resin(ABR)/(XJ8-80)	10%	10%	5%	5%	0%	0%
Agarose Overlay	N/A	Moderate	N/A	Moderate	N/A	Moderate
1XMEM Elute	Severe	N/A	Mild	N/A	None	N/A

TABLE VIII

Cytotoxicity, Antibacterial Activity and Mechanical Properties of Formulated Composites Containing Antibacterial Resin						
Composite Compositions	IJ1-115	IJ1-118	IJ1-117	IJ1-137	IJ1-139	IJ1-138
Resin Blend	IJ1-115 17.83%	IJ1-118 17.85%	IJ1-117 17.75%	IJ1-137 17.81%	IJ1-112 17.84%	IJ1-111 17.93%
Filler Blend (XJ8-148)	82.17%	82.15%	82.25%	82.19%	82.16%	82.07%
Antibacterial Resin(ABR) (XJ8-80)	1.78%	1.78%	0.89%	0.89%	0%	0%
Compr. St. (MPa)	322 ± 12	310 ± 12	330 ± 14	318 ± 8	339 ± 10	353 ± 9
Compr. Mod. (MPa)	6570 ± 150	6530 ± 230	6530 ± 100	6390 ± 330	6410 ± 40	6320 ± 380
Flex. St. (MPa)	99 ± 6	97 ± 6	114 ± 8	120 ± 13	119 ± 9	106 ± 8
Flex. Mod. (MPa)	8070 ± 640	9190 ± 940	9080 ± 670	10330 ± 1330	10600 ± 1310	11320 ± 1390
Agarose Overlay	N/A	Mild	N/A	Slight	N/A	None
1XMEM Elute	Slight	N/A	Slight	N/A	None	N/A
Antibacterial Activity Vs <i>S. aureus</i>	N/A	1.75 × 10 ⁵	N/A	1.75 × 10 ⁵	N/A	1.75 × 10 ⁵
24 hrs/CFU Reduction, %	N/A	<5	N/A	5	N/A	2.10 × 10 ⁶
		>99.999		99.999		None

TABLE IX

Mechanical Properties of Formulated Resins Containing Antibacterial Resin						
Resin Compositions	IJ1-206	IJ1-208	IJ1-207	IJ2-1	IJ1-112 (XJ8-135)	IJ1-111
Isosorbide-based Urethane Resin (999993/EBR10224)	81%	81%	85.5%	85.5%	90%	90%
TEGDMA (487170/110207)	9%	9%	9.5%	9.5%	10%	10%
Antibacterial Resin(ABR)/(XJ8-152)	10%	10%	5%	5%	0%	0%
CQ	0.165%	0.165%	0.165%	0.165%	0.165%	0.165%
EDAB	0.300%	0%	0.300%	0%	0.300%	0%
LTPO	0%	0.40%	0%	0.40%	0%	0.40%
BHT	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%
Viscosity @ 20° C. Pa · s	35	35	40	40	40	35
Compr. Mod. (MPa)	2530 ± 40	2550 ± 50	2620 ± 60	2640 ± 100	2640 ± 40	2680 ± 40
Flex. St. (MPa)	68 ± 3	92 ± 2	74 ± 3	89 ± 3	80 ± 2	94 ± 2
Flex. Mod. (MPa)	1740 ± 140	2430 ± 110	1680 ± 120	2160 ± 130	1850 ± 100	2190 ± 130

TABLE X

Mechanical Properties of Formulated Composites Containing Antibacterial Resin						
Composite Compositions	IJ2-39	IJ2-41	IJ2-40	IJ2-42	IJ1-139	IJ1-138
Resin Blend	IJ1-206 18.63%	IJ1-208 18.31%	IJ1-207 18.27%	IJ2-1 18.57%	IJ1-112 17.84%	IJ1-111 17.93%
Filler Blend (XJ8-148)	81.37%	81.69%	81.76%	81.43%	82.16%	82.07%

TABLE X-continued

Mechanical Properties of Formulated Composites Containing Antibacterial Resin						
Composite Compositions	IJ2-39	IJ2-41	IJ2-40	IJ2-42	IJ1-139	IJ1-138
Antibacterial Resin(ABR) (XJ8-152)	1.86%	1.83%	0.92%	0.93%	0%	0%
Compr. St. (MPa)	300 ± 6	296 ± 20	313 ± 10	324 ± 12	339 ± 10	353 ± 9
Compr. Mod. (MPa)	6300 ± 40	6250 ± 230	6450 ± 150	6570 ± 160	6410 ± 40	6320 ± 380
Flex. St. (MPa)	108 ± 8	115 ± 6	114 ± 8	120 ± 8	119 ± 9	106 ± 8
Flex. Mod. (MPa)	9800 ± 340	9910 ± 490	8790 ± 660	10800 ± 780	10600 ± 1310	11320 ± 1390

TABLE XI

Mechanical Properties of Formulated Resins Containing Antibacterial Resin						
Resin Compositions	IJ2-178	IJ2-180	IJ2-179	IJ2-181	IJ2-131	IJ2-132
Isosorbide-based Urethane Resin (999993/EBR10224)	81%	81%	85.5%	85.5%	90%	90%
TEGDMA (487170/110207)	9%	9%	9.5%	9.5%	10%	10%
Antibacterial Resin(ABR) (XJ8-160)	10%	10%	5%	5%	0%	0%
CQ	0.165%	0.165%	0.165%	0.165%	0.165%	0%
EDAB	0.300%	0%	0.300%	0%	0%	0%
LTPO	0%	0.40%	0%	0.40%	0%	0.40%
BHT	0.030%	0.030%	0.030%	0.030%	0.030%	0.030%
Viscosity @ 20° C. Pa · s	35	35	35	35	40	40
Compr. St. (MPa)	2500 ± 30	2440 ± 00	2290 ± 40	2580 ± 40	N/A	2640 ± 30
Compr. Mod. (MPa)						
Flex. St. (MPa)	63 ± 6	77 ± 5	70 ± 4	82 ± 5	N/A	97 ± 1
Flex. Mod. (MPa)	1560 ± 210	1850 ± 250	1690 ± 200	1850 ± 220	N/A	2280 ± 60

TABLE XII

Properties of Formulated Composites Containing Antibacterial Resin						
Composite Compositions	IJ2-189	IJ2-191	IJ2-190	IJ2-192	IJ2-170	IJ2-171
Resin Blend	IJ2-178 17.52%	IJ2-180 17.43%	IJ2-179 17.57%	IJ2-181 17.22%	IJ2-131 17.48%	IJ2-132 17.76%
Filler Blend (XJ8-148)	82.48%	82.57%	82.43%	82.78%	82.52%	82.24%
Antibacterial Resin(ABR) (XJ8-160)	1.75%	1.74%	0.88%	0.86%	0%	0%
Compr. St. (MPa)	322 ± 11	313 ± 9	328 ± 14	339 ± 12	295 ± 13	332 ± 16
Compr. Mod. (MPa)	6350 ± 90	6520 ± 120	6140 ± 180	6610 ± 90	5690 ± 120	6350 ± 120
Flex. St. (MPa)	121 ± 3	138 ± 13	129 ± 13	136 ± 8	96 ± 8	118 ± 16
Flex. Mod. (MPa)	9390 ± 610	11800 ± 690	10850 ± 1130	12320 ± 660	6720 ± 650	10840 ± 1170
Antibacterial Activity Vs <i>S. aureus</i>	1.65×10^5 5	1.65×10^5 <5	1.65×10^5 <5	1.65×10^5 <5	N/A	1.65×10^5 1.85×10^4
24 hrs/CFU Reduction, %	99.973	>99.973	>99.973	>99.973		N/A

TABLE XIII

Compositions of Formulated Resins Containing Different Antibacterial Resins					
Resin Compositions	IJ2-201	IJ12-202	IJ2-203	IJ2-204	IJ2-132
Isosorbide-based Urethane Resin (999993/EBR10224)	81%	81%	81%	81%	90%
TEGDMA (487170/110207)	9%	9%	9%	9%	10%

TABLE XIII-continued

Compositions of Formulated Resins Containing Different Antibacterial Resins					
Resin Compositions	IJ2-201	IJ2-202	IJ2-203	IJ2-204	IJ2-132
Antibacterial Resin (ABR)					
XJ8-88	10%				0%
XJ8-94		10%			
XJ8-54			10%		
XJ8-114				10%	
CQ	0.165%	0.165%	0.165%	0.165%	0%
EDAB	0%	0%	0%	0%	0%
LTPO	0.40%	0.40%	0.40%	0.40%	0.40%
BHT	0.030%	0.030%	0.030%	0.030%	0.030%
Viscosity @ 20° C. Pa · s	40	40	40	40	40
Compr. St. (MPa)	2460 ± 30	2490 ± 70	2480 ± 50	N/A	2640 ± 30
Compr. Mod. (MPa)					
Flex. St. (MPa)	80 ± 2	86 ± 3	86 ± 3	N/A	97 ± 1
Flex. Mod. (MPa)	2030 ± 100	2330 ± 120	2210 ± 150	N/A	2280 ± 60

TABLE XIV

Antibacterial Activities and Properties of Formulated Composites Containing Antibacterial Resin					
Composite Compositions	IJ2-205	IJ2-206	IJ2-207	IJ2-208	IJ2-171
Resin Blend					
	IJ2-201	IJ2-202	IJ2-203	IJ2-204	IJ2-132
	18.18%	18.23%	18.02%	18.57%	17.76%
Filler Blend (XJ8-148)					
	81.83%	81.77%	81.98%	81.43%	82.24%
Antibacterial Resins (ABR)					
	1.82%	1.82%	1.80%	1.86%	0%
Compr. St. (MPa)	335 ± 11	325 ± 14	328 ± 8	340 ± 15	332 ± 16
Compr. Mod. (MPa)	6620 ± 80	6520 ± 120	6560 ± 180	6380 ± 220	6350 ± 120
Flex. St. (MPa)	148 ± 11	146 ± 11	149 ± 7	147 ± 13	118 ± 16
Flex. Mod. (MPa)	13840 ± 410	13390 ± 1390	11900 ± 880	11350 ± 1140	10840 ± 1170
Antibacterial Activity Vs <i>S. aureus</i>	2.05×10^5	2.05×10^5	2.05×10^5	2.05×10^5	2.05×10^5
24 hrs/CFU Reduction, %	99.998	99.942	>99.973	99.233	N/A

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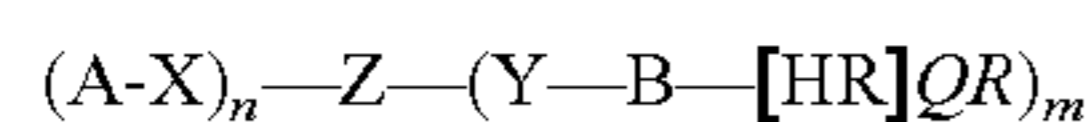
It will be appreciated that various of the above-disclosed and other features and functions, or alternatives thereof, may be desirably combined into many other different systems or applications. Also, various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, and are also intended to be encompassed by the following claims.

What I claim is:

1. A [dental] curable antimicrobial composition comprising:

[from about 0.1 weight percent to about 5.0 weight percent of] an imidazolium-based polymerizable resin[; from about 5 weight percent to about 60 weight percent of a non-imidazolium-based polymerizable resin; from about 0.005 weight percent to about 5 weight percent of at least one of a photoinitiator, a thermal/redox initiator or other additive; from about 40 weight percent to about 90 weight percent of a glass filler having a particle size of from about 10 nm to about 100 microns; and an optional inert solvent]

wherein the imidazolium-based polymerizable resin has a formula of:



wherein A is a polymerizable moiety selected from the group consisting of methacrylate, acrylate, epoxy and vinyl ether,

wherein B is an [imidazole or a methyl imidazole] imidazolium moiety,

wherein R is a hydrogen atom or an alkyl group having from 1 to 22 carbon atoms,

wherein [H] Q is [a halogen atom, a chlorine atom, a bromine atom or an iodine atom] an imidazolium counter ion,

wherein X and Y are the same or different and are an ether, ester, amide, imide, direct link, alkyl, or aromatic,

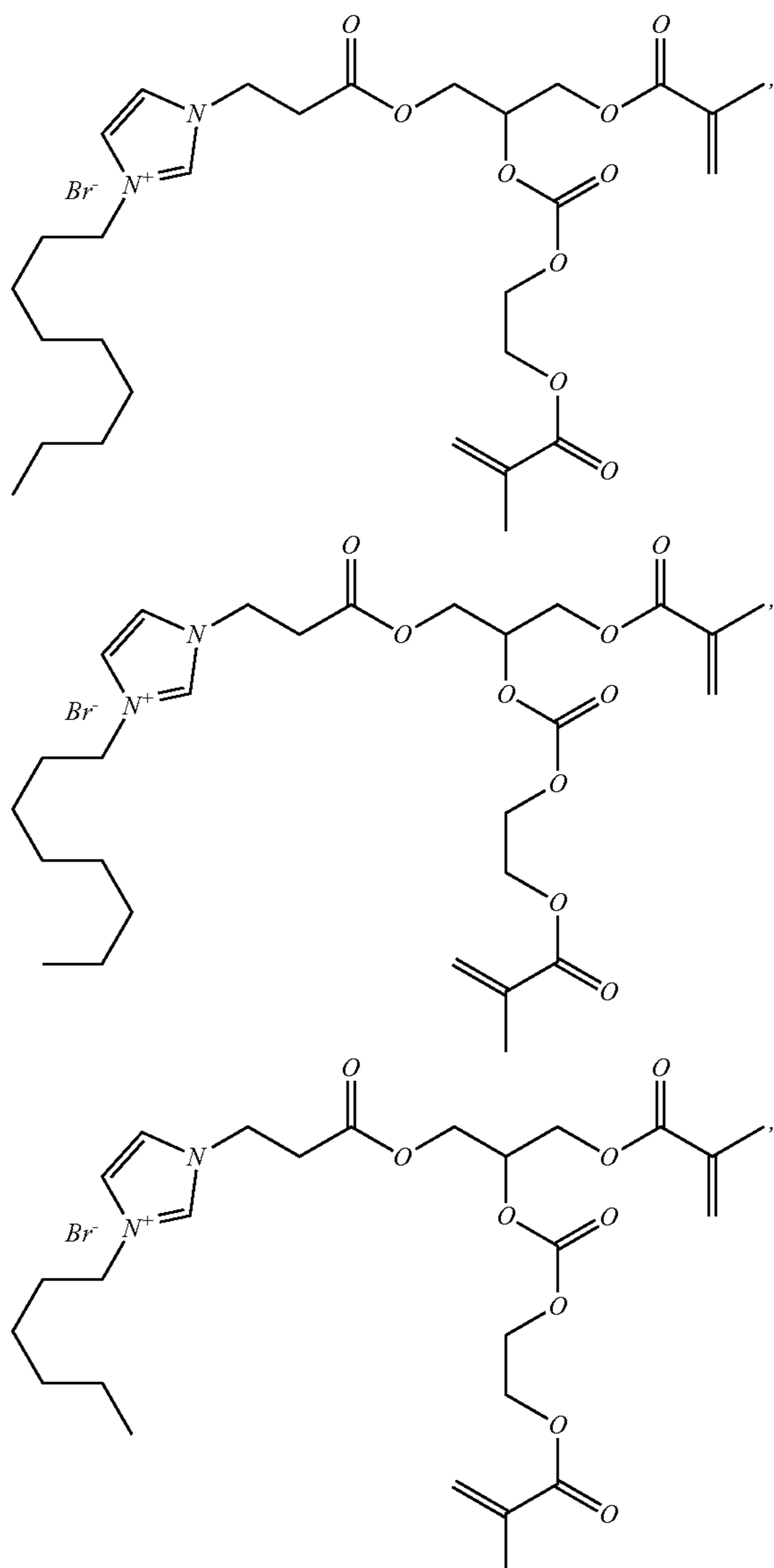
wherein Z is an alkyl or an aromatic, and wherein n and m are integers of at least 1.

2. The [dental] curable antimicrobial composition according to claim 1, wherein the imidazolium-based polymerizable resin demonstrates antibacterial activity capable of killing at least 99 percent of *S. mutans*.

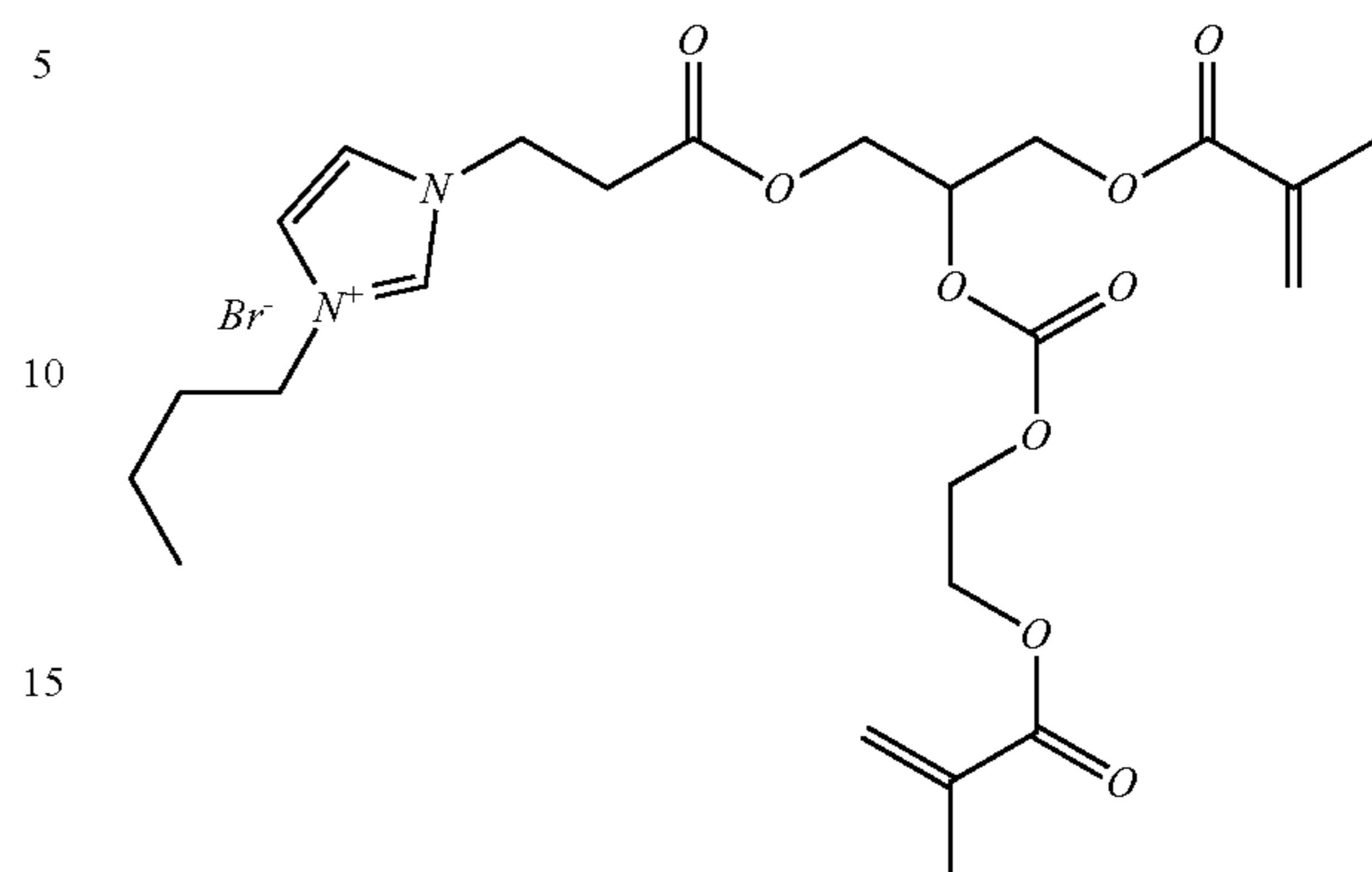
3. The [dental] curable antimicrobial composition according to claim 1, wherein the [dental composition in its entirety is capable of an] imidazolium-based polymerizable resin demonstrates antibacterial activity capable [to] of killing more than 99 percent of *S. mutans* and *S. aureus*.

4. A curable antimicrobial composition according to claim 1, wherein the imidazolium-based polymerizable resin is an alkylimidazoliumbromide-dimethacrylate resin having a formula selected from:

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-continued
and

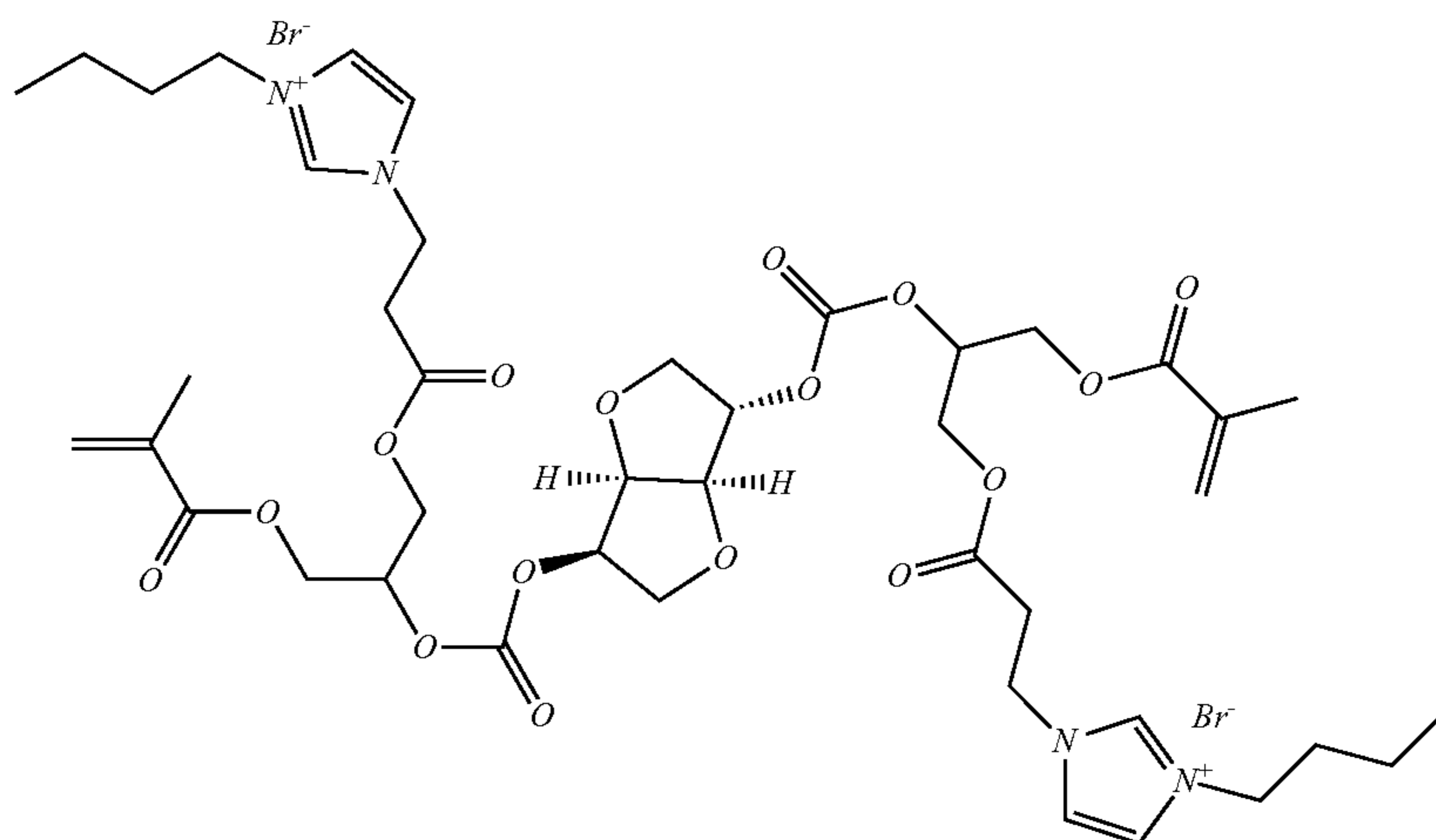
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5. A curable antimicrobial composition comprising: at least one ionic imidazolium moiety, and a polymerizable moiety, the imidazolium-based polymerizable resin selected from a HEMA-based monoimidazoliumbromide-dimethacrylate resin, a 3-dodecanylimidazoliumbromide-dimethacrylate resin, a bis(3-dodecanylimidazoliumbromide)-bisacrylate resin, a bis(3-butylimidazoliumbromide)-bisacrylate resin, a EGAMA-based monoimidazoliumbromide-monomethacrylate resin, a 3-dodecanylimidazoliumbromide-monomethacrylate resin, a AMAHP-based monoimidazolium-methacrylate resin, a isosorbide-based bisimidazoliumbromide-dimethacrylate resin, a isosorbide-based bis(3-butylimidazoliumbromide)-dimethacrylate resin, and a 1,6-hexane-bisimidazoliumbromide-dimethacrylate resin.

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6. A curable antimicrobial composition according to claim 5, wherein the imidazolium-based polymerizable resin having a formula selected from:

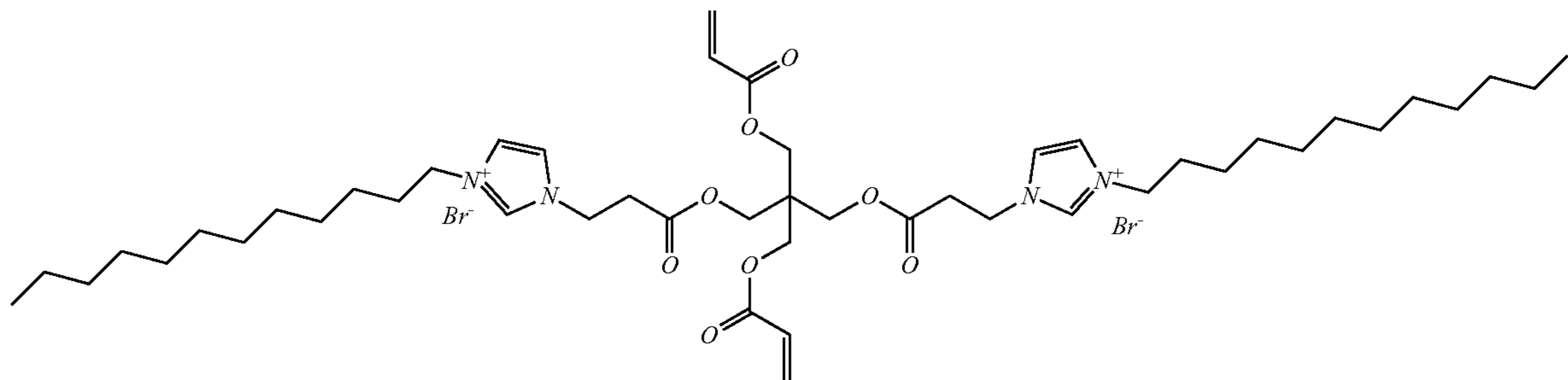
- (a) a bisimidazolium-dimethacrylate resin that has a formula selected from one of a:
an isosorbide-based bisimidazoliumbromide-dimethacrylate resin



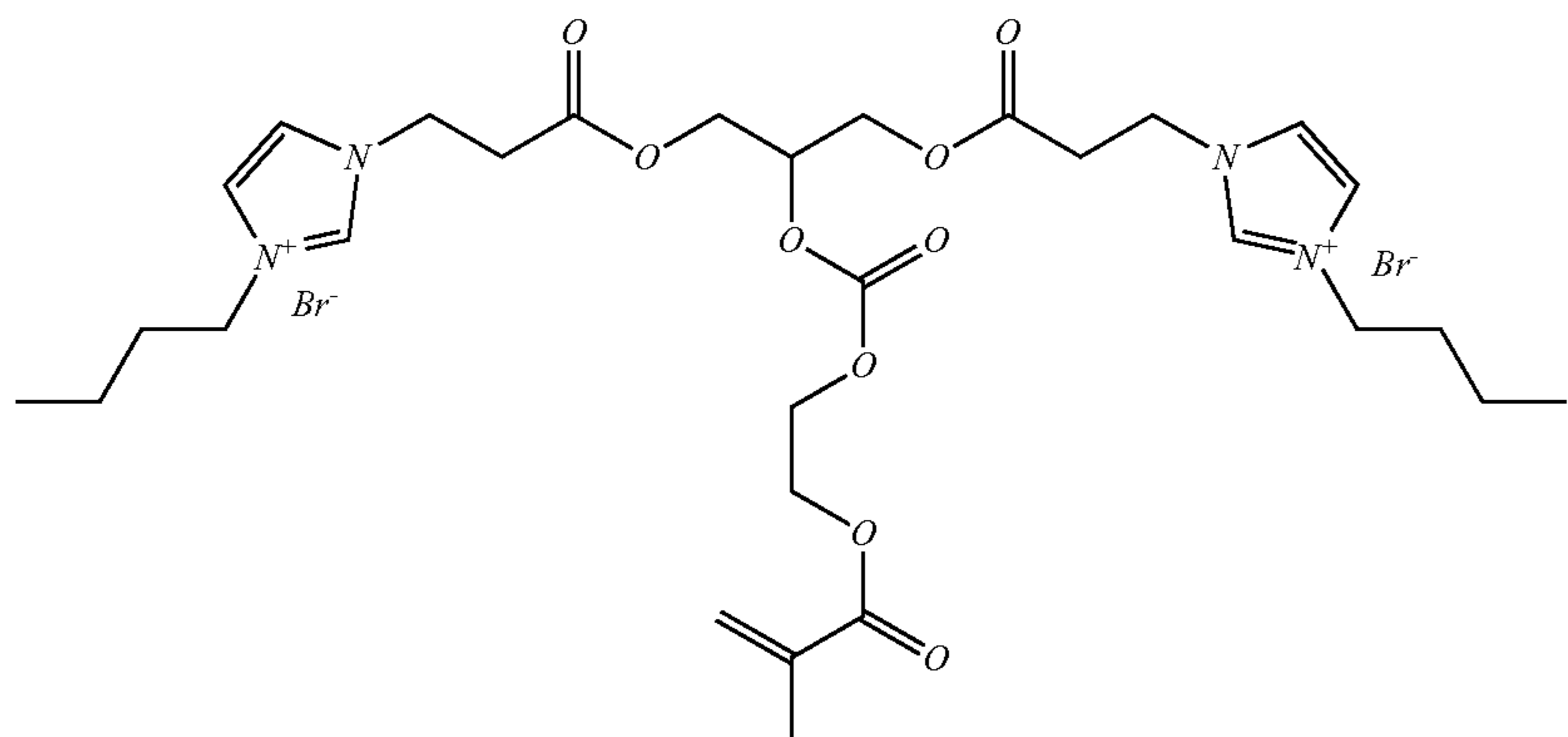
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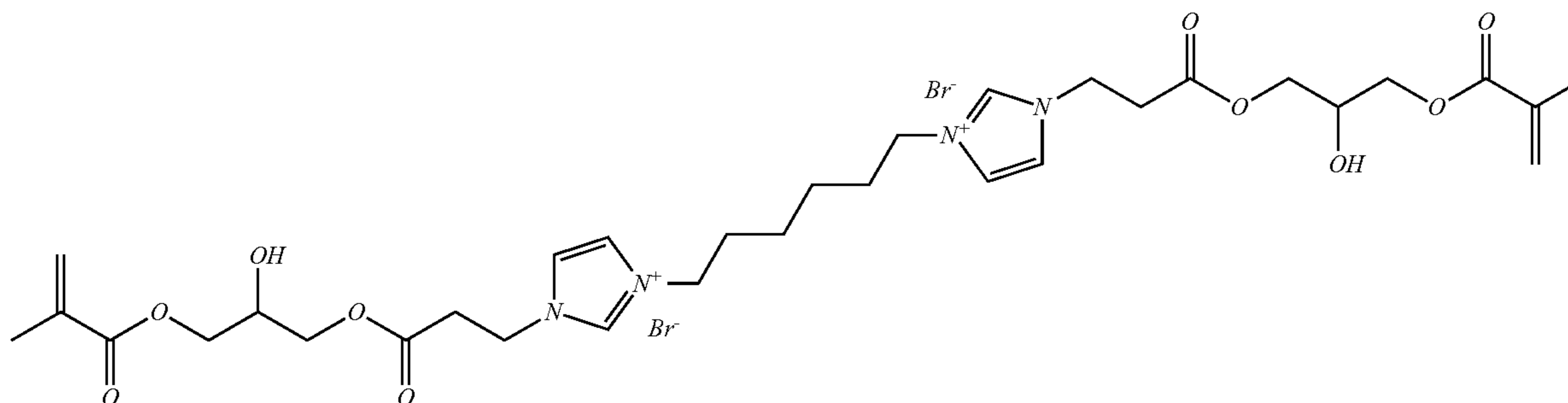
a bis(3-dodecanylimidazoliumbromide)-bisacrylate resin



a bis(3-butyylimidazoliumbromide)-bisacrylate resin

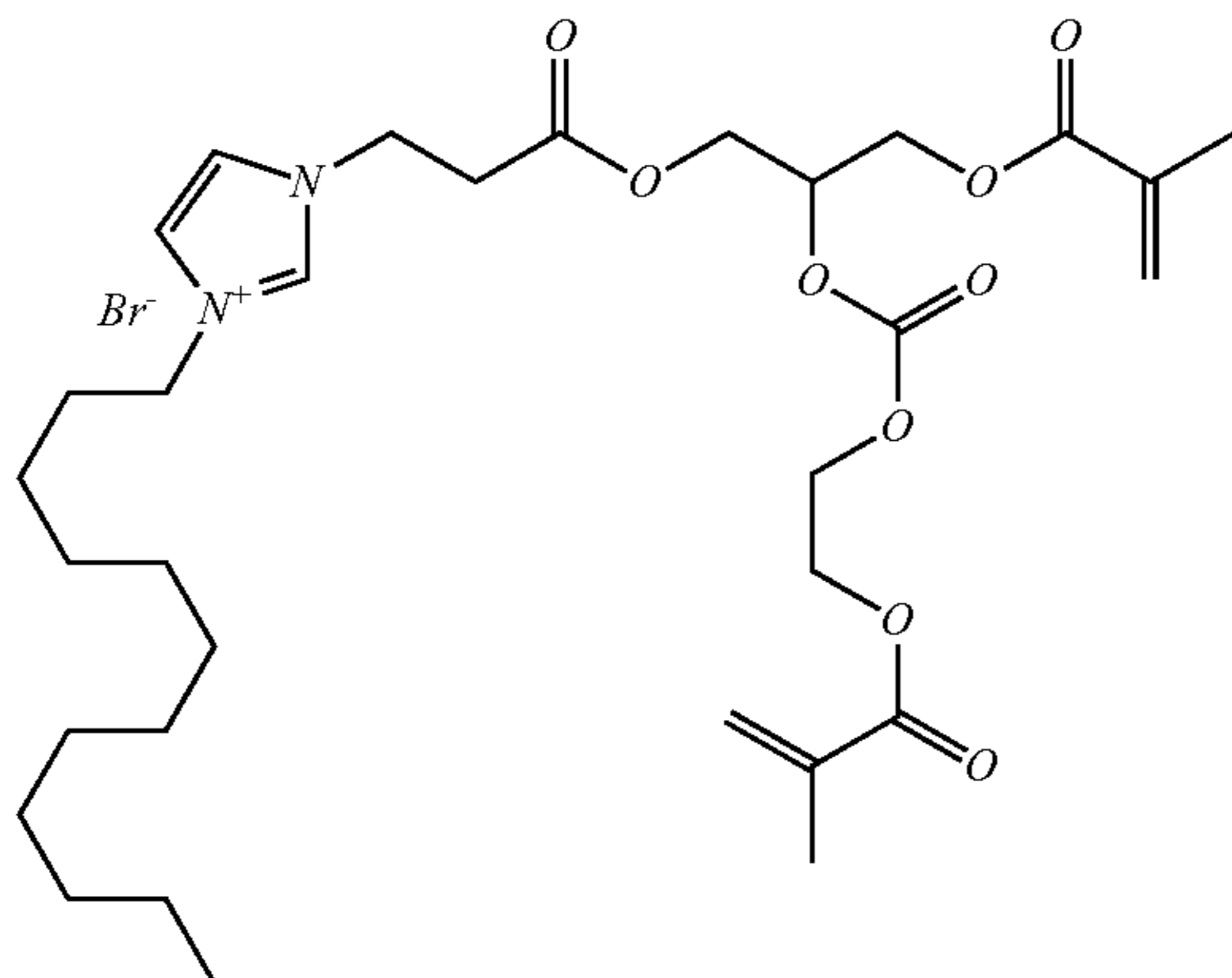


A 1,6-hexane-bisimidazoliumbromide-dimethacrylate resin

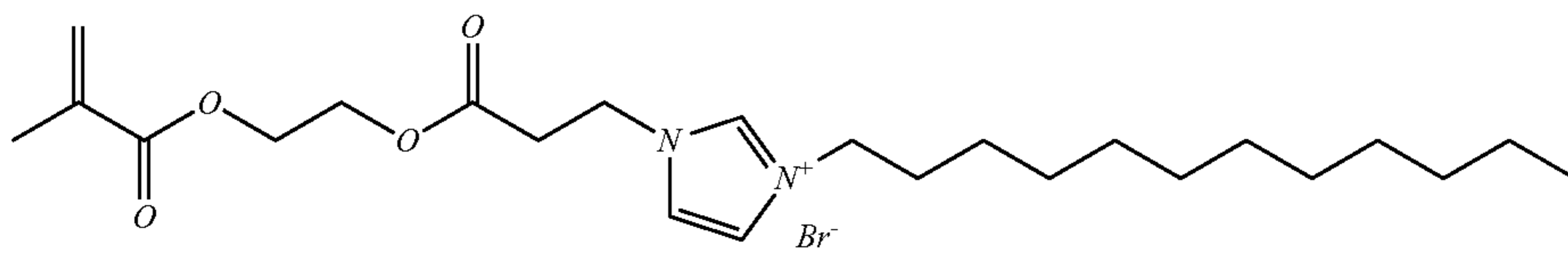


(b) a monoimidazolium-dimethacrylate resin that has a formula of a HEMA-based monoimidazoliumbromide-dimethacrylate resin

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(c) a monoimidazolium-dimethacrylate resin that has a formula of a EGAMA-based monoimidazoliumbromide-monomethacrylate resin



7. A curable antimicrobial composition according to claim 5, wherein the imidazolium-based polymerizable resin is present from about 0.1 weight percent to about 20.0 weight percent, based on the total weight of the composition.

8. A curable antimicrobial composition according to claim 7, comprising: one or more acidic resins or polymers, or reactive acidic glass powders complexed with the imidazolium-based polymerizable resin to form one of a soluble liquid resin, soft gel, hard gel and highly-crosslinked solid.

9. A curable antimicrobial composition according to claim 8, comprising:

about 5 weight percent to about 99 weight percent of a non-imidazolium based polymerizable resin;

from about 0.001 weight percent to about 5 weight percent initiators and other additives;

from about 40 weight percent to about 90 weight percent of filler particles having a size of from about 10 nm to about 100 micron,

an optional inert solvent,

wherein all weight percents are based on the total weight of the curable antimicrobial composition.

10. A curable antimicrobial composition according to claim 8, comprising:

from about 5 weight percent to about 60 weight percent of a non-imidazolium-based polymerizable resin;

from about 0.005 weight percent to about 5 weight percent of at least one of a photoinitiator, a thermal/redox initiator or other additive;

wherein the imidazolium-based polymerizable resin is present from about 0.1 weight percent to about 5.0 weight percent, and

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wherein all weight percents are based on the total weight of the curable antimicrobial composition.

11. A curable antimicrobial composition according to claim 10, comprising

about 80 weight percent of a glass filler having a particle size of from about 10 nm to about 100 microns; and wherein the imidazolium-based polymerizable resin is present from about 0.9 weight percent to about 1.8 weight percent, and

wherein all weight percents are based on the total weight of the curable antimicrobial composition.

12. A curable antimicrobial composition comprising: an imidazolium-based polymerizable resin comprising:

at least one polymerizable group, and

at least one imidazolium moiety comprising a linear long alkyl chain of from eight to fourteen carbon atoms.

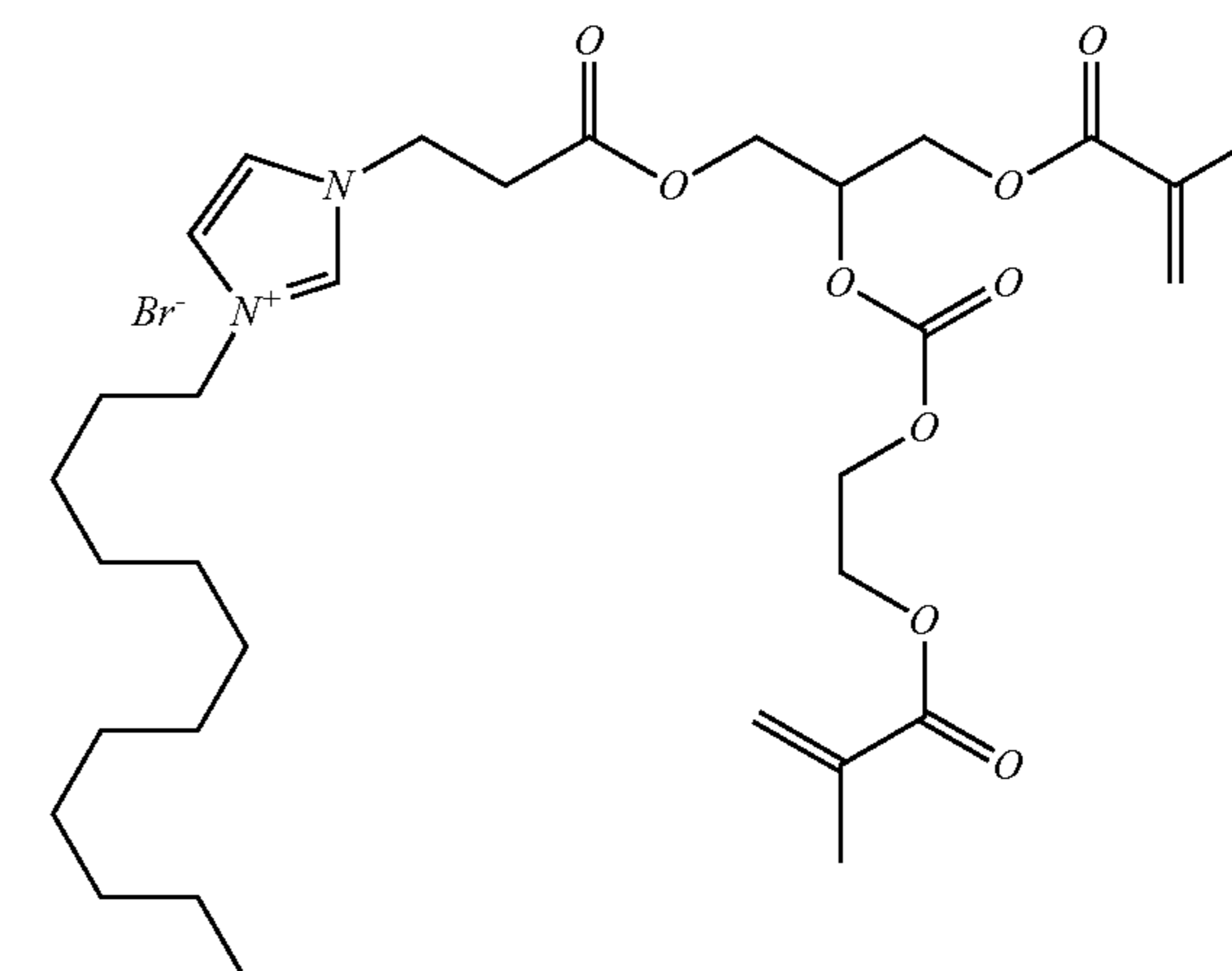
13. A curable antimicrobial composition according to claim 12, the at least one polymerizable group selected from methacrylate, acrylate, epoxy and vinylether.

14. A curable antimicrobial composition according to claim 12, the at least one polymerizable group selected from acrylate, methacrylate and polyacrylate.

15. A curable antimicrobial composition according to claim 14, the at least one polymerizable group comprising two methacrylate groups, and the at least one imidazolium moiety comprising a linear alkyl chain of twelve carbon atoms.

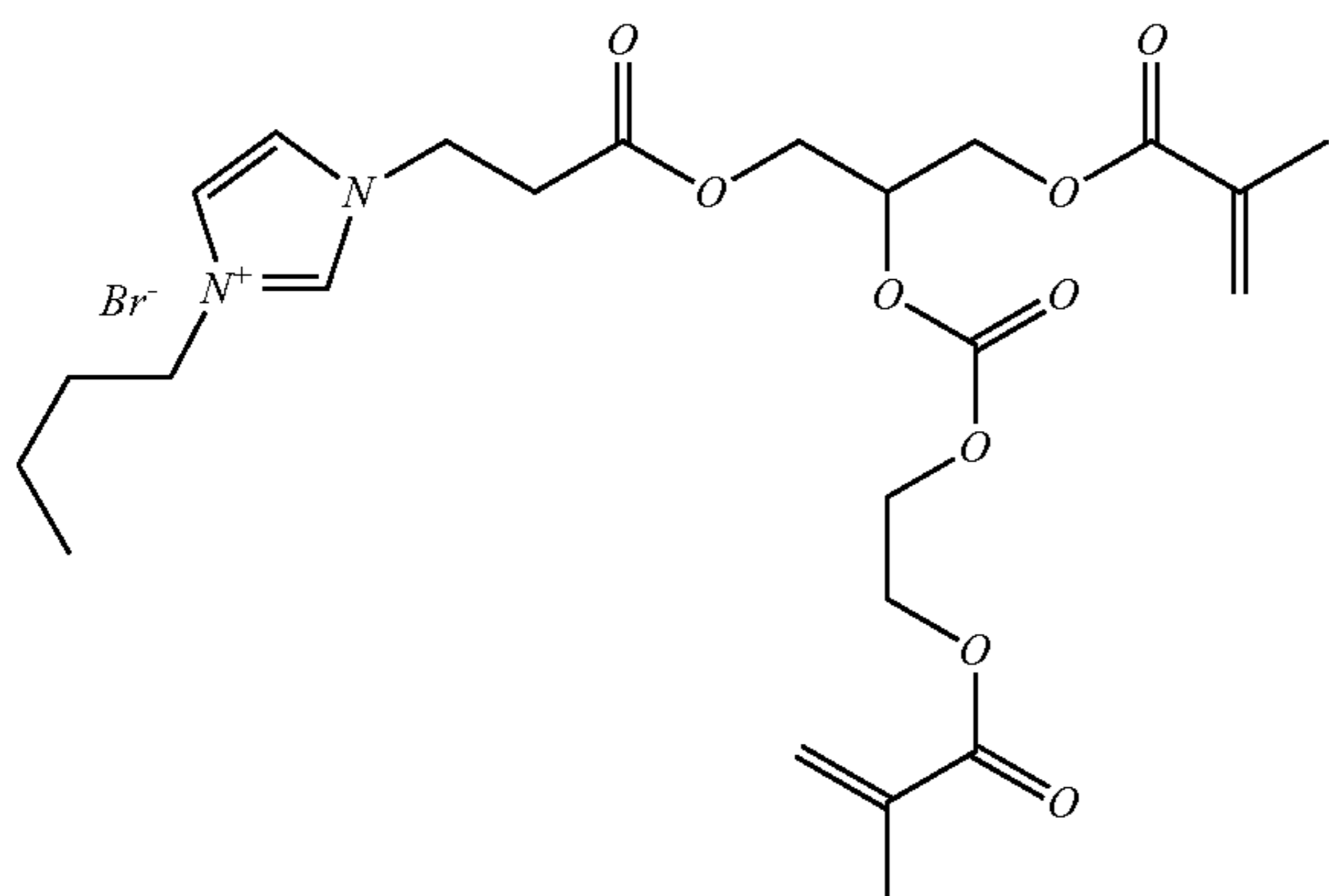
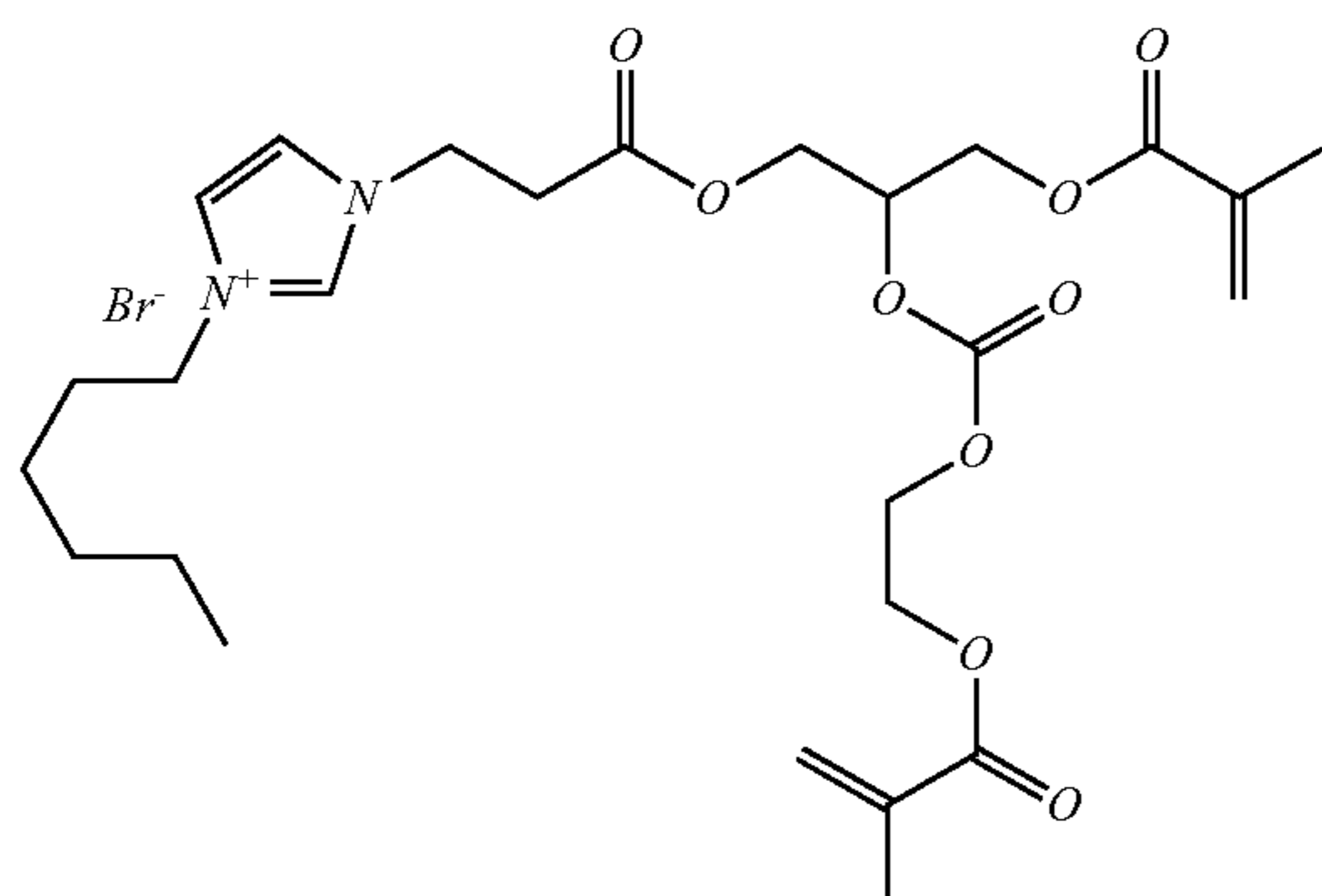
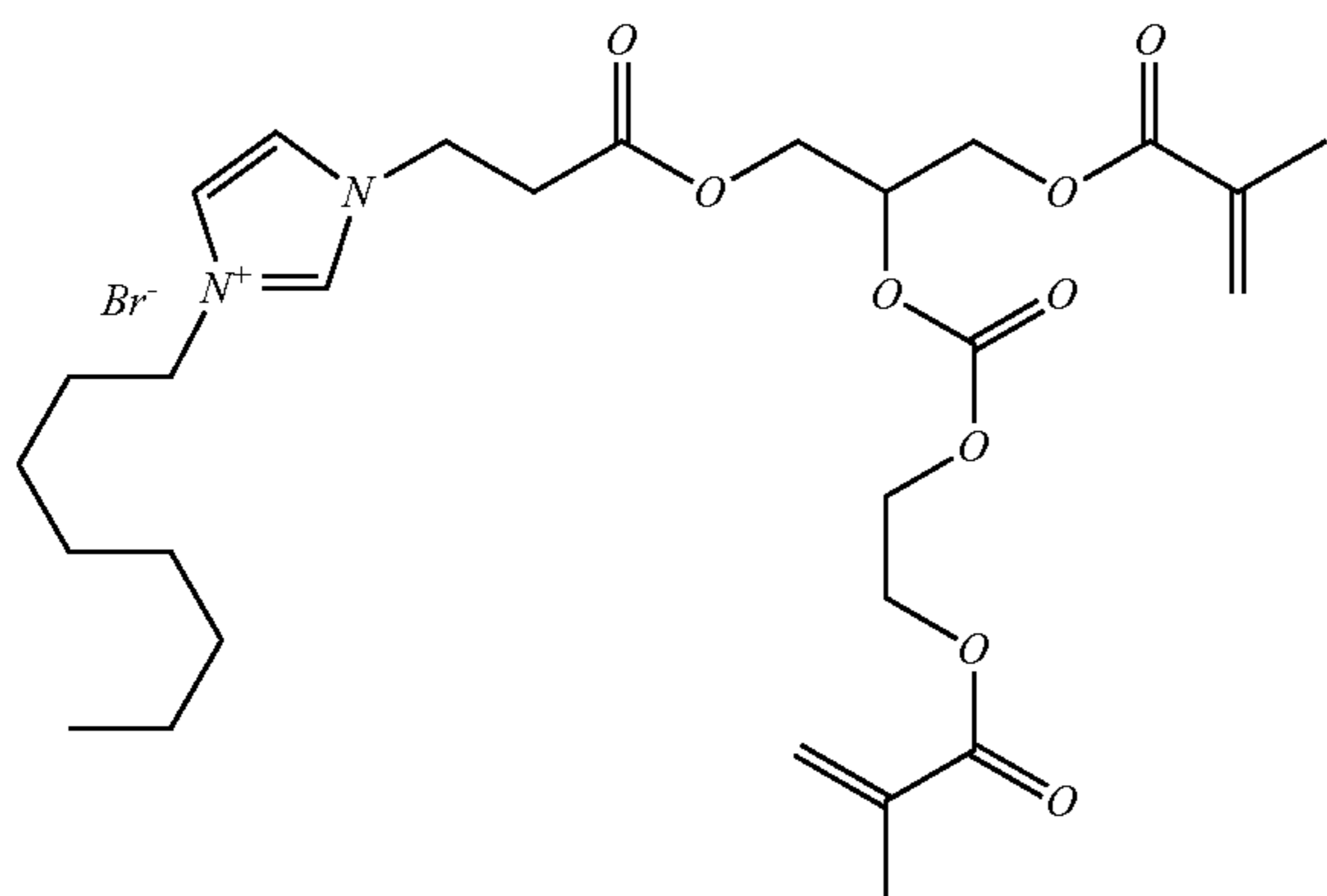
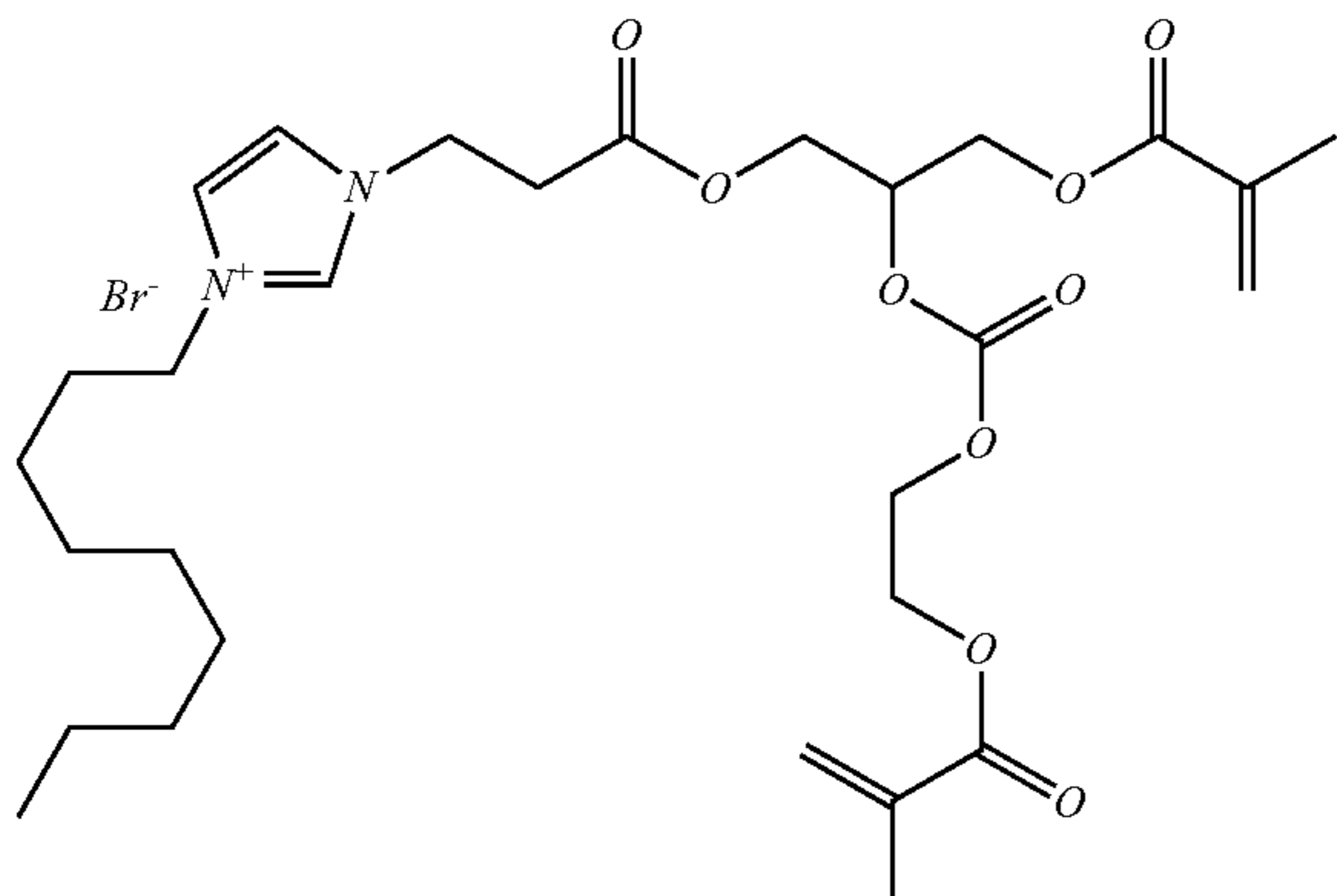
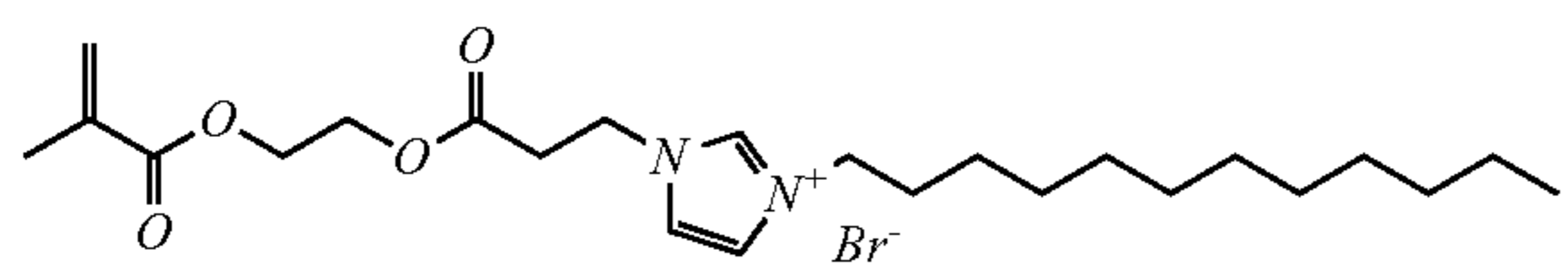
16. A curable antimicrobial composition according to claim 12 having a formula selected from:

a HEMA-based monoimidazoliumbromide-dimethacrylate resin



a EGAMA-based monoimidazoliumbromide-monomethacrylate resin

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17. A curable antimicrobial composition according to claim 12, wherein the imidazolium-based polymerizable resin is present from about 0.1 weight percent to about 20.0 weight percent based on the total weight of the composition.

18. A curable antimicrobial composition according to claim 17, comprising: one or more acidic resins or polymers, or reactive acidic glass powders complexed with the imidazolium-based polymerizable resin to form one of a soluble liquid resin, a gel, and a crosslinked solid.

19. A curable antimicrobial composition according to claim 18, comprising:

about 5 weight percent to about 99 weight percent of a non-imidazolium based polymerizable resin;

from about 0.001 weight percent to about 5 weight percent initiators and other additives;

from about 40 weight percent to about 90 weight percent of filler particles having a size of from about 10 nm to about 100 micron,

an optional inert solvent,

wherein all weight percents are based on the total weight of the curable antimicrobial composition.

20. A curable antimicrobial composition according to claim 18, comprising:

from about 5 weight percent to about 60 weight percent of a non-imidazolium-based polymerizable resin;

from about 0.005 weight percent to about 5 weight percent of at least one of a photoinitiator, a thermal/redox initiator or other additive;

wherein the imidazolium-based polymerizable resin is present from about 0.1 weight percent to about 5.0 weight percent, and

wherein all weight percents are based on the total weight of the curable antimicrobial composition.

21. A curable antimicrobial composition according to claim 20, comprising

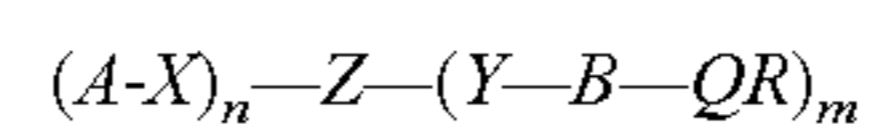
about 80 weight percent of a glass filler having a particle size of from about 10 nm to about 100 microns; and

wherein the imidazolium-based polymerizable resin is present from about 0.9 weight percent to about 1.8 weight percent, and

wherein all weight percents are based on the total weight of the curable antimicrobial composition.

22. A curable antimicrobial composition according to claim 12,

wherein the imidazolium-based polymerizable resin has a formula of:



wherein A is a polymerizable moiety selected from the group consisting of methacrylate, acrylate, epoxy and vinyl ether,

wherein B is an imidazole or a methyl imidazole,

wherein R is a hydrogen atom or an alkyl group having from 1 to 22 carbon atoms,

wherein Q is an imidazolium counter ion,

wherein X and Y are the same or different and are an ether, ester, amide, imide, direct link, alkyl, or aromatic,

wherein Z is an alkyl or an aromatic, and

wherein n and m are integers of at least 1.

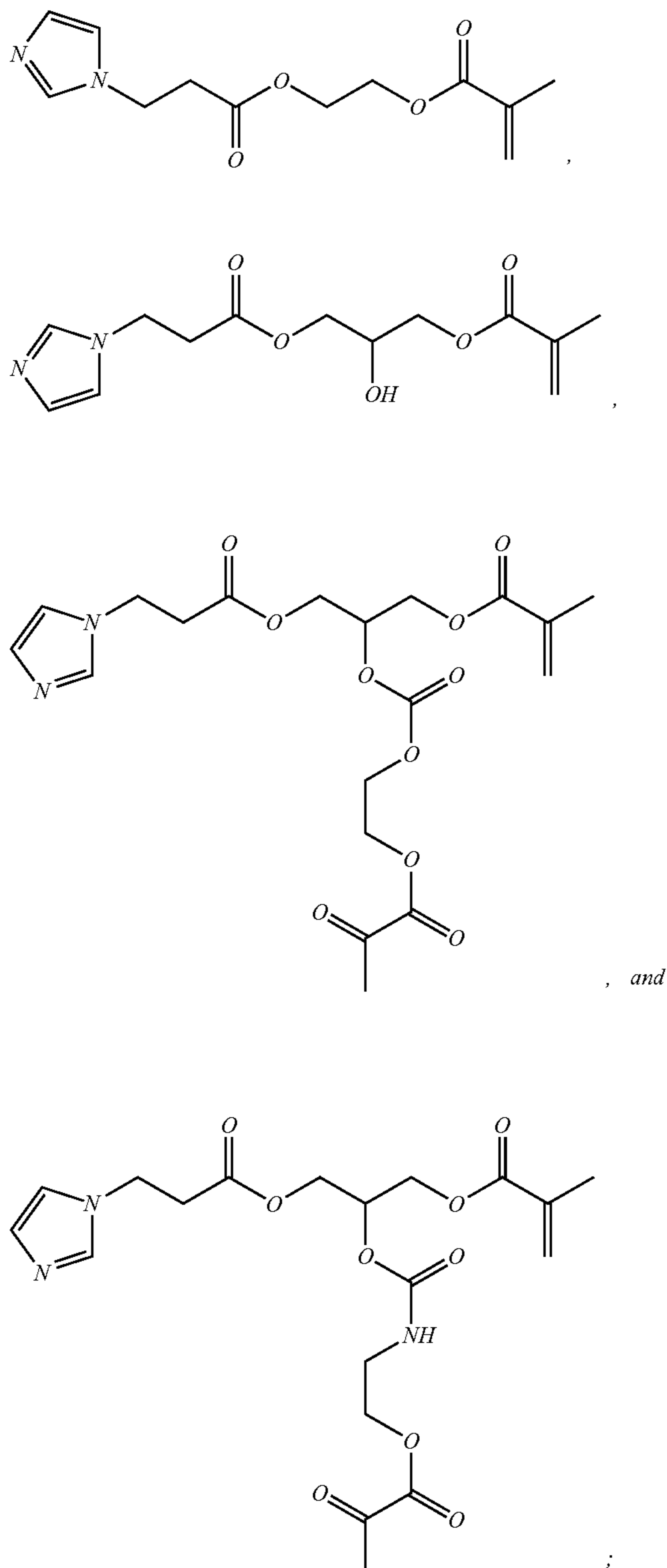
23. A curable antimicrobial composition according to claim 22, wherein Q is a halogen.

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24. A curable antimicrobial composition according to claim 22, wherein Q is selected from chlorine, bromine, and iodine.

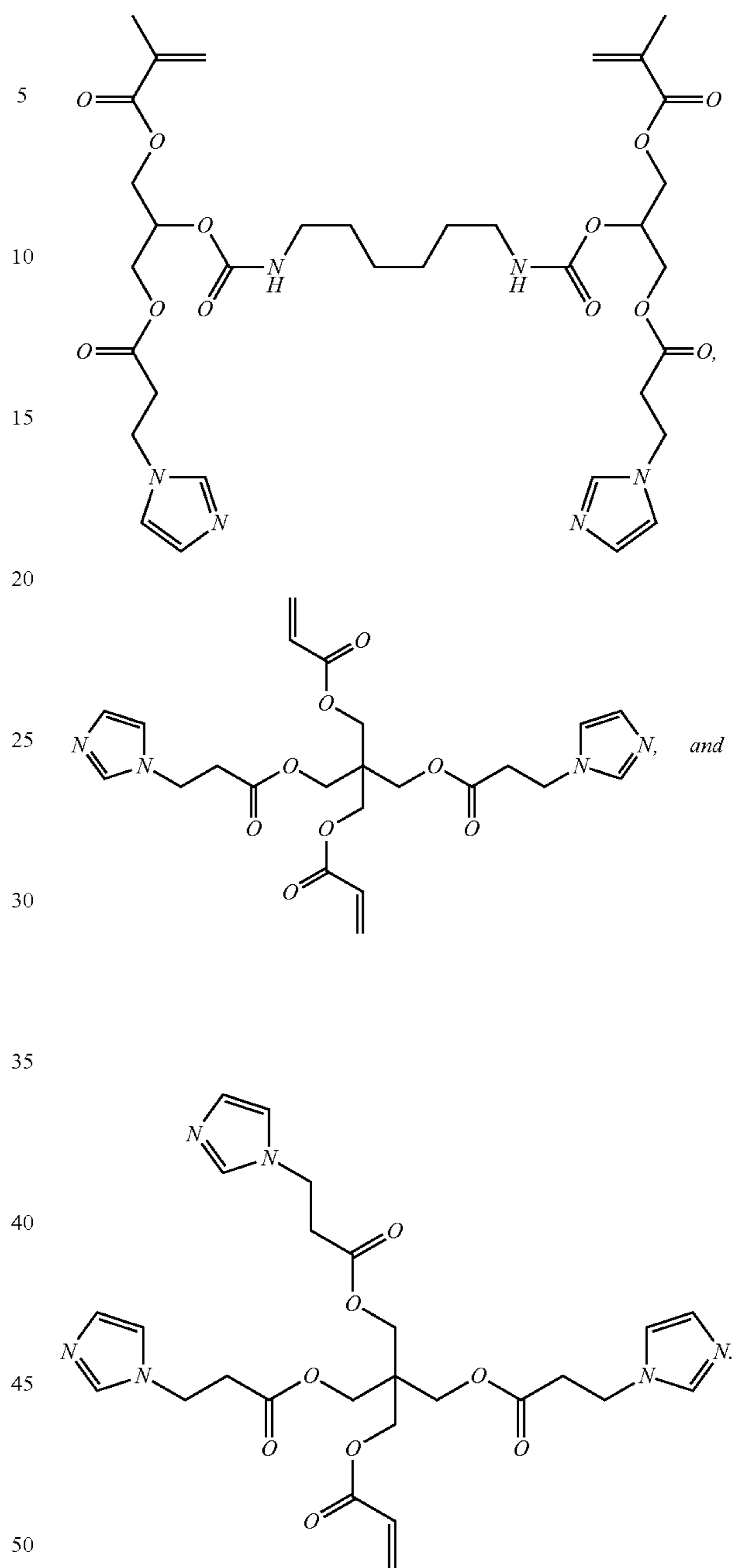
25. An imidazole-based precursor for forming an imidazolium-based polymerizable resin, comprising:

a polymerizable imidazole-based resin selected from a monoimidazole resin and a polyimidazole(meth)acrylate resin, the moniomidazole resin having a formula selected from:



the polyimidazole(meth)acrylate resin having a formula selected from:

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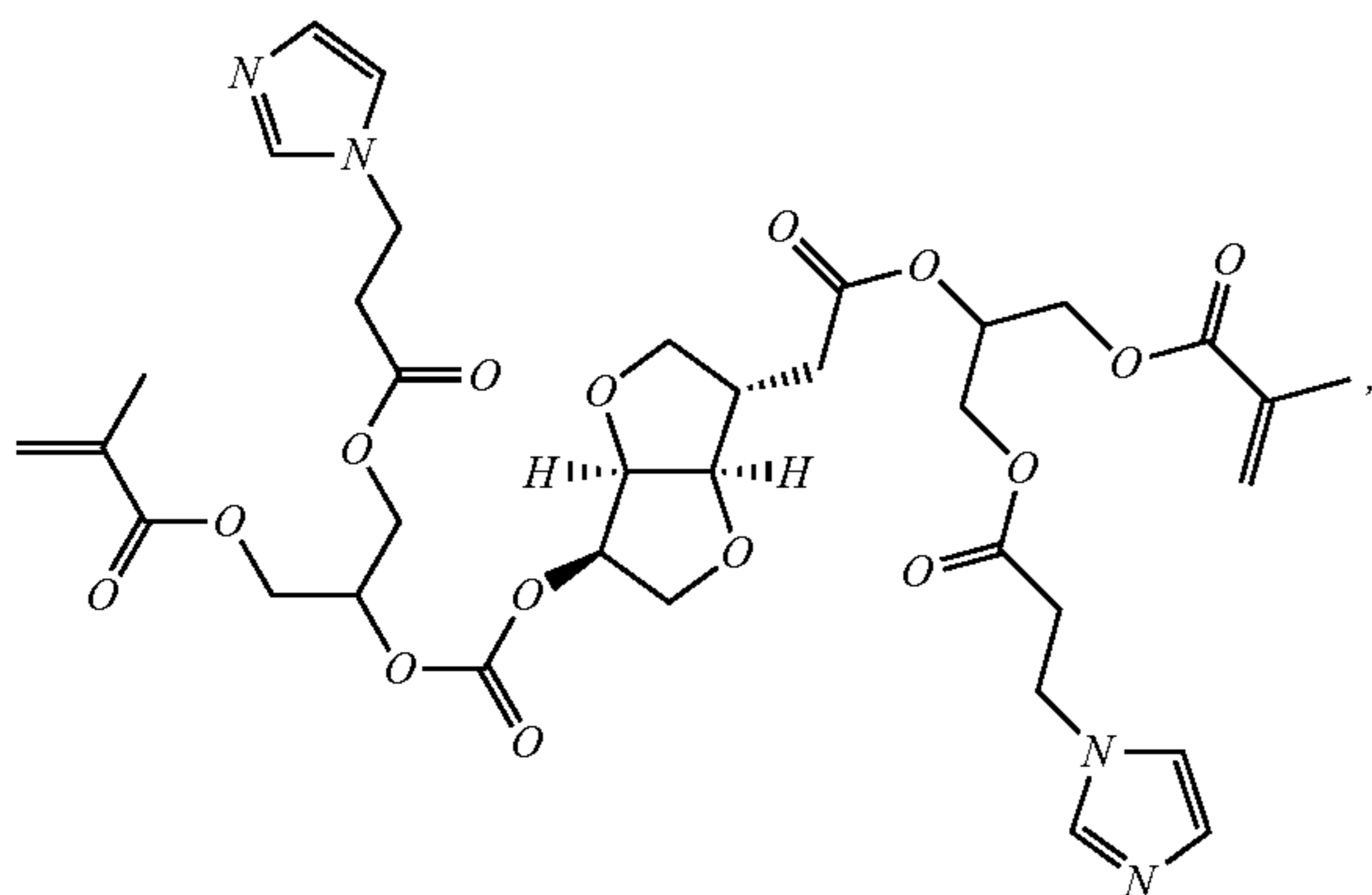


26. An imidazole-based polymerizable resin comprising: an imidazole moiety, the imidazole-based polymerizable resin selected from a isosorbide-based bisimidazole-dimethacrylate resin, a TCDC-based bisimidazole-dimethacrylate resin, a butanediol-based bisimidazole-dimethacrylate resin, a TCDC-based bisimidazole-dimethacrylate resin, a paraxylenediol-based bisimidazole-dimethacrylate resin, a HEMA-based monoimidazole-dimethacrylate Resin, a AMAHP-based monoimidazole-monomethacrylate resin, and a EGAMA-based monoimidazole-monomethacrylate.

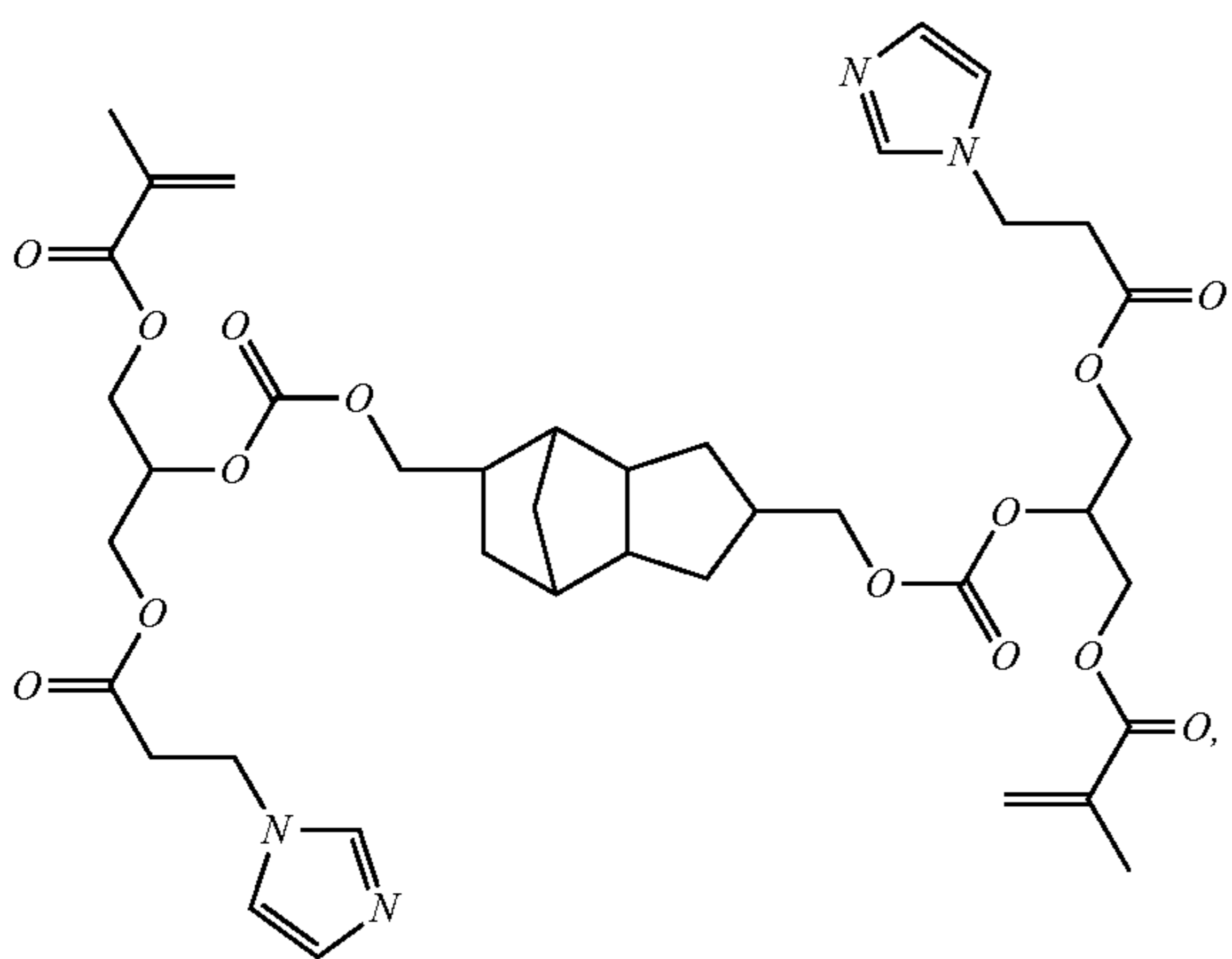
27. A curable antimicrobial composition according to claim 26, wherein the imidazole based polymerizable resin has a formula selected from:

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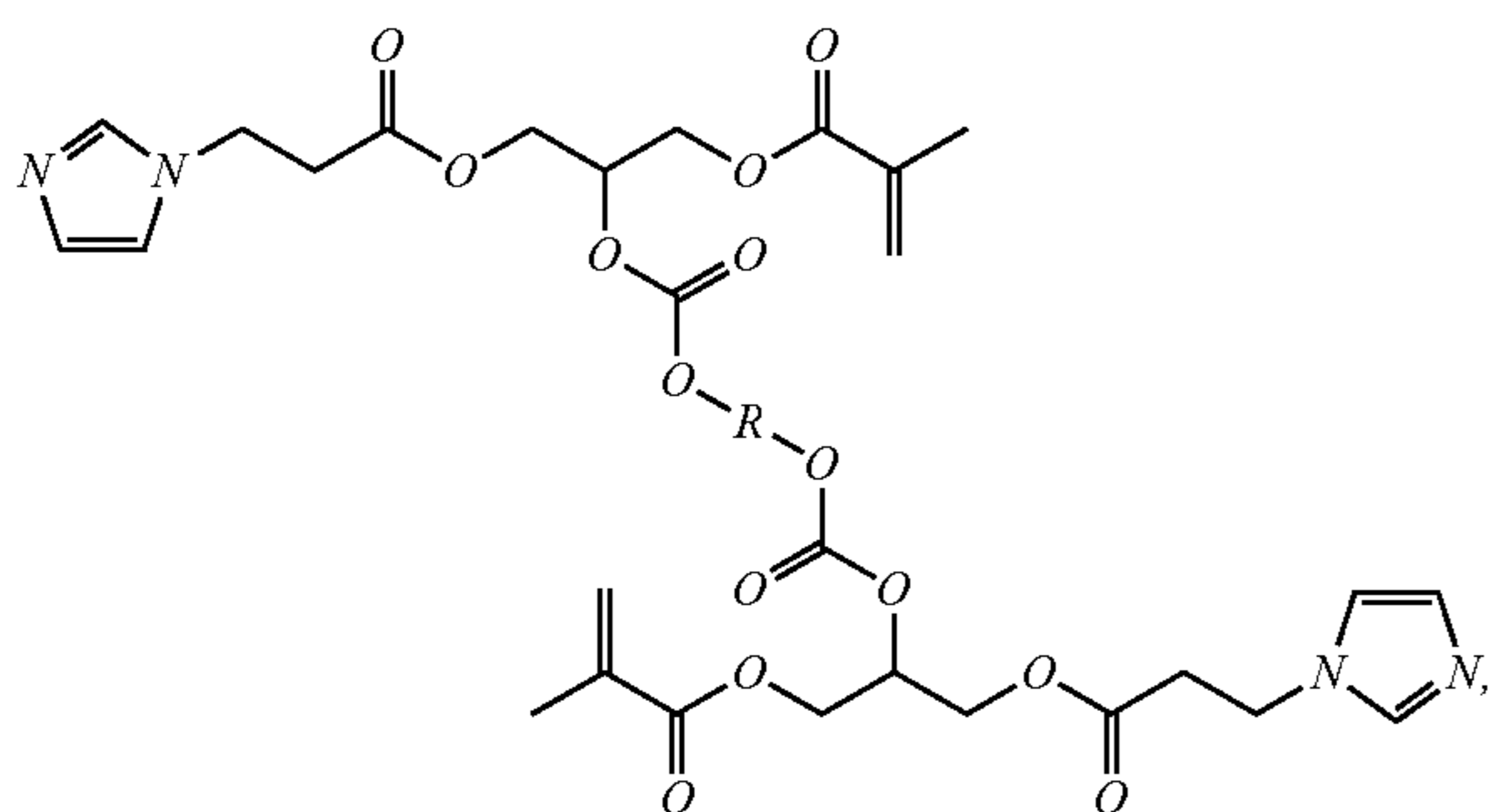
(a) a bisimidazole-dimethacrylate resin that has a formula selected from:
 a isosorbide-based bisimidazole-dimethacrylate resin



a TCDC-based bisimidazole-dimethacrylate resin

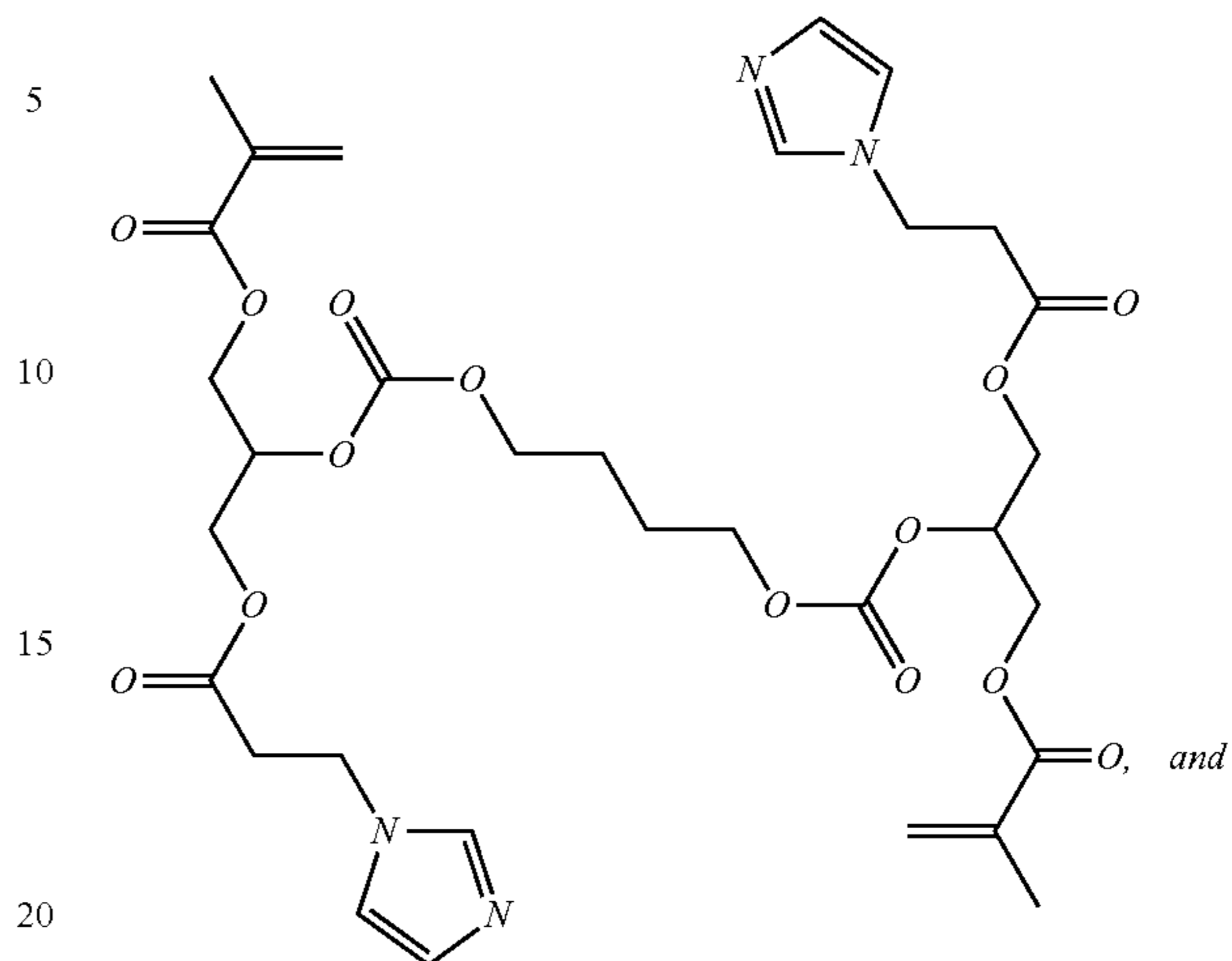


CDI-based reaction pathways to bisimidazole-dimethacrylate resins

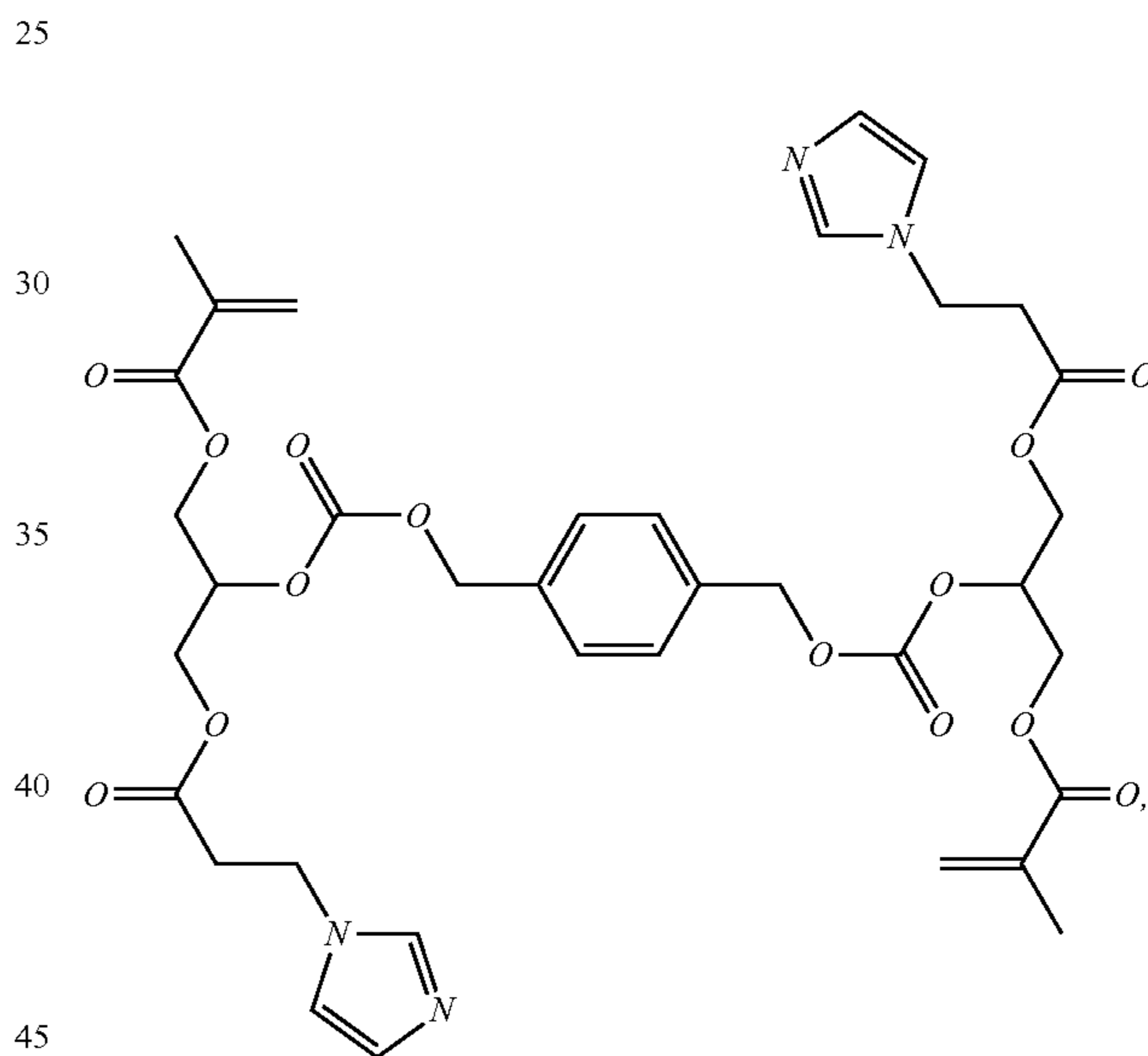


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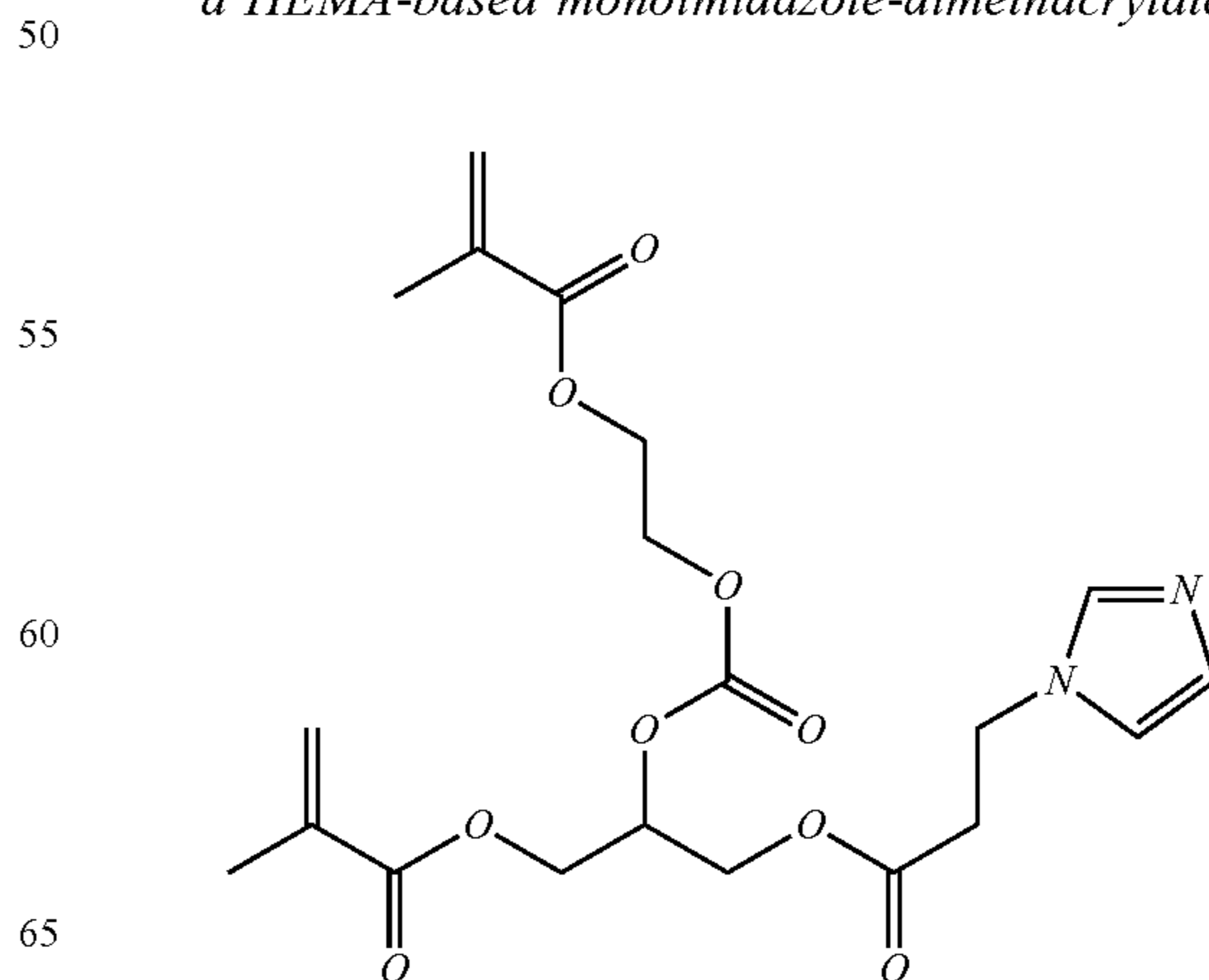
a butanediol-based bisimidazole-dimethacrylate resin



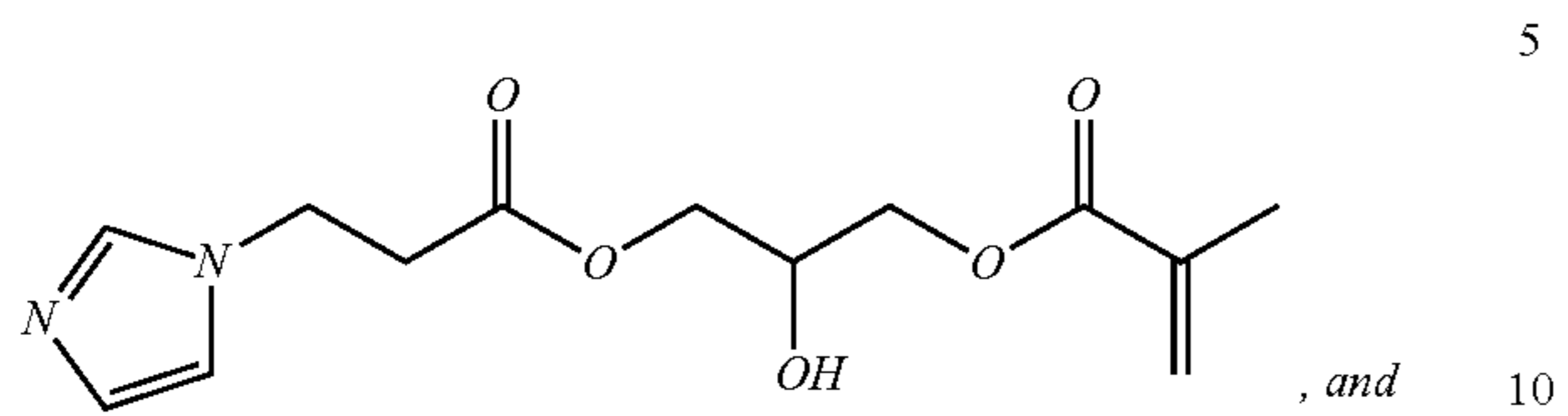
a paraxylenediol-based bisimidazole-dimethacrylate resin



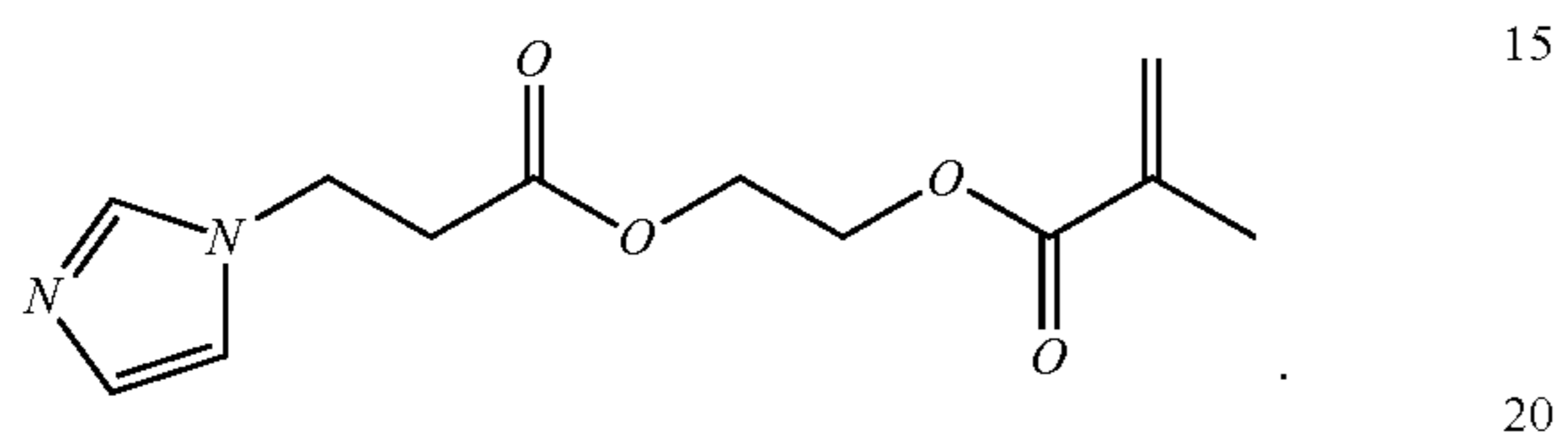
(b) a Monoimidazole-dimethacrylate resin that has a formula:
 a HEMA-based monoimidazole-dimethacrylate resin



(c) a monoimidazole-methacrylate resin that has a formula selected from:
 a AMAHP-based monoimidazole-methacrylate resin



a EGAMA-based monoimidazole-methacrylate resin



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