COPOLYMERS INCLUDING ULTRAVIOLET ABSORBING GROUPS AND FLUOROPOLYMER COMPOSITIONS INCLUDING THEM

Cross Reference to Related Application

This application claims priority to U.S. Provisional Application No. 61/740,125, filed December 20, 2012, the disclosure of which is incorporated by reference in its entirety herein.

Background

Fluoropolymers are known to have a variety of useful properties, including cleanability, weather resistance, and chemical resistance. Such beneficial properties render fluoropolymers useful, for example, for a variety of outdoor applications including signage, films or coatings for architectural coverings, and protective coverings for photovoltaic modules.

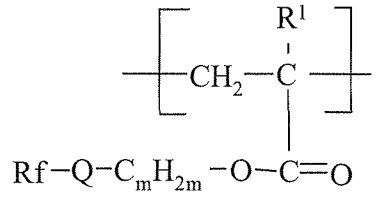
It may be desirable to incorporate ultraviolet absorbers (UVAs) into materials exposed to ultraviolet (UV) radiation, for example, to protect a topcoat or topsheet or an underlying substrate or adhesive from UV degradation. Some UVAs can be dispersed into some compositions, but sometimes they can be lost due to volatilization or migration to the surface. Covalent incorporation of UVAs into certain compositions has been proposed. See, e.g., U.S. Pat. Appl. Pub. No. 2011/0297228 (Li et al.).

It has been reported that common UVAs can be incompatible with fluoropolymers. See, e.g., U.S. Pat. No. 6,251,521 (Eian et al.). This incompatibility can lead to degradation of physical or optical properties (e.g., loss of clarity or increased fogginess) as well as increased or accelerated loss of the UVA by migration, bleeding, or blooming.

Summary

The present disclosure provides a copolymer that includes a first divalent unit with a pendent ultraviolet absorbing group and a second divalent unit that is fluorinated. These copolymers are generally quite compatible with fluoropolymers such that the copolymers and fluoropolymers are readily blended together. Compositions including the fluoropolymers and copolymers provide protection to ultraviolet light and have good transparency to visible and infrared light. These properties are typically well maintained even after accelerated UV exposure and exposure to high temperature and humidity conditions.

~~In one aspect, t~~The present disclosure provides a copolymer that includes a first divalent unit having a pendent ultraviolet absorbing group and a second divalent unit represented by formula:

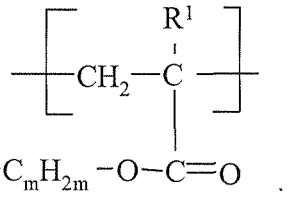


In this formula, Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group. R^1 is hydrogen or methyl. Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen, and m is an integer from 0 to 11. The copolymer is a thermoplastic copolymer or is not covalently crosslinked.

In one aspect, the present disclosure provides a copolymer comprising:

a first divalent unit comprising a pendent ultraviolet absorbing group comprising a triazine; and

a second divalent unit represented by formula:



;

wherein

Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen; and

m is an integer from 0 to 11,

wherein the copolymer is not covalently crosslinked.

In another aspect, the present disclosure provides a composition comprising a fluoropolymer and the copolymer in any of its embodiments described above or below.

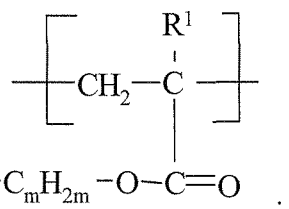
In another aspect, the present disclosure provides a composition comprising:

a fluoropolymer;

a copolymer comprising:

a first divalent unit comprising a pendent ultraviolet absorbing group; and

a second divalent unit represented by formula:



;

wherein

Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen; and

m is an integer from 0 to 11,

wherein the copolymer is not crosslinked; and

a second copolymer, wherein the second copolymer is a copolymer of methyl methacrylate and an acrylate- or methacrylate-functional ultraviolet absorbing group.

In another aspect, the present disclosure provides a photovoltaic device comprising the composition in any of its embodiments described above or below.

In another aspect, the present disclosure provides a method of making a composition. The method includes blending the copolymer in any of its embodiments described above or below with a fluoropolymer to make the composition.

In another aspect, the present disclosure provides a method of making a film. The method includes providing the composition in any of its embodiments and extruding the composition into a film.

As described above, compositions including the fluoropolymers and copolymers typically provide protection to ultraviolet light and have good transparency to visible and infrared light. Accordingly, the present disclosure provides a photovoltaic device include the composition according to the present disclosure in any of its embodiments.

In this application:

Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terms "a", "an", and "the" are used interchangeably with the term "at least one".

The phrase "comprises at least one of" followed by a list refers to comprising any one of the items in the list and any combination of two or more items in the list. The phrase "at least one of" followed by a list refers to any one of the items in the list or any combination of two or more items in the list.

The term “ultraviolet absorbing group” refers to a covalently attached ultraviolet absorber (UVA). UVAs are known to those skilled in the art as being capable of dissipating absorbed light energy from UV rays as heat by reversible intramolecular proton transfer. UVAs are selected such that the copolymer in any of the embodiments of copolymers or second copolymers disclosed herein absorbs at least 70%, 80%, or 90% of incident light in a wavelength range from 180 nanometers (nm) to 400 nm.

"Alkyl group" and the prefix "alk-" are inclusive of both straight chain and branched chain groups and of cyclic groups. Unless otherwise specified, alkyl groups herein have up to 20 carbon atoms. Cyclic groups can be monocyclic or polycyclic and, in some embodiments, have from 3 to 10 ring carbon atoms.

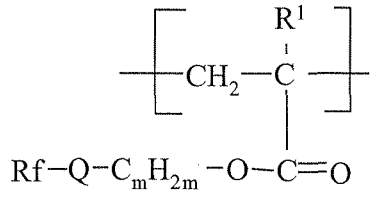
5

What is claimed is:

1. A copolymer comprising:

a first divalent unit comprising a pendent ultraviolet absorbing group comprising a triazine; and

a second divalent unit represented by formula:



;

wherein

Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

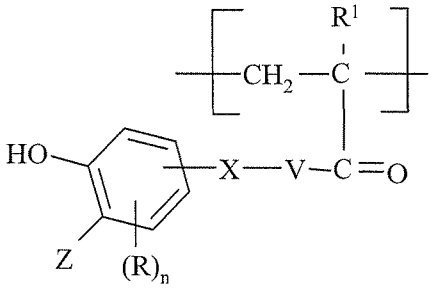
Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen; and

m is an integer from 0 to 11,

wherein the copolymer is not covalently crosslinked.

~~2. The copolymer of claim 1, wherein the pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.~~

~~3~~2. The copolymer of claim ~~2~~1, wherein the first divalent unit is represented by formula:



,

wherein

R^1 is hydrogen or methyl;

V is O or NH;

X is alkylene or alkyleneoxy group having from 1 to 10 carbon atoms and optionally interrupted by one or more –O- groups and optionally substituted by a hydroxyl group;

R is alkyl having from one to four carbon atoms;

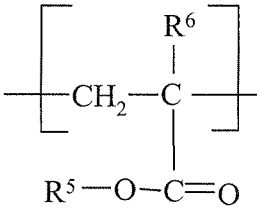
n is 0 or 1; and

Z is ~~a benzoyl group,~~ a 4,6-bisphenyl[1,3,5]triazin-2-yl group, ~~or a 2H-benzotriazol-2-yl group,~~ wherein the ~~benzoyl group,~~ 4,6-bisphenyl[1,3,5]triazin-2yl group~~, and 2H-benzotriazol2-yl group are~~is optionally substituted by one or more alkyl, aryl, alkoxy, hydroxyl, or halogen substituents, or a combination of these substituents.

~~4. The copolymer of any one of claims 1 to 3, wherein the pendent ultraviolet absorbing group comprises a triazine.~~

~~5~~3. The copolymer of ~~any one of~~ claim~~s~~ 1 ~~to~~ or ~~4~~2, wherein Rf represents a perfluoroalkyl group having up to 4 carbon atoms.

~~6~~4. The copolymer of any one of claims 1 to ~~5~~3, further comprising a third divalent unit represented by formula:



wherein

R^6 is hydrogen or methyl; and

R^5 is alkyl having from 1 to 4 carbon atoms.

~~7~~5. The copolymer of any one of claims 1 to ~~6~~4, wherein the second divalent unit is present in the copolymer in an amount of up to 50 percent by weight, based on the total weight of the copolymer.

~~8~~6. The copolymer of any one of claims 1 to ~~7~~5, wherein the copolymer is an oligomer with a number average molecular weight of up to 50,000 grams per mole.

~~9~~7. The copolymer of claim ~~8~~6, wherein the oligomer has a number average molecular weight greater than 5000 grams per mole.

~~10~~8. The copolymer of claim ~~8~~6 or ~~9~~7, wherein the oligomer has a number average molecular weight of less than 20000 grams per mole.

~~11~~9. A composition comprising a fluoropolymer and the copolymer of any one of claims 1 to ~~10~~8.

~~12~~10. The composition of claim ~~11~~9, further comprising poly(methyl methacrylate).

~~13~~11. The composition of claim ~~11~~9 or ~~12~~10, wherein the fluoropolymer is present in the composition in an amount of at least 50 percent by weight, based on the total weight of the composition.

~~14~~12. The composition of any one of claims ~~11~~9 to ~~13~~11, wherein the copolymer is present in the composition in an amount up to 10 percent by weight, based on the total weight of the composition.

~~15~~13. The composition of any one of claims ~~11~~9 to ~~14~~12, further comprising a second copolymer comprising the first divalent unit and at least one of the second or third divalent units.

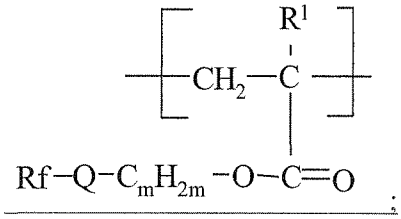
~~16~~14. ~~The composition of claim 15~~A composition comprising:

a fluoropolymer;

a copolymer comprising:

a first divalent unit comprising a pendent ultraviolet absorbing group; and

a second divalent unit represented by formula:



;

wherein

Rf represents a fluoroalkyl group having from 1 to 6 carbon atoms optionally interrupted by one -O- group, or Rf represents a polyfluoropolyether group;

R^1 is hydrogen or methyl;

Q is a bond, $-SO_2-N(R)-$, or $-C(O)-N(R)-$, wherein R is alkyl having from 1 to 4 carbon atoms or hydrogen; and

m is an integer from 0 to 11,

wherein the copolymer is not crosslinked; and

a second copolymer, wherein the second copolymer is a copolymer of methyl methacrylate and an acrylate- or methacrylate-functional ultraviolet absorbing group.

15. The composition of claim 14, wherein the pendent ultraviolet absorbing group comprises a triazine, a benzophenone, or a benzotriazole.

16. The composition of claim 15, wherein the pendent ultraviolet absorbing group comprises a triazine.

17. The composition of any one of claims ~~15~~ 13 ~~or~~ to 16, wherein the copolymer and the second copolymer are present in the composition in an amount up to 10 percent combined weight, based on the total weight of the composition.

18. The composition of any one of claims ~~11~~ 9 to 17, wherein the composition is essentially free of volatile organic solvent.

19. The composition of any one of claims ~~11~~ 9 to 18, wherein the fluoropolymer is selected from the group consisting of ethylene-tetrafluoroethylene copolymer, a tetrafluoroethylene-hexafluoropropylene copolymer, a tetrafluoroethylene-hexafluoropropylene-vinylidene fluoride copolymer, or polyvinylidene fluoride.

20. The composition of any one of claims ~~11~~ 9 to 19 in the form of a film.

21. The composition of claim 20, wherein the film is a multilayer film.

22. The composition of claim 21, wherein the film is a multilayer optical film.

23. A photovoltaic device comprising the composition of any one of claims ~~11~~ 9 to 22.

24. A method of making a film, the method comprising providing the composition of any one of claims ~~11~~ 9 to 19 and extruding the composition into the film.

25. A method of making a composition, the method comprising blending the copolymer of any one of claims 1 to ~~10~~ 8 with a fluoropolymer to make the composition.