

Patent #3002.EEM

OXETANE COMPOUNDS CONTAINING CINNAMYL FUNCTIONALITY

FIELD OF THE INVENTION

[0001] This invention relates to oxetane compounds containing cinnamyl functionality.

BACKGROUND OF THE INVENTION

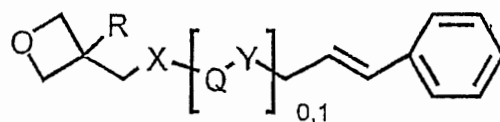
[0002] Oxetanes are highly reactive cyclic ethers that can undergo both cationic and anionic ring opening homopolymerization. Cinnamyl compounds are capable of free radical polymerization.

SUMMARY OF THE INVENTION

[0003] This invention relates to compounds that contain an oxetane functionality and a cinnamyl functionality. These compounds can be homopolymerizable in reactions in which the oxetane can undergo cationic or anionic ring opening, or polymerizable with compounds such as electron acceptor compounds. The dual functionality allows for dual cure processing, both thermal cure or radiation cure. This capability makes them attractive for use in many applications, such as, adhesives, coatings, encapsulants, and composites.

DETAILED DESCRIPTION OF THE INVENTION

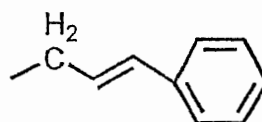
[0004] In one embodiment, the compounds of this invention can be represented by the formula



in which R is a methyl or ethyl group, X and Y independently are a direct bond, provided both are not direct bonds, or an ether, ester, or carbamate group, and Q is a divalent hydrocarbon. The actual configuration of the Q portion will depend on the configuration of the starting compounds.

[0005] The starting cinnamyl compound can be small molecule, for example, cinnamyl alcohol or cinnamyl chloride, or can be an oligomeric or polymeric molecule, prepared by reacting cinnamyl alcohol or cinnamyl chloride with one functionality on a difunctional oligomer or polymer.

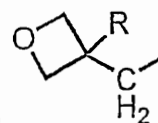
[0006] Whether the starting cinnamyl compound is a small molecule or an oligomeric or polymeric material, it will contain a cinnamyl functionality



represented by the structural formula

and a second functionality reactive with a second functionality on the starting oxetane compound. For example, the cinnamyl starting materials disclosed above contain halogen or hydroxyl functionality in addition to the cinnamyl functionality.

[0007] The starting oxetane compound can be a small molecule or an oligomeric or polymeric molecule, prepared, for example, by reacting one of the small molecule oxetane starting compounds disclosed below with one functionality on a difunctional oligomer or polymer. In either case, it will



contain an oxetane functionality represented by the structure

and a second functionality reactive with the second functionality on the cinnamyl starting compound.

[0008] Suitable starting oxetane compounds that are small molecules include, for example,

[0009] (a) alcohols, such as, 3-methyl-3-hydroxymethyloxetane, 3-ethyl-3-hydroxymethyloxetane;



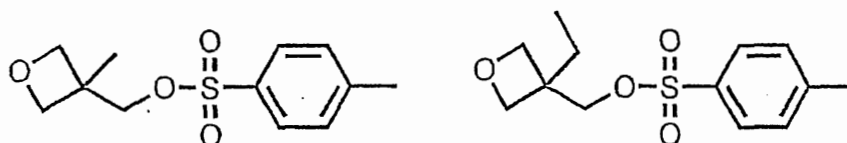
[0010] (b) halides, such as, 3-methyl-3-bromomethyloxetane, 3-ethyl-3-bromomethyloxetane, which can be prepared by the reaction of an alcohol from (a) with CBr₄ as is known in the art;



[0011] (c) alkyl halides, such as, 3-methyl-3-alkylbromomethyloxetane, 3-ethyl-3-alkylbromomethyloxetane, which can be prepared from the reaction of an alkyl dibromide compound with an oxetane alcohol from (a) as is known in the art;



[0012] and (d) tosylates, such as, 3-methyl-3-tosylmethyloxetane, 3-ethyl-3-tosylmethyl-oxetane, which can be prepared from *p*-toluenesulfonyl chloride:



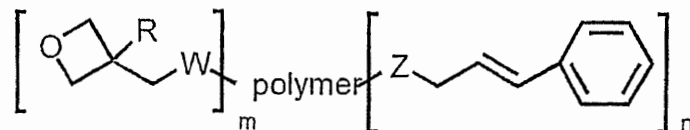
[0013] When a longer chain and higher molecular weight compound containing cinnamyl and oxetane is desired, either the starting cinnamyl compound or the starting oxetane compound, or both, may be reacted with a difunctional oligomeric or polymeric material. The second functionality on this oligomeric or polymeric material must be reactive with the oxetane starting compound if the first reaction was between the cinnamyl starting compound and the difunctional oligomeric or polymeric material, and with the cinnamyl starting compound if the first reaction was between the oxetane starting compound and the difunctional oligomeric or polymeric material. Examples of suitable and commercially available oligomers and polymers include dimer diol and poly(butadiene) with terminal hydroxyl functionality.

[0014] In the case in which both the oxetane and cinnamyl starting compounds are oligomeric or polymeric, Q may also contain a functionality, for example, an ether, ester, carbamate, or urea functionality, resulting from the reaction of the two oligomeric or polymeric starting materials.

[0015] In general, the inventive compounds containing oxetane and cinnamyl functionality are prepared by reacting together a starting compound containing oxetane functionality and a second functionality and a starting compound containing cinnamyl functionality and a second functionality reactive with the second functionality on the oxetane compound. Typical reaction schemes include well known addition, substitution, and condensation reactions.

[0016] In a further embodiment, the compounds of this invention include polymeric compounds that contain more than one oxetane and more than one cinnamyl functionality. Such compounds are prepared from a polymeric starting compound from which depend functionalities that are reactive with the starting oxetane compound and the starting cinnamyl compound.

[0017] The polymeric compound will have the structure .



in which polymer represents a polymeric backbone from which depend the oxetane and cinnamyl functionalities, m and n are integers that will vary with the level of oxetane and cinnamyl functionality added by the practitioner and typically each will be from 2 to 500, R is methyl or ethyl, and W and Z are independently an ether, ester, or carbamate group (formed through the reaction of a pendant functionality on the polymer and a corresponding reactive functionality on the starting oxetane compound or starting cinnamyl compound).

[0018] The pendant functionalities on the polymer may be connected to the polymeric backbone by a hydrocarbon, for example, one having one to twenty carbons, that itself is dependent from the polymeric backbone. For purposes of this specification, those dependent moieties will be deemed to be part of the polymeric backbone.

[0019] An example of a commercially available and suitable polymeric backbone is poly(butadiene) having pendant hydroxyl groups. The pendant hydroxyl groups can be reacted with the oxetane starting compound containing the tosyl leaving group and with cinnamyl chloride. In this case, the linking groups W and Z will be an ether functionality.

[0020] As a further example, a poly(butadiene) having pendant carboxylic acid functionality can react with the hydroxyl functionality on either of the hydroxyl oxetane starting materials and with the hydroxyl functionality on cinnamyl alcohol. In this case, the W and Z groups will be an ester functionality.

[0021] Polymeric starting material can be purchased commercially, for example, there are available acrylonitrile-butadiene rubbers from Zeon Chemicals and styrene-acrylic copolymers from Johnson Polymer. The pendant functionalities from these polymers are hydroxyl or carboxylic acid functionality.

[0022] Other starting polymeric materials can be synthesized from acrylic and/or vinyl monomers using standard polymerization techniques known to those skilled in the art. Suitable acrylic monomers include α,β -unsaturated mono and dicarboxylic acids having three to five carbon atoms and acrylate ester monomers (alkyl esters of acrylic and methacrylic acid in which the alkyl groups contain one to fourteen carbon atoms).

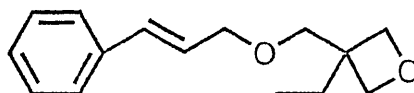
[0023] Examples are methyl acrylate, methyl methacrylate, n-octyl acrylate, n-nonyl methacrylate, and their corresponding branched isomers, such as, 2-ethylhexyl acrylate. Suitable vinyl monomers include vinyl esters, vinyl ethers, vinyl halides, vinylidene halides, and nitriles of ethylenically unsaturated hydrocarbons. Examples are vinyl acetate, acrylamide, 1-octyl acrylamide, acrylic acid, vinyl ethyl ether, vinyl chloride, vinylidene chloride, acrylonitrile, maleic anhydride, and styrene.

[0024] Other polymeric starting materials can be prepared from conjugated diene and/or vinyl monomers using standard polymerization techniques known to those skilled in the art. Suitable conjugated diene monomers include butadiene-1,3,2-chlorobutadiene-1,3, isoprene, piperylene and conjugated hexadienes. Suitable vinyl monomers include styrene, α -methylstyrene, divinylbenzene, vinyl chloride, vinyl acetate, vinylidene chloride, methyl methacrylate, ethyl acrylate, vinylpyridine, acrylonitrile, methacrylonitrile, methacrylic acid, itaconic acid and acrylic acid.

[0025] Those skilled in the art have sufficient expertise to choose the appropriate combination of those monomers and subsequent reactions to

be able to add pendant functionality, for example, hydroxyl and carboxyl functionality, for adding the oxetane and cinnamyl functionalities as disclosed in this specification.

[0026] EXAMPLE 1: Preparation of cinnamyl ethyl oxetane.



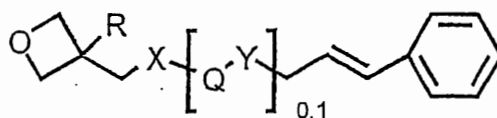
[0036] 3-Ethyl-3-oxetane methanol (27.03 g, 0.2326 mole), toluene (100 ml), tetrabutyl ammonium hydrogen sulfate (17.38 g, 0.0512 mole) and 50% sodium hydroxide solution (300 ml) were combined in a 1L 4-neck round bottom flask equipped with a condenser, mechanical mixer and oil bath. The mixture was stirred vigorously and the oil bath was heated to 90°C at which temperature the solids were totally dissolved.

[0037] Cinnamyl chloride (35.50 g, 0.2326 mole) was added over approximately 35 minutes. The reaction was heated at 90°C with mixing for an additional 1.25 hour and then allowed to cool to room temperature. The organic phase was isolated in a separatory funnel and washed four times with 20% sodium chloride solution (200 ml each). As a result, the washes changed from cloudy yellow to hazy colorless and the pH of the washes dropped from 12 to 6. The last of four more washes (200 ml) using distilled water was an emulsion, which separated over night. After the emulsion separated, a clear orange organic fraction was collected and mixed for one hour with silica gel (60 g). Solids were then filtered out, and the reaction solution was stripped of toluene in *vacuo* resulting in a clear orange liquid with a viscosity of <100 cPs at 25°C, and a volatility of 93% at 200°C as measured by thermogravimetric analysis (TGA).

[0038] ^1H -NMR: δ 7.15-7.51 (m, 5H), 6.12-6.25 (d, 1H), 6.30-6.42 (m, 1H), 4.51-4.71 (d, 2H), 4.41-4.51 (d, 2H), 4.15-4.25 (d, 2H), 3.65 (s, 2H), 1.85-1.90 (m, 2H), 1.85-1.95 (t, 3H).

WHAT IS CLAIMED IS:

1. A compound containing oxetane and cinnamyl functionality having the structure



in which

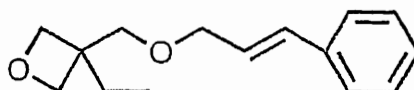
R is a methyl or ethyl group,

X and Y are independently a direct bond, an ether, ester, or carbamate group,

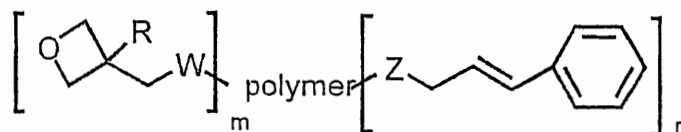
Q is a divalent hydrocarbon, and

provided that X and Y will not both be direct bonds.

2. The compound according to claim 1 having the structure



3. A compound containing cinnamyl and oxetane functionality having the structure



in which

polymer is a polymeric backbone,

m and n are integers for 2 to 500, carbamate group,

R is methyl or ethyl, and

W and Z are independently an ether, ester, or carbamate group.