PLASTIC MODIFIERS

FIELD OF THE INVENTION

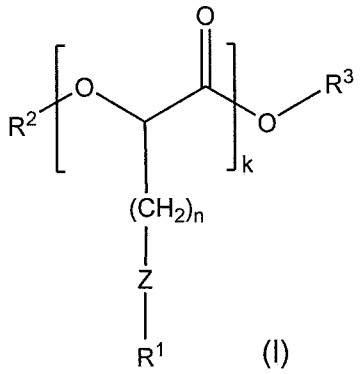
[0001] The present disclosure generally relates to hydrocarbyl terminated polyester compounds having sulfur-containing repeat units that are useful as plastic modifiers. In particular, the disclosure relates to the polyester compounds, polymer blends comprising polymers and the polyester compounds, and methods of using the polyester compounds to modify performance properties of polymers.

BACKGROUND OF THE INVENTION

[0002] Non-biodegradable polymers, such as polyvinyl chloride (PVC), are used in a wide variety of consumer products. The functional properties of many polymers can be improved by the addition of additives such as plasticizers. Phthalates are the most commonly used plasticizers, but their use is being phased out because of concerns about health and environmental risks. Thus, there is a need for new functional and environmentally friendly plasticizers that provide the same performance benefits as phthalates and/or improve the performance properties of polymers such as PVC. For biodegradable polymers made from polylactide (PLA), a plasticizer is appreciated in terms of improving PLA performances and reducing production cycle time without sacrificing biodegradability of the end consumer products.

SUMMARY

[0003] The present disclosure provides a polyester composition comprising compounds of Formula (I):



(I)

wherein:

R^1 and R^3 independently are hydrocarbyl or substituted hydrocarbyl;

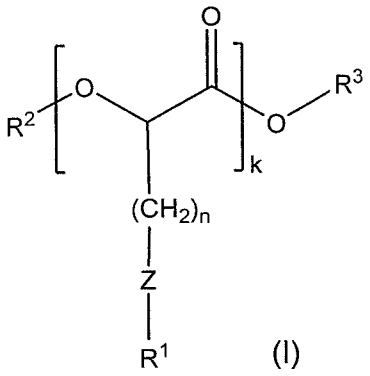
R^2 is R^4CO- or R^4, wherein R^4 is hydrocarbyl or substituted hydrocarbyl;

Z is sulfur, sulfoxide, or sulfone;

k is an integer of 1 or greater; and

n is an integer of 1 or greater.

[0003a] One aspect of the present disclosure provides a composition comprising compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

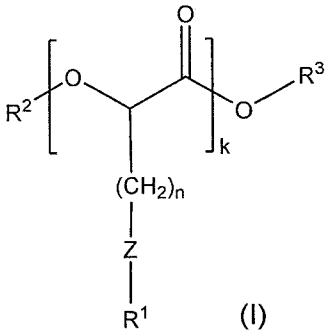
R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

Z is sulfur;

k is an integer from 1 to 20; and

n is an integer of 1 or 2.

[0004] The present disclosure encompasses a polymer blend composition comprising a polymer and a polyester composition comprising compounds of Formula (I):



(I)

wherein:

R^1 and R^3 independently are hydrocarbyl or substituted hydrocarbyl;

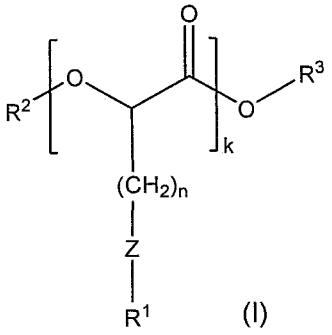
R^2 is hydrogen, R^4CO-, or R^4, wherein R^4 is hydrocarbyl or substituted hydrocarbyl;

Z is sulfur, sulfoxide, or sulfone;

k is an integer of 1 or greater; and

n is an integer of 1 or greater.

[0004a] Another aspect of the present disclosure encompasses a polymer blend composition comprising a polymer and a composition comprising compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

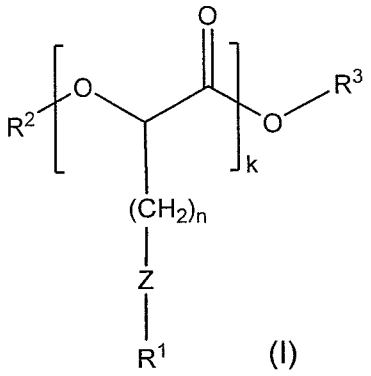
R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

Z is sulfur;

k is an integer from 1 to 20; and

n is an integer of 1 or 2.

[0005] The present disclosure provides a process for modifying performance properties of polymers. The process comprises contacting a polymer with a polyester composition comprising compounds of Formula (I) to form a polymer blend composition, wherein the polymer blend composition has an improved performance property relative to an unmodified polymer, the compounds of Formula (I):



(I)

wherein:

R^1 and R^3 independently are hydrocarbyl or substituted hydrocarbyl;

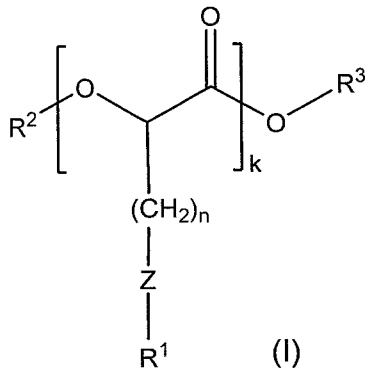
R^2 is hydrogen, R^4CO-, or R^4, wherein R^4 is hydrocarbyl or substituted hydrocarbyl;

Z is sulfur, sulfoxide, or sulfone;

k is an integer of 1 or greater; and

n is an integer of 1 or greater.

[0005a] Another aspect of the present disclosure provides a process for modifying performance properties of polymers, the process comprising contacting a polymer with a composition comprising compounds of Formula (I) to form a polymer blend composition, wherein the polymer blend composition has an improved performance property relative to an unmodified polymer, the compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

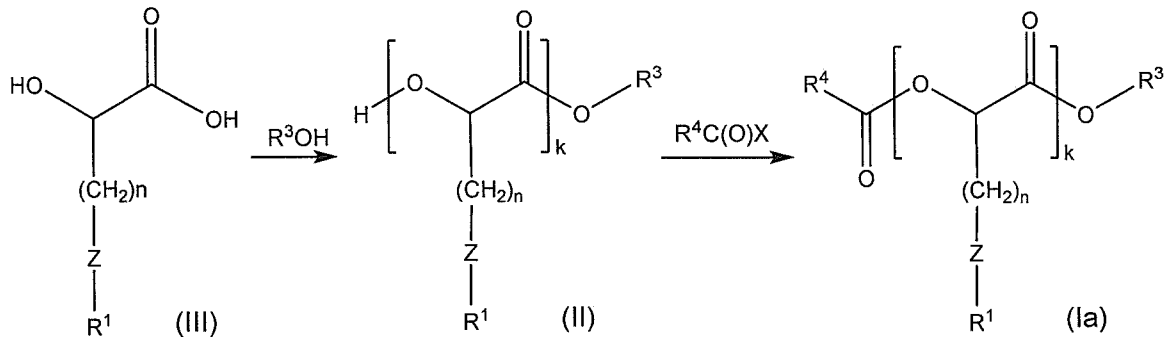
R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

Z is sulfur;

k is an integer from 1 to 20; and

n is an integer of 1 or 2.

[0006] The present disclosure encompasses a process for preparing a polyester composition comprising compounds of Formula (Ia) from a compound of Formula (III). The process comprises (a) contacting the compound of Formula (III) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II) and (b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the polyester composition comprising compounds of Formula (Ia), according to the following reaction scheme:



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

X is a halide ion or a hydroxyl group;

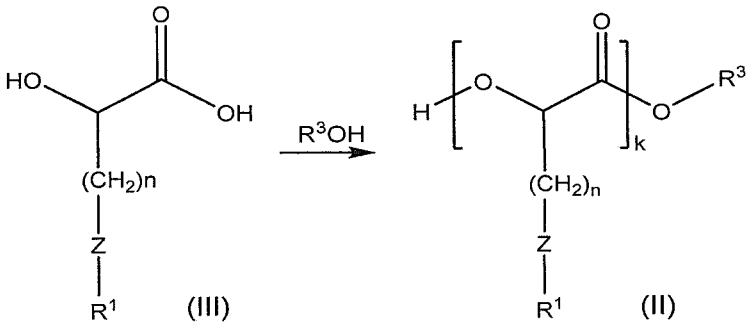
Z is sulfur, sulfoxide, or sulfone;

k is an integer of 1 or greater; and

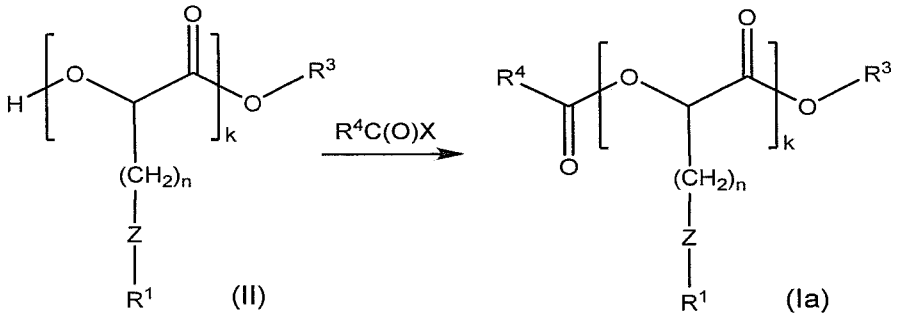
n is an integer of 1 or greater.

[0006a] Another aspect of the present disclosure encompasses a process for preparing a composition comprising compounds of Formula (Ia) from a compound of Formula (III), the process comprising:

(a) contacting the compound of Formula (III) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II); and



(b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the composition comprising compounds of Formula (Ia);



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

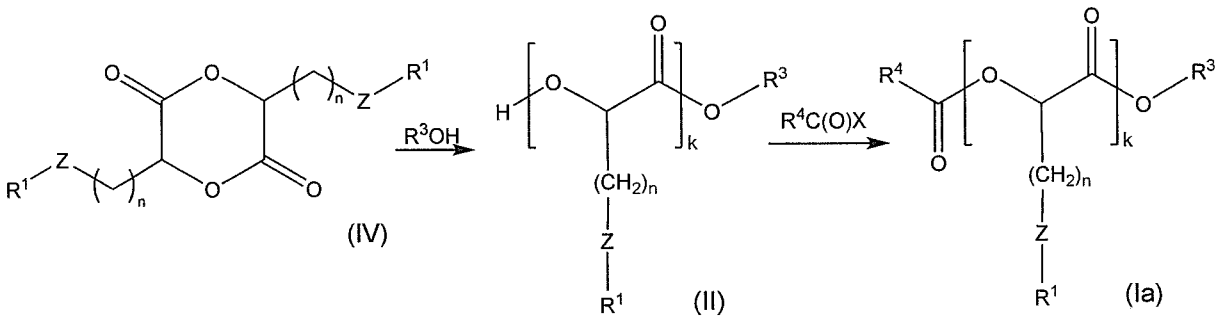
X is a halide ion or a hydroxyl group;

Z is sulfur, sulfoxide, or sulfone;

k is an integer from 1 to 20; and

n is an integer of 1 or 2.

[0007] The present disclosure provides a process preparing a polyester composition comprising compounds of Formula (Ia) from a compound of Formula (IV). The process comprises (a) contacting the compound of Formula (IV) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II) and (b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the polyester composition comprising compounds of Formula (Ia), according to the following reaction scheme:



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

X is a halide ion or a hydroxyl group;

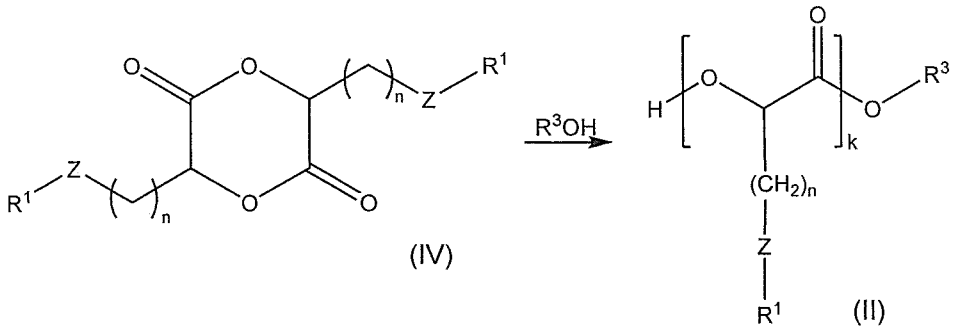
Z is sulfur, sulfoxide, or sulfone;

k is an integer of 1 or greater; and

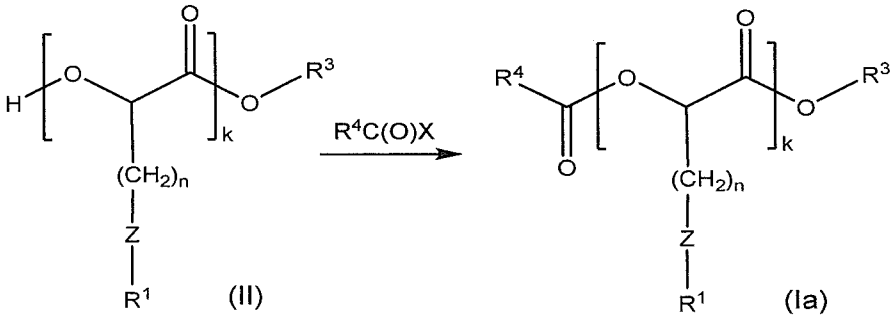
n is an integer of 1 or greater.

[0007a] Another aspect of the present disclosure provides a process for preparing a composition comprising compounds of Formula (Ia) from a compound of Formula (IV), the process comprising:

(a) contacting the compound of Formula (IV) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II); and



(b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the composition comprising compounds of Formula (Ia);



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

X is a halide ion or a hydroxyl group;

Z is sulfur, sulfoxide, or sulfone;

k is an integer from 1 to 20; and

n is an integer of 1 or 2.

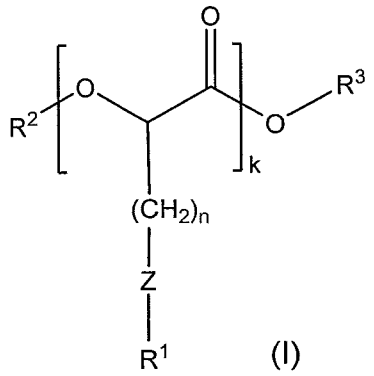
[0008] Other features and iterations of the disclosure are described in more detail below.

DETAILED DESCRIPTION OF THE INVENTION

[0009] The present disclosure provides hydrocarbyl terminated polyester compounds comprising sulfur-containing repeat units that are useful as plastic modifiers. In particular, the polyester compounds disclosed herein can be used to

CLAIMS
What is claimed is:

1. A composition comprising compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

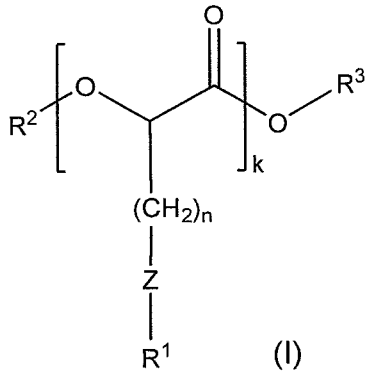
Z is sulfur;

k is an integer from 1 to 20 ; and

n is an integer of 1 or 2 .

2. The composition of claim 1, wherein R^1 is methyl; k is from 1 to 10; and n is 2.

3. A polymer blend composition comprising a polymer and a composition comprising compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

Z is sulfur;

k is an integer from 1 to 20 ; and

n is an integer of 1 or 2.

4. The polymer blend composition of claim 3, wherein herein R1 is methyl; k is from 1 to 10; and n is 2.

5. The polymer blend composition of claims 3 or 4, wherein the polymer is chosen from polyvinyl chloride, polylactide, poly(acrylic acid), poly(methacrylic acid), poly(methyl acrylate), poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl alcohol), polyethylene, polystyrene,

polypropylene, polycaprolactone, polyhydroxyalkanoate, polyurethane, cellulosics, copolymer thereof, or combination thereof.

6. The polymer blend composition of any one of claims 3 to 5 , wherein the polymer composition has a reduced glass transition temperature, reduced cold crystallization temperature, increased elongation at break, improved tensile modulus, improved reduced tensile strength at break, or combination thereof, relative to that of an unblended polymer.

7. The polymer blend composition of any one of claims 3 to 6 , wherein the polymer is polyvinyl chloride and the composition comprising compounds of Formula (I) is present at a concentration from 5 to 100 parts by weight per hundred parts by weight of the polymer.

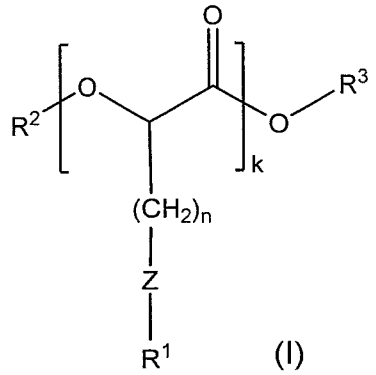
8. The polymer blend composition of any one of claims 3 to 6, wherein the polymer is polylactide and the composition comprising compounds of Formula (I) is present at a concentration from 5 wt% to 50 wt% by weight of the polymer blend composition.

9. The polymer blend composition of any one of claims 3 to 8, further comprising at least one additive chosen from a heat stabilizer, a UV/light stabilizer, a flame retardant/smoke suppressor, an antioxidant, a biocide, a processing aid, a thermal modifier, an impact modifier, a blowing agent, a filler, a lubricant/co-stabilizer, a pigment, or a nucleating agent.

10. The polymer blend composition of any one of claims 3 to 9, wherein the polymer blend composition is a powder, a granular material, or a pelletized material.

11. A process for modifying performance properties of polymers, the process comprising contacting a polymer with a composition comprising compounds of Formula (I) to form a polymer blend composition, wherein the

polymer blend composition has an improved performance property relative to an unmodified polymer, the compounds of Formula (I):



(I)

wherein:

R^1 is C_1 to C_6 alkyl;

R^3 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl;

R^2 is R^4CO-, wherein R^4 is C_1 to C_{30} alkyl or C_1 to C_{30} alkenyl ;

Z is sulfur;

k is an integer from 1 to 20 ; and

n is an integer of 1 or 2 .

12. The process of claim 11, wherein R1 is methyl; k is from 1 to 10; and n is 2.

13. The process of claims 11 or 12, wherein the polymer is chosen from polyvinyl chloride, polylactide, poly(acrylic acid), poly(methacrylic acid), poly(methyl acrylate), poly(methyl methacrylate), poly(vinyl acetate), poly(vinyl alcohol), polyethylene, polystyrene, polypropylene,

polycaprolactone, polyhydroxyalkanoate, polyurethane, cellulosics, copolymer thereof, or combination thereof.

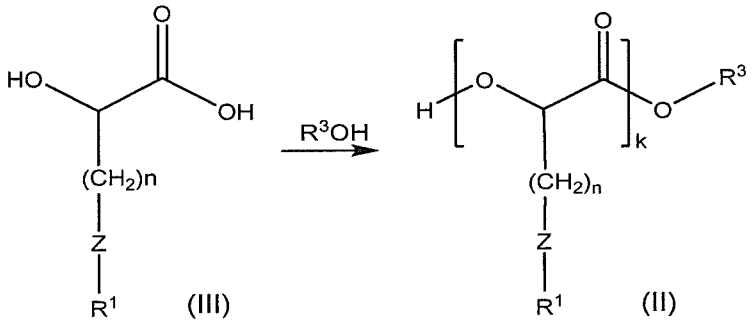
14. The process of any one of claims 11 to 13, wherein the improved performance property is reduced glass transition temperature, reduced cold crystallization temperature, increased elongation at break, reduced tensile modulus, reduced tensile strength at break, or combination thereof.

15. The process of any one of claims 11 to 14 , wherein the polymer is polyvinyl chloride and the composition comprising compounds of Formula (I) is present at a concentration from 5 to 100 parts by weight per hundred parts by weight of the polymer.

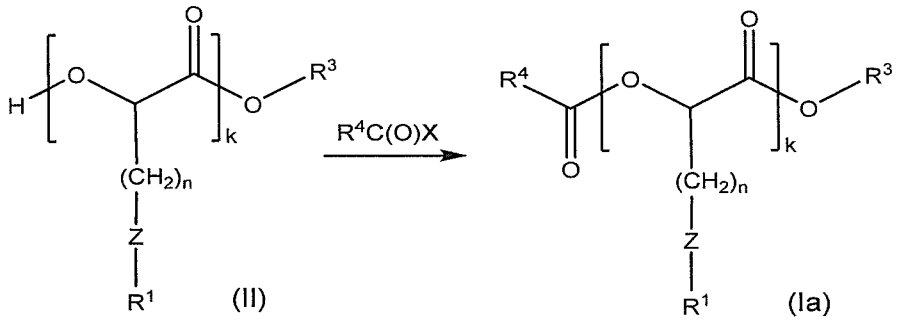
16. The process of any one of claims 11 to 14 , wherein the polymer is polylactide and the composition comprising compounds of Formula (I) is present at a concentration from 5 wt% to 50 wt% by weight of the polymer blend composition.

17. A process for preparing a composition comprising compounds of Formula (Ia) from a compound of Formula (III), the process comprising:

(a) contacting the compound of Formula (III) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II); and



(b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the composition comprising compounds of Formula (Ia);



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

X is a halide ion or a hydroxyl group;

Z is sulfur, sulfoxide, or sulfone;

k is an integer from 1 to 20 ; and

n is an integer of 1 or 2 .

18. The process of claim 17, wherein R1 is alkyl; and R3 and R4 independently are alkyl, substituted alky, alkenyl, or substituted alkenyl.

19. The process of either claims 17 or 18, wherein R1 is C1 to C6 alkyl; and R3 and R4 independently are C1 to C30 alkyl or C1 to C30 alkenyl.

20. The process of any one of claims 17 to 19, wherein R1 is methyl; Z is sulfur; k is from 1 to 20; and n is 2.

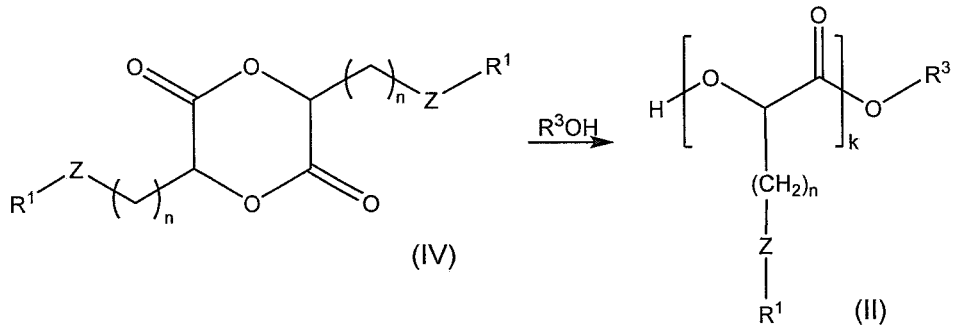
21. The process of any one of claims 17 to 20, wherein the compound of Formula (III) and the alcohol, R3OH, are present at a mole-to-mole ratio of 1:0.1 to 1:10; and the compounds of Formula (II) and R4C(O)Xare present at a mole-to-mole ratio of 1:0.8 to 1:1.5

22. The process of any one of claims 17 to 21, wherein step (a) is conducted in the presence of a catalyst and at a temperature of 80°C to 150°C; and step (b) is conducted at a temperature of 70°C to about 90°C.

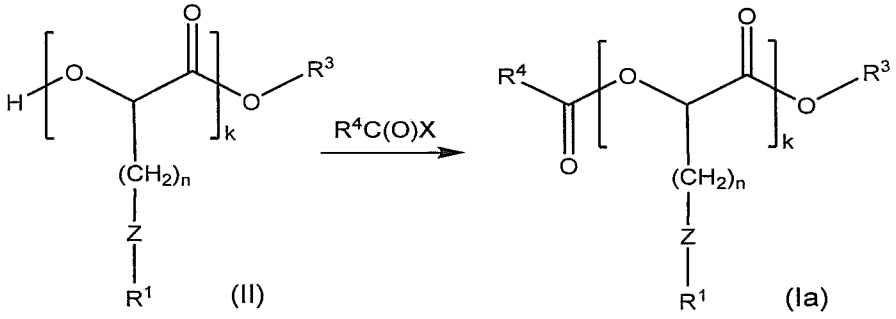
23. The process of any one of claims 17 to 22, wherein the process further comprises contacting the composition comprising compounds of Formula (Ia) with one or more agents to remove color bodies and/or odor.

24. A process for preparing a composition comprising compounds of Formula (Ia) from a compound of Formula (IV), the process comprising:

(a) contacting the compound of Formula (IV) with an alcohol, R^3OH, to form a distribution of compounds of Formula (II); and



(b) contacting the distribution of compounds of Formula (II) with an acyl halide or its acid analog, $R^4C(O)X$, to form the composition comprising compounds of Formula (Ia);



wherein:

R^1, R^3, and R^4 independently are hydrocarbyl or substituted hydrocarbyl;

X is a halide ion or a hydroxyl group;

Z is sulfur, sulfoxide, or sulfone;

k is an integer from 1 to 20 ; and

n is an integer of 1 or 2 .

25. The process of claim 24, wherein R1 is alkyl; and R3 and R4 independently are alkyl, substituted alky, alkenyl, or substituted alkenyl.

26. The process of either claims 24 or 25, wherein R1 is C1 to C6 alkyl; and R3 and R4 independently are C1 to C30 alkyl or C1 to C30 alkenyl.

27. The process of any one of claims 24 to 26, wherein R1 is methyl; Z is sulfur; k is from 1 to 10; and n is 2.

28. The process of any one of claims 24 to 27, wherein the compound of Formula (IV) and the alcohol, R3OH, are present at a mole-to-mole ratio of 1:0.1 to 1:10; and the compound of Formula (II) and R4C(O)X are present at a mole-to-mole ratio of 1:0.8 to 1:1.5

29. The process of any one of claims 24 to 28, wherein step (a) is conducted in the presence of a catalyst and at a temperature of 80°C to 150°C; and step (b) is conducted at a temperature of 70°C to 90°C.

30. The process of any one of claims 24 to 29, wherein the process further comprises contacting the composition comprising compounds of Formula (Ia) with one or more agents to remove color bodies and/or odor .