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(54) Titre : COMPOSITIONS DE RESINE MACROCYCLIQUES POLYMERISABLES RADICALES PRESENTANT UNE FAIBLE CONTRAINTE DE POLYMERISATION

(54) Title: RADICAL POLYMERIZABLE MACROCYCLIC RESIN COMPOSITIONS WITH LOW POLYMERIZATION STRESS

(57) Abrégé/Abstract:
Free radical polymerizable macrocylic compounds are needed for a wide range of problems in many different fields such as microelectronics, coatings and restorative dentistry. Production of such compounds under mild conditions is desirable. A process for preparing a free radical polymerizable macrocyclic oligomer is described which includes activating the condensation groups of BisGMA with carbonyldiimidazole to obtain an activated form of BisGMA. This activated form is reacted with 1,10-decanediol as a coupling agent to obtain the polymerizable macrocyclic oligomer under pseudo-high-dilution conditions.

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ABSTRACT

Free radical polymerizable macrocylic compounds are needed for a wide range of problems in many different fields such as microelectronics, coatings and restorative dentistry. Production of such compounds under mild conditions is desirable. A process for preparing a free radical polymerizable macrocyclic oligomer is described which includes activating the condensation groups of BisGMA with carbonyldiimidazole to obtain an activated form of BisGMA. This activated form is reacted with 1,10-decanediol as a coupling agent to obtain the polymerizable macrocyclic oligomer under pseudo-high-dilution conditions.

RADICAL POLYMERIZABLE MACROCYCLIC RESIN COMPOSITIONS WITH LOW POLYMERIZATION STRESS

Field of the Invention

[0001] This invention relates to free radical polymerizable macrocyclic compounds and composition, which feature by their low shrinkage and low contraction stress upon polymerization. Such low shrinkage and low stress resin could find their wide range of applications, especially in microelectronic, special coating and restorative dentistry where the dimensional stability and contraction stress within cured materials are critical to the total performance.

Background of the Invention

[0002] The polymerization shrinkage of curable material is referred to the dimensional contraction during polymerization or curing, because the formation of covalent bonding during polymerization bring the molecules closer each other than that while they are free in van der Walls distance. The origin of polymerization stress, on the other hand, comes from a restrained polymerization or shrinking during curing. Therefore, it is not only related to polymerization shrinkage, but also is dependent on the polymerization kinetics.

[0003] It is well known that with increasing molecular weight, the mobility of polymeric chain would be limited, the diffusion is becoming the rate control factor. In addition, such a limited mobility in a cross-linking system appear to come earlier in comparison with linear system, which means extra reaction would lead to an

increasing polymerization stress. There are different ways to control the stress generation and development:

1. Slow down the polymerization rate;
    - Introducing a special rate controller like stable radicals;
    - Creating different polymerization zones from which the stress developed in a polymerized zone could be transferred to its adjacent unpolymerized zone and got relief like segmental polymerization technique;
    - Employing different polymerization groups;
    - Using large-size macromonomer to limited its reactivity at the early stage;
2. Reduce the conversion;
    - Pre-building a 2D or 3D structure like macrocyclics, dendrimers or hyperbranches;
3. Limiting the cross-link density to offer acceptable mechanical property.

[0004] To reduce polymerization shrinkage and stress in the specific dental restorative composite, all of above approaches are taking into account. In this invention, however, the objective is to present a general method to produce a macrocyclic oligomer which would be converted into 3D network via free radical polymerization.

[0005] US patent, 4,644,053, disclosed a method to synthesize single macrocyclic compounds. Then various macrocyclics oligomers, including carbonates, esters, amides, ethers, imides, sulfides, et al, have been prepared. However, high temperature ring-opening reaction has to be involved to convert these macrocyclics into high molecular weight polymers.

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[0006] US patent, 5,047,261, disclosed a composition containing a five-member carbonate cyclic group for fast copolymerization with methacrylate.

[0007] US patent, 5,792,821, disclosed polymerizable cyclidextrin (CD) derivatives, in which methacrylate was attached on CD.

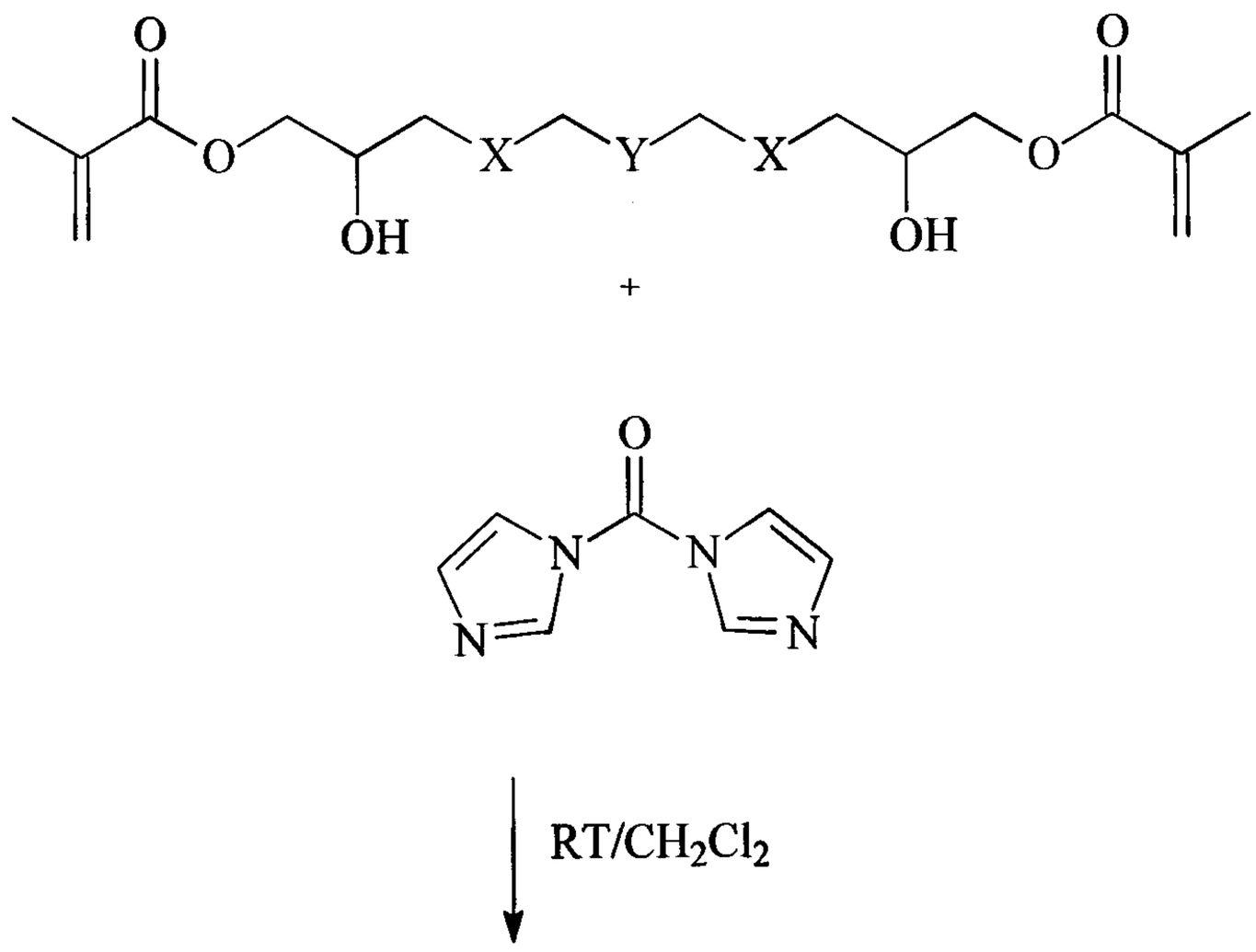
[0008] US patent, 5,962,703, disclosed functionalized bicyclic methacrylate with norboneyl or norbonadienl group.

[0009] US patent, 6,043,361, disclosed polymerizable cyclic allylic sulfides is used for low shrinkage materials.

Summary of the Invention

[0009.1] According to one aspect of the present invention, there is provided a process for preparing a free radical polymerizable macrocyclic oligomer with at least one polymerizable group for use in restorative dentistry, which comprises

(i) activating the condensation groups of a reactive and free radical polymerizable precursor according to the following scheme,



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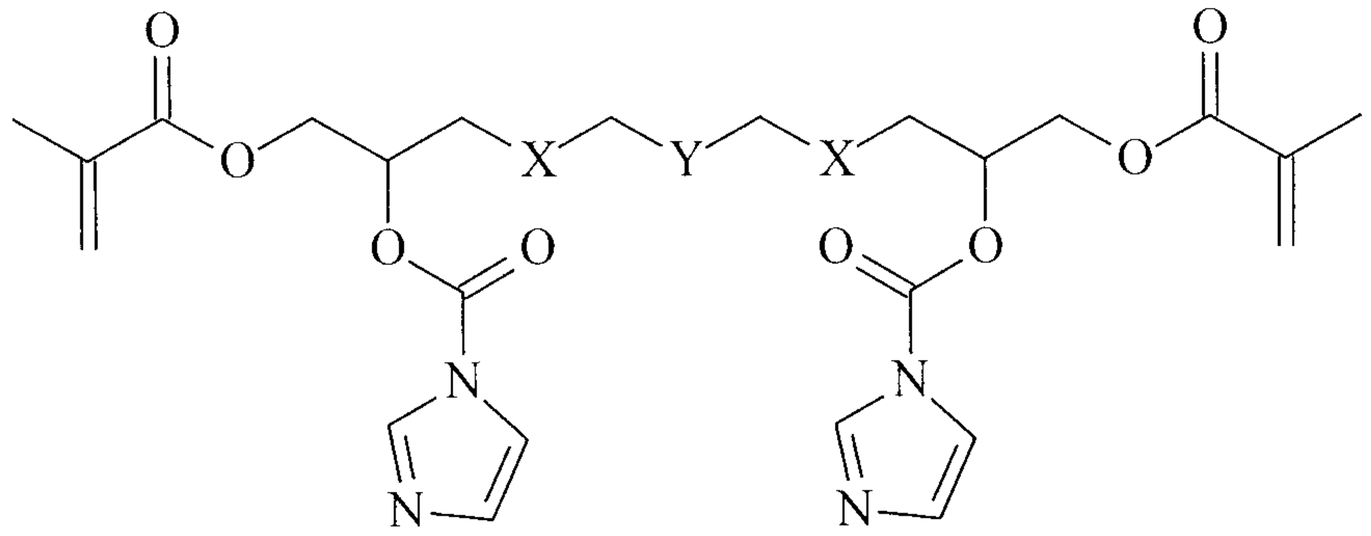


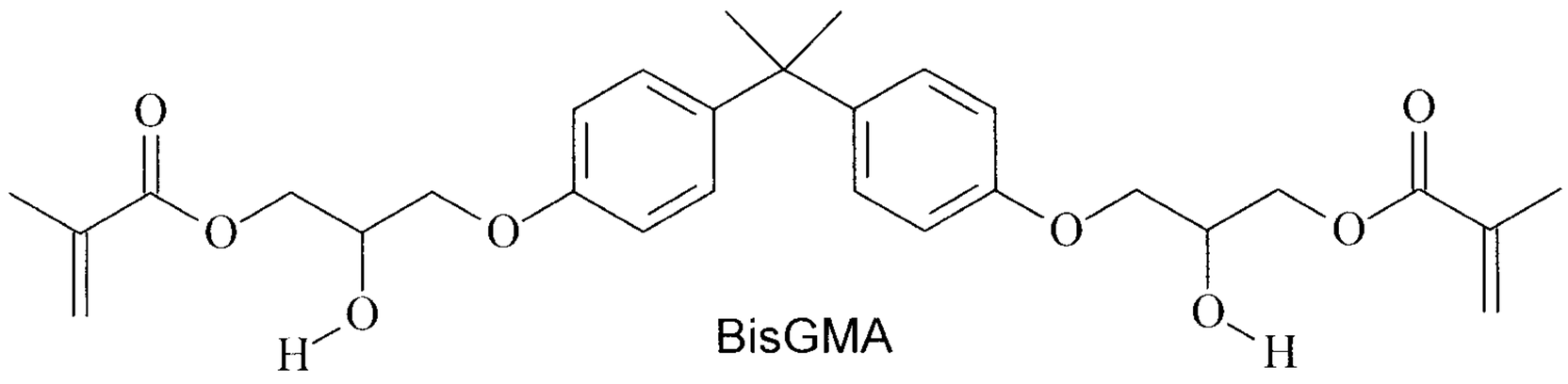
Y: Ar, cyclohexyl,

X: O, COO, and

(ii) preparing the free radical polymerizable macrocyclic oligomer under pseudo-high-dilution conditions *via* a condensation between the activated, reactive and free radical polymerizable precursor and a coupling agents to afford carbonate, ester, siloxane, phosphonate linkages.

According to one aspect of the present invention, there is provided a process for preparing a free radical polymerizable macrocyclic oligomer with at least one polymerizable group for use in restorative dentistry, which comprises

(i) activating the condensation groups of BisGMA according to the following scheme,



BisGMA

+

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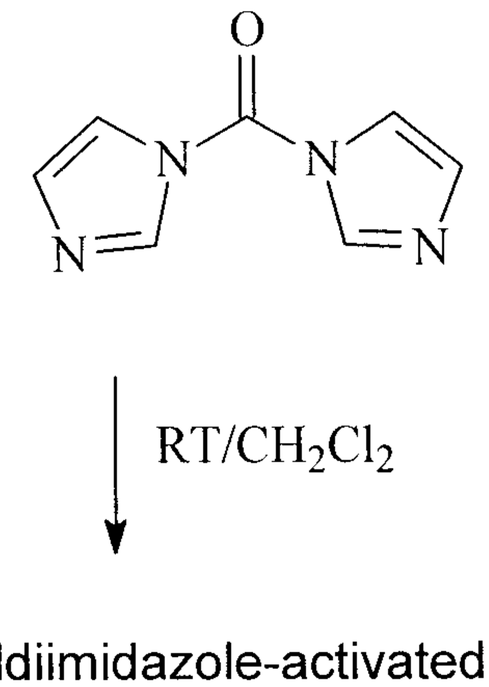

carbonyldiimidazole-activated BisGMA

(ii) preparing the free radical polymerizable macrocyclic oligomer under pseudo-high-dilution conditions *via* a condensation between the carbonyldiimidazole-activated BisGMA and 1,10-decanediol as a coupling agent to afford ester linkages.

According to another aspect of the present invention, there is provided the process as described herein, wherein the carbonyldiimidazole-activated BisGMAis a liquid, a crystalline solid or a combination thereof.

According to still another aspect of the present invention, there is provided the free radical polymerizable macrocyclic oligomer as described herein, which is C10-CYCBGM of the following formula:

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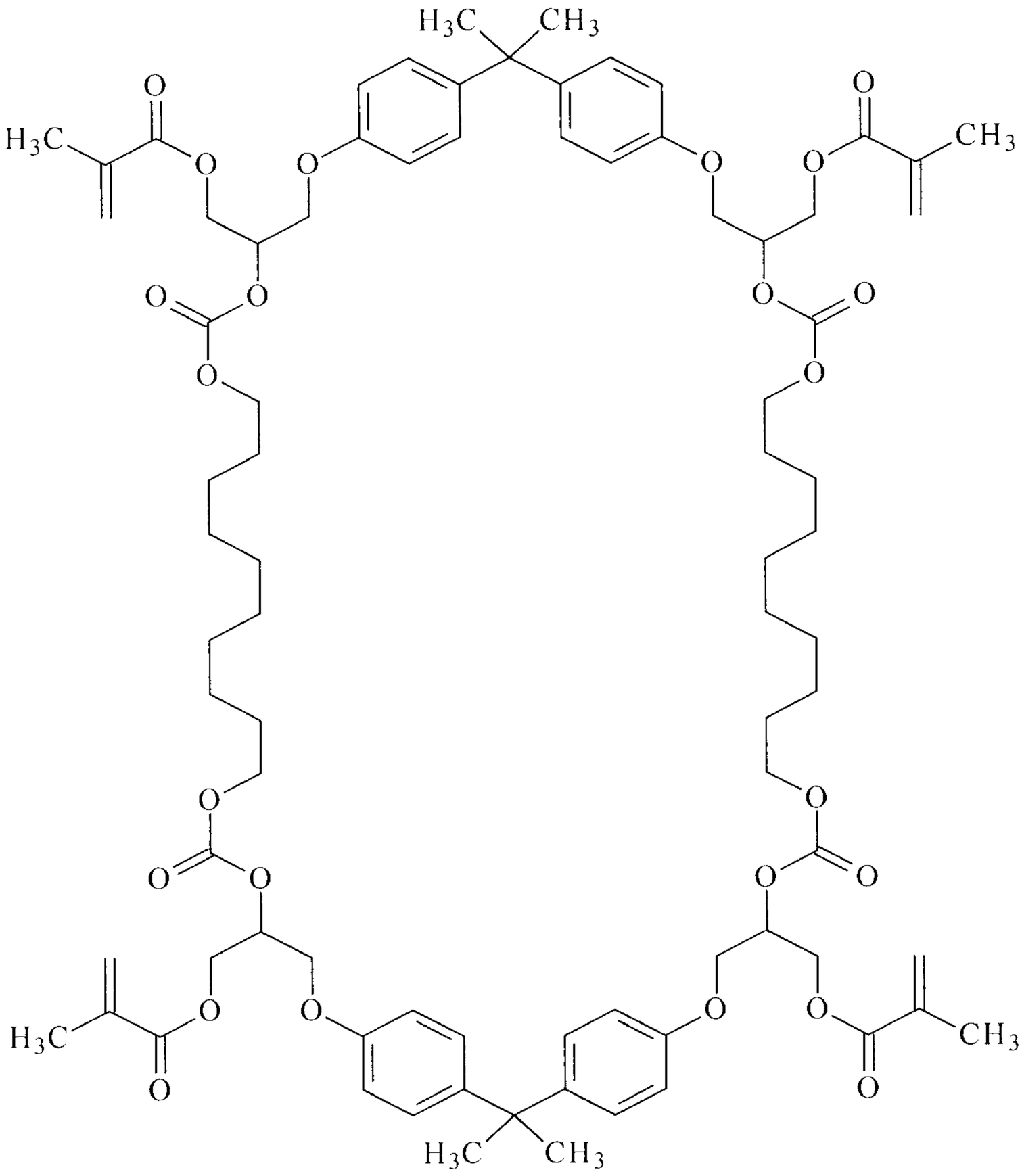

C10-CYCBGM

[0009.2] According to another aspect of the present invention, there is provided a free radical polymerizable macrocyclic oligomer with at least one polymerizable group for use in restorative dentistry, wherein said free radical polymerizable macrocyclic oligomer is obtained as described herein.

Approach

[0010] The macrocyclic oligomers are prepared under pseudo-high-dilution condition via a condensation between a reactive and free radical polymerizable precursor and various coupling agents to afford carbonate, ester, siloxane,

phosphonate, et al linkages to result in macrocyclic oligomers. To avoid the premature polymerization of methacrylate groups, the condensation groups usually have to be activated to assure a mild reaction for cyclization with the coupling monomers.

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[0011] BisGMA is one of widely used dental resin and it contains two free radical polymerizable group, methacrylate and two hydroxyl groups. This turns BisGMA an ideal candidate for polymerizable macrocyclic oligomer, although the presence of BisGMA isomer would make more complicated to this approach. As shown in Scheme I, carbonyldiimidazol (CDI, 1), was used to selectively reacted with the secondary alcohol in BisGMA (2) to give an activated BisGMA, DIZ-BisGMA(3). It was isolated and the chemical structure of DIZ-BisGMA was fully characterized with FITR and NMR. Actually, it has recently been reported that CDI and its intermediates could exhibit surprisingly specificity towards primary, secondary, tertiary functional groups, of the same type, during the controlled formation of various well-defined molecular sequence. Our idea is to adopt same chemistry of CDI and to activate the two secondary hydroxyl group. Furthermore, an activated precursor, DIZ-BisGMA, was made to react with various primary diols 1,10-decanediol, under a pseudo high-dilution condition, as shown in Scheme III. Both reactants were simultaneously charged into the system in a high-dilution condition via slowly, precisely controlled addition to ensure a favorable formation of cyclic product. Since the product, C10-CYCBGM (5), is accumulated with a final concentration of 0.02M, which is much higher than the classical high dilution condition (0.001M), this procedure is, therefore, referred as *pseudo-high-dilution* approach. Since imidazol is produced from both precursor and cyclization steps, a continuous process was successfully developed without direct separation of DIZ-BisGMA.

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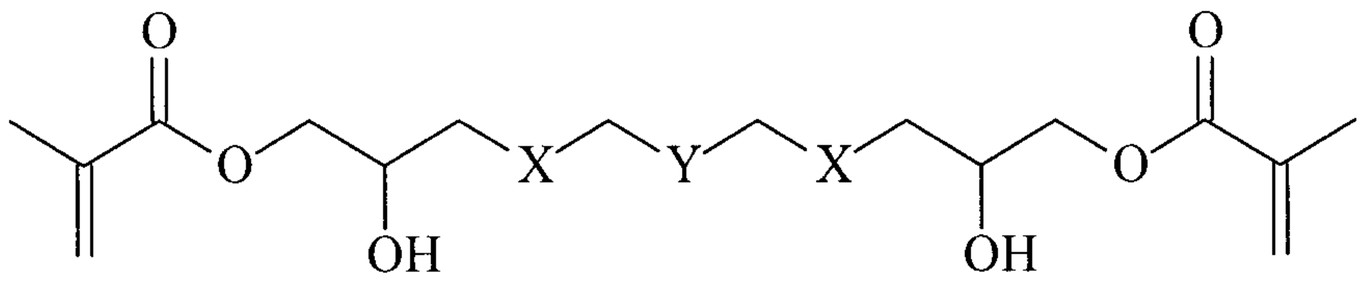
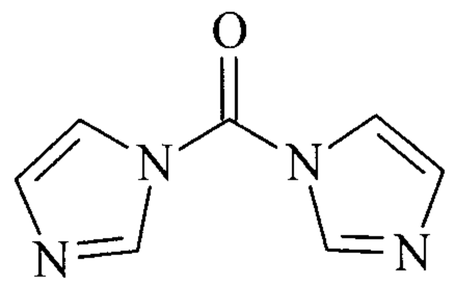
Scheme I: Preparation of Free Readical Polymerizable Macrocyclic Oligomer

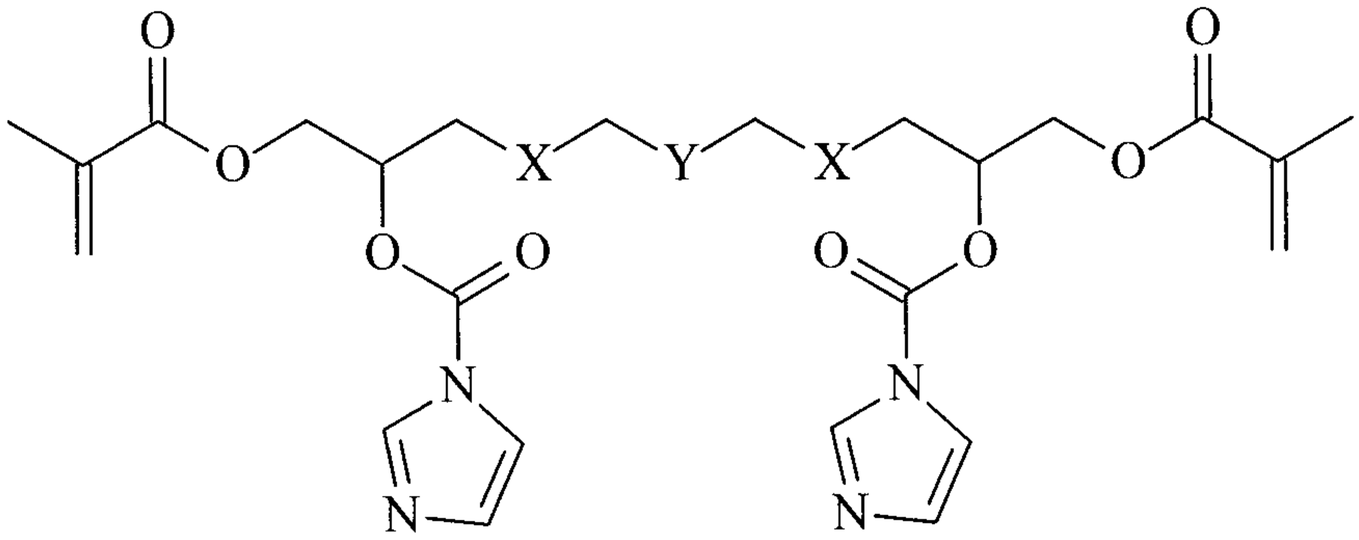


BisGMA(2)



CDI(1)

RT/CH_2Cl_2



DIZ-BisGMA(3)

Y: Ar, cyclohexyl,

X: O, COO,

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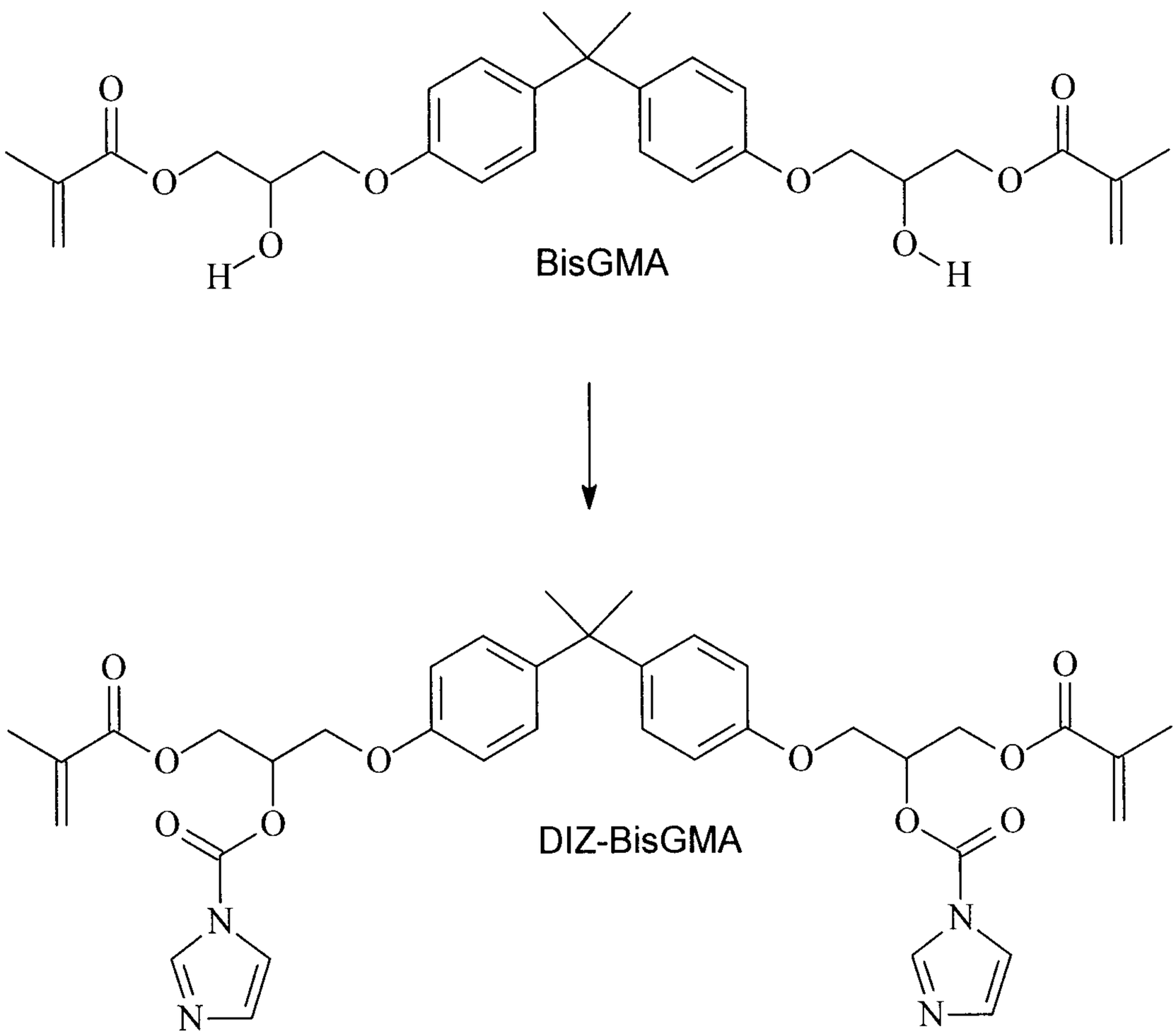
Scheme II: Preparation of Activated BisGMA(DIZ-BisGMA)



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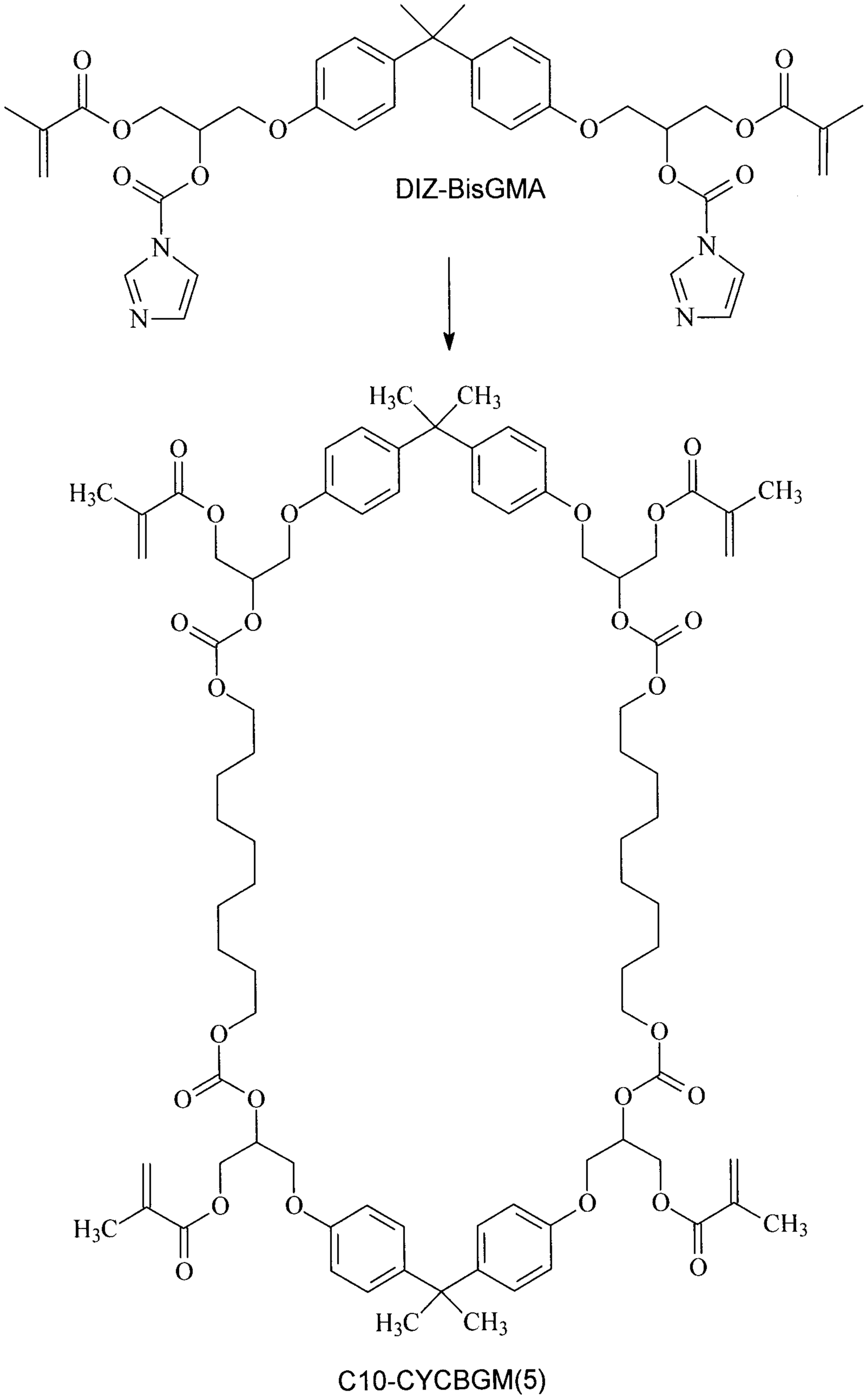
Scheme III: C10-CYCBGM Preparation



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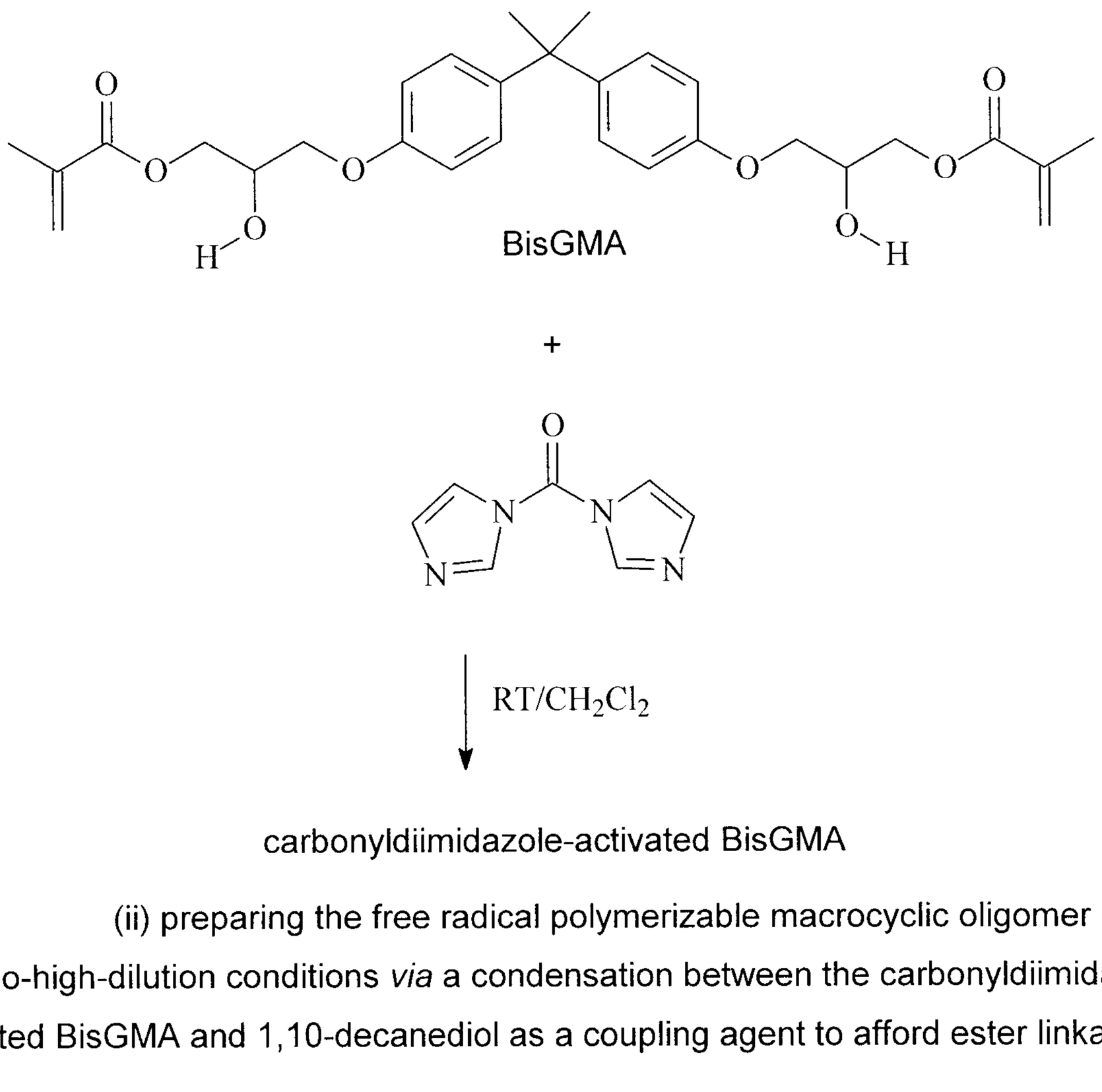
CLAIMS:

1. A process for preparing a free radical polymerizable macrocyclic oligomer with at least one polymerizable group for use in restorative dentistry, which comprises

(i) activating the condensation groups of BisGMA according to the following scheme,



carbonyldiimidazole-activated BisGMA

(ii) preparing the free radical polymerizable macrocyclic oligomer under pseudo-high-dilution conditions *via* a condensation between the carbonyldiimidazole-activated BisGMA and 1,10-decanediol as a coupling agent to afford ester linkages.

2. The process according to claim 1, wherein the carbonyldiimidazole-activated BisGMAis a liquid, a crystalline solid or a combination thereof.

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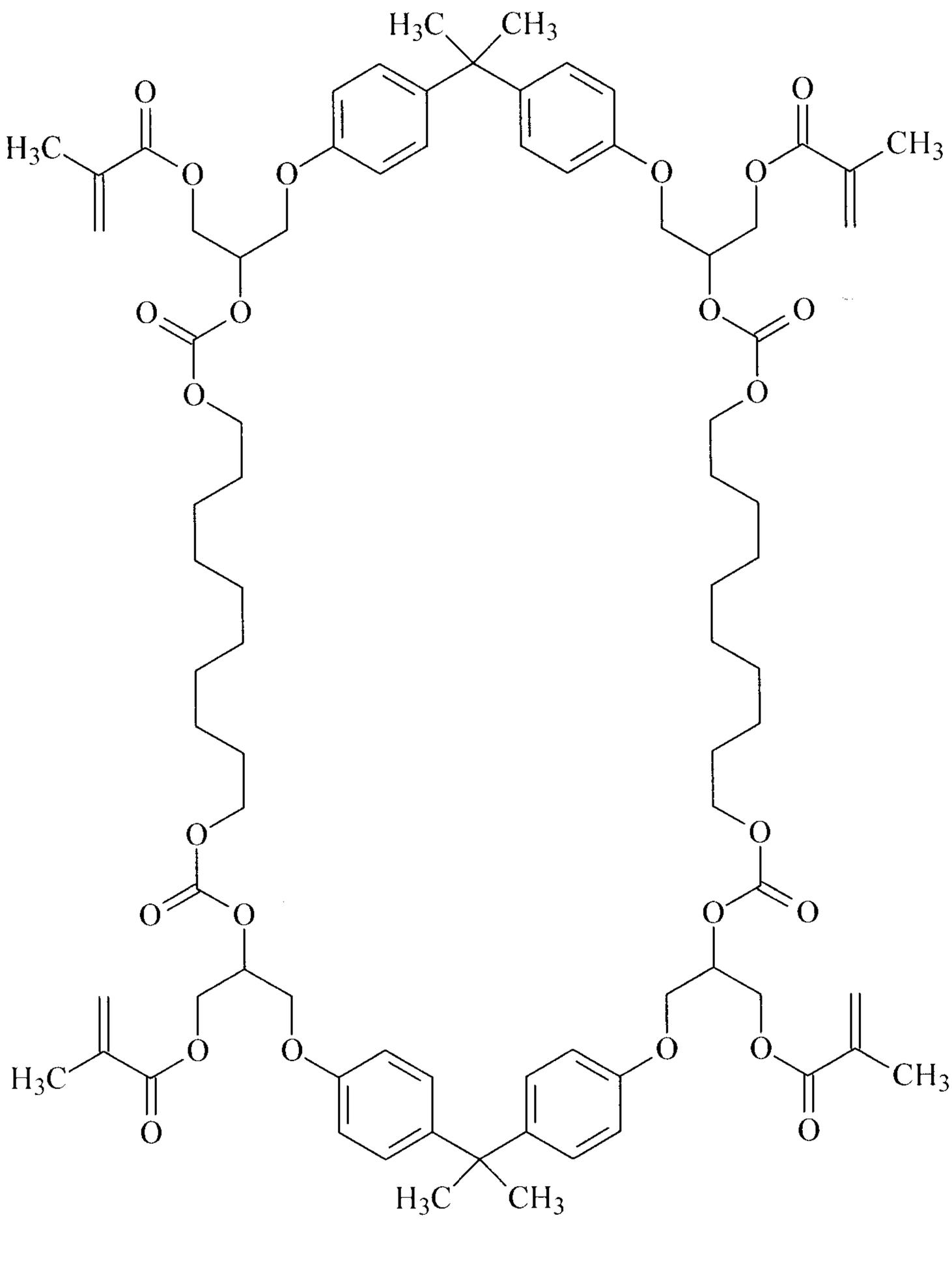
3. A free radical polymerizable macrocyclic oligomer with at least one polymerizable group for use in restorative dentistry, wherein said free radical polymerizable macrocyclic oligomer is obtained according to the process of claim 1 or 2.

4. The free radical polymerizable macrocyclic oligomer according to claim 3, which is C10-CYCBGM of the following formula:



C10-CYCBGM