DESCRIPTION

POLY(NON-CONJUGATED DIENE) BASED SUNSCREENS

The subject invention was made with government support under a research project supported by National Science Foundation Private Investigator Grant, Contract No. DMR-0703261 and 0314110. The government has certain rights to this invention.

BACKGROUND OF INVENTION

UV radiation penetrates the ozone layer over two wavelength regimes, UVB (290-320nm) and UVA (320-400nm). UVB acts directly on biological molecules, causing the familiar delayed sunburn that arises 12-24 hours after exposure, skin aging, skin cancer (melanoma) and eye photokeratities. UVA acts indirectly with the skin by forming reactive oxygen species, causing an "immediate" sunburn that diminishes within 2 hours after exposure. UVA potentially plays a role in delayed sunburn and skin cancer. Although less energetic, UVA, which accounts for about 5.6% of sunlight, penetrates the skin more deeply, even into the dermis, than does UVB radiation, about 0.5% of sunlight, which generally is limited to the epidermis.

Melanoma has experienced the most rapid increase in the number of cases of all forms of cancer with more than 51,000 cases reported in America each year. As most cases have been attributed to sun exposure, the market for sunscreens presently exceeds $1 billion a year. Sunscreens are substances used to protect the skin by absorbing, reflecting and/or scattering damaging ultraviolet (UV) radiation. Sunscreens are typically used as a component in a cream or lotion. Sunscreen formulations are an article intended for the prevention of a disease and are regulated as an over-the counter (OTC) drug.

In a Final Monograph of May 21, 1999, entitled "Sunscreen Drug Products for Over-The-Counter Human Use" by the U.S. Food and Drug Administration (FDA), conditions were established under which OTC sunscreen drug products are generally recognized as safe and effective and not misbranded as part of FDA's ongoing review of OTC drug products. The Monograph established that an active ingredient of sunscreen products consists of any of the following (within the concentration specified for each ingredient when the finished product provides a minimum SPF value of not less than 2 as measured by a testing procedures

established in the Monograph): Aminobenzoic acid (PABA) (15%); Avobenzone (3%); Cinoxate (3%); Dioxybenzone (3%); Homosalate (15%); Menthyl anthranilate (5%); Octocrylene (10%); Octyl methoxycinnamate (7.5%); Octyl salicylate (5%); Oxybenzone (6%); Padimate O (8%); Phenylbenzimidazole sulfonic acid (4%); Sulisobenzone (10%); Titanium dioxide (25%); Trolamine salicylate (12%); and Zinc oxide (25%). Since 1999 Ecamsule (10%) and Phenylbenzimidazole sulfonic acid (4%) have been approved for use as sunscreens. Also approved for use in Europe are: 4-Methylbenzylidene camphor (4%); Bisoctrizole (10%); Bemotrizinol (10%); Bisdisulizole disodium (10%); Drometrizole trisiloxane (15%); Benzophenone-9 (10%); Ethylhexyl triazone (5%); Diethylamino hydroxybenzoyl hexyl benzoate (10%); Iscotrizinol (10%); Polysilicone-15 (10%); and Isoamyl p-Methoxycinnamate (10%).

Of these sunscreens, only Polysilicone-15 is a silicon based polymeric sunscreen with the IUPAC name a-(trimethylsilyl)-ω-(trimethylsilyloxy)poly[oxy(dimethyl)silylene]-co-[oxy-(methyl)(2-{4-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy}-1-methyleneethyl)silylene]-co-[oxy-(methyl)(2-(4-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy)prop-1-enyl)silylene] with about 55 oxy(dimethyl)silylene units, about 4 oxy(methyl)(2-{4-[2,2-bis(ethoxycarbonyl)vinyl]phenoxy}-1-methyleneethyl) silylene units and about 1 oxy(methyl)(2-(4-[2,2-bis(ethoxycarbonyl) vinyl]phenoxy)prop-1-enyl)silylene units on average with an average molecular weight of 6,070. Statistically the random copolymer should have more than one percent of the chains that have no UV absorbing chromophores. An equivalent polymer of about 1,000 molecular weight would have less than half of the chains containing any UV absorbing chromophores. Polymeric sunscreens have the potential to provide a simple mode of distribution of the sunscreen in a vehicle, and reduce or eliminate absorption of the sunscreen by the skin to which it is applied. Many examples of polymeric sunscreens have been disclosed in the patent literature.

US Patents 7,291,322, 6,376,679, 6,312,673, 6,251,373, 6,221,343, 6,214,324, 6,200,557, 6,159,456, and 5,753,209, and US Patent Application Publications 2007/0020204, 2004/0213746, 2002/0054860, and 2001/0026789 are directed to silicone based polymeric sunscreens that are random copolymers similar to Polysilicone-15 with various UV absorbing chromophores. Another form of polymeric sunscreens is random acrylic copolymers, as disclosed in US Patents 5,741,924, 5,487,885, 5,099,027 and 4,524,061 (which also discloses the polymers from a cyclic lactams). Substantive polymers are prepared by random vinyl

copolymerization are disclosed in US Patent 7,087,692 and US Patent Application Publication 2004/0101498 or by random condensation copolymerization, as disclosed in US Patents 4,004,074 and 3,864,473. Water dispersible polymeric sunscreens have been prepared by a random condensation copolymerization with polyethylene glycol monomers, as disclosed in 5,250,652, 5,243,021, and 5,134,223. An acrylamide homopolymer having UV active chromophores at every repeating unit is disclosed in US Patent 4,233,430. US Patent Application Publication 2005/0186152 discloses a polyanhydride modified by the addition of nucleophilic UV active chromophores to place the chromophores on every repeating unit of the polymer chain with the formation of an equal amount of carboxylic acid groups on the polymer chain. US Patents 6,962,692, 6,926,887, 6,919,473, 6,899,866, 6,890,521, 6,800,274, and 5,993,789, discloses a homo-polyester sunscreen where UV active chromophores are on every repeating unit of the polymer.

As disclosed polymeric sunscreens have very high levels of UV absorbing chromophores that can result in a non-uniform distribution of the chromophores in the vehicles as in homopolymer or with random copolymers where molecular weights or UV absorbing chromophores are limited to those where a high molecular weights or high levels of UV absorbing units. Hence a polymeric system where the UV absorbing chromophore's distribution through out the polymer can be controlled with every polymer chain having the same proportion of UV absorbing chromophores independent of the molecular weight is attractive for a polymeric sunscreen.

BRIEF SUMMARY

Embodiments of the invention are directed to poly(non-conjugated diene) based sunscreens where the polymer has a plurality of one or more repeating units where each repeating unit has a chromophore unit having at least one UV absorbing chromophore situated between two mono-ene units. The mono-ene units of the polymer are separated from the chromophore unit by chains. In embodiments of the invention the chains can be a plurality of methylene units. The UV absorbing chromophores absorbs light in the UVA and/or UVB region of the electromagnetic spectrum. The UV absorbing chromophores can be equivalents to and derived from the conjugated group of the approved sunscreens: Aminobenzoic acid; Avobenzone; Cinoxate; Dioxybenzone; Homosalate; Menthyl anthranilate; Octocrylene; Octyl

methoxycinnamate; Octyl salicylate; Oxybenzone; Padimate O; Phenylbenzimidazole sulfonic acid; Sulisobenzone; Trolamine salicylate; Ecamsule; Phenylbenzimidazole sulfonic acid; 4-Methylbenzylidene camphor; Bisoctrizole; Bemotrizinol; Bisdisulizole disodium; Drometrizole trisiloxane; Benzophenone-9; Ethylhexyl triazone; Diethylamino hydroxybenzoyl hexyl benzoate; Iscotrizinol; or Isoamyl p-Methoxycinnamate. The chromophore units can have bridging groups to connect the UV absorbing chromophores to the chromophore units. In embodiments of the invention, the bridging groups can include an alkylene group and a linking functionality that is a residue of an addition or a condensation reaction between functionality on the alkylene group and the UV absorbing chromophore.

Depending on the structures of the repeating units included in the poly(non-conjugated diene) based sunscreen, in some embodiments the UV absorbing chromophore can be periodically displaced along the backbone of the poly(non-conjugated diene). In other embodiments of the invention, the UV absorbing chromophore can be quasi-periodically or pseudo-randomly placed within the backbone of the poly(non-conjugated diene). In some embodiments of the invention, one or more functionality to impart: substantive properties; dispersivity; and/or an ability to specifically interact with particles or chemicals can be incorporated into at least one repeating unit, or can be attached at one or both terminal mono-enes of the poly(non-conjugated diene).

Other embodiments of the invention are directed to monomers for the preparation of the above poly(non-conjugated diene) based sunscreens. The monomers have two terminal ene units connected by a chain to a chromophore unit that has one or more UV absorbing chromophores that independently absorb light in the UVA and/or UVB regions of the electromagnetic spectrum. In one embodiment of the invention, the chains between the ene units and chromophore units of the monomers are of equal length and composition, which allows the formation of a periodic poly(non-conjugated diene). In another embodiment of the invention, the chains can be of different lengths and compositions in the same monomer to permit formation of a quasi-periodic poly(non-conjugated diene). The monomers can include functionality that can impart substantive properties, dispersivity, and/or an ability to specifically interact with particles or chemicals.

Other embodiments of the invention are directed to a method of preparing a poly(non-conjugated diene) based sunscreens where one or more of the above monomers are polymerized

in the presence of a catalyst to promote acyclic olefin metathesis where ethylene is removed until a desired molecular weight is achieved. Olefin metathesis catalysts that can be use include Schrock's catalyst or Grub's catalyst.

Other embodiments of the invention are directed to sunscreen drug products where the poly(non-conjugated diene) based sunscreens are included with a vehicle. The vehicle can include a solvent for the poly(non-conjugated diene) or can include a combination of a non-solvent and a dispersing agent to emulsify or suspend the poly(non-conjugated diene) in the non-solvent vehicle.

Another embodiment of the invention is a method to prevent sunburn by providing a poly(non-conjugated diene) based sunscreen which is applied to skin. The poly(non-conjugated diene) based sunscreen can be provided as a component of a fluid that is a solution or a dispersion.

BRIEF DESCRIPTION OF DRAWINGS

Figures 1 shows a) a representation of current sunscreen technology and b) a polymer having a unit that acts as a sunscreen according to embodiments of the invention.

Figure 2 shows three poly(non-conjugated diene) based sunscreens with a UV absorbing chromophore on every ninth carbon along the backbone where the bridging group is: a) an ester; b) an amide; and c) an oligoether ester in accordance with embodiments of the invention.

Figure 3 shows a monomer for preparing a poly(non-conjugated diene) based sunscreen that has a chromophore unit that is a 5 to 10 carbon unit with two different UV absorbing chromophores attached at the ends of the carbon by a spacer group.

Figure 4 shows a specific monomer according to that illustrated in Figure 3 where the UV absorbing chromophores are derived from Avobenzone and Octocrylene type of sunscreen components and connected to a 5 carbon chromophore unit where one bridging group is a methylene spacer with a carbonate functional group and the other bridging group is a methylene spacer with an ester functional group.

Figure 5 shows the synthesis of a monomer and its polymerization to a poly(non-conjugated diene) based sunscreen in accordance with embodiments of the invention.

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