



US 20140288332A1

(19) **United States**

(12) **Patent Application Publication**
Carlson et al.

(10) **Pub. No.: US 2014/0288332 A1**

(43) **Pub. Date: Sep. 25, 2014**

(54) **ALKYL ETHER COMPOSITIONS AND METHODS OF USE**

Publication Classification

(71) Applicant: **Empire Technology Development LLC**,
Wilmington, DE (US)

(51) **Int. Cl.**
C07C 43/115 (2006.01)
C07C 43/04 (2006.01)

(72) Inventors: **William B. Carlson**, Seattle, WA (US);
Gregory D. Phelan, Cortland, NY (US)

(52) **U.S. Cl.**
CPC **C07C 43/115** (2013.01); **C07C 43/04**
(2013.01)
USPC **568/593**; 568/601; 568/866

(21) Appl. No.: **14/297,990**

(22) Filed: **Jun. 6, 2014**

(57) **ABSTRACT**

Related U.S. Application Data

(63) Continuation of application No. 13/761,512, filed on
Feb. 7, 2013, now Pat. No. 8,779,070.

Foreign Application Priority Data

Jul. 31, 2012 (US) PCT/US2012/048980

A polymer includes a linker represented by Formula I
([OR¹OCH₂OR²OCH₂]_m), where R¹ and R² are, indepen-
dently, alkylene, alkenylene, arylene, heteroarylene, or alky-
larylalkylene; and the polymer has a weight average molecu-
lar weight of about 500 g/mol to about 2,000,000 g/mol, and
m is 1 to 1000.

ALKYL ETHER COMPOSITIONS AND METHODS OF USE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of U.S. patent application Ser. No. 13/761,512, filed on Feb. 7, 2013, which in turn claims the benefit of International Application Serial No. PCT/US2012/048980, filed on Jul. 31, 2012, the entire disclosure of which is hereby incorporated by reference for all purposes in its entirety as if fully set forth herein.

FIELD

[0002] The present technology relates to polymers that are degradable and recyclable and plastic materials that are made from such polymers.

BACKGROUND

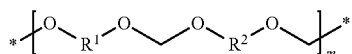
[0003] The following description is provided to assist the understanding of the reader. None of the information provided or references cited is admitted to be prior art to the present technology.

[0004] Commercially relevant packaging materials are constantly evolving to meet consumer demand for improved products by combining numerous physical characteristics, such as flexibility, light weight, or strength into such packaging materials. Unfortunately, despite improvements in product performance, most of these commercially relevant packaging materials remain difficult or impractical to recycle. Unless it is biodegradable, the discarded packaging materials accumulate in landfills and waterways, where they may eventually harm ecosystems and wildlife. Consequently, the food packaging industry is seeking packaging materials that satisfy the evolving demands of consumers, yet can be more readily degraded and recycled.

SUMMARY

[0005] The present technology provides for a recyclable polymer that includes monomers joined by acid-sensitive $\text{—OCH}_2\text{O—}$ linkers that can be cleaved upon exposure to acidic conditions. The recyclable polymer, having monomers joined by acid-sensitive $\text{—OCH}_2\text{O—}$ linkers, can be incorporated into plastic materials such as, for example, food packaging or consumer packaging materials. After the plastic materials have been used by a consumer they can readily be degraded by subjecting the plastic materials to acidic conditions. Upon treatment with acid, the $\text{—OCH}_2\text{O—}$ linkers within the polymers are hydrolyzed, the monomers are released, and the plastic materials are thus degraded. The resulting monomers can be recombined with additional acid-sensitive $\text{—OCH}_2\text{O—}$ linkers to regenerate the polymer and recycle the plastic materials.

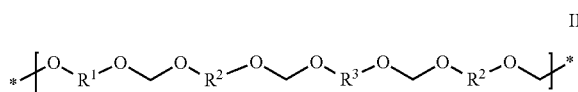
[0006] In one aspect a polymer is provided including a linker represented by Formula I:



In Formula I, R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene. In

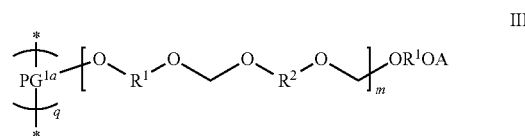
some embodiments, the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol, and m is 1 to 1000. In some embodiments, R^1 is $\text{C}_2\text{--C}_{10}$ alkylene; and R^2 is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0007] In another aspect a polymer is provided including a linker represented by Formula II:



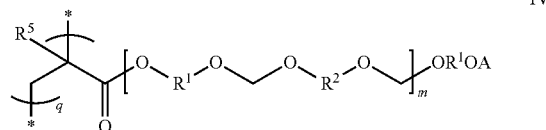
In Formula II, R^1 , R^2 , and R^3 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; and R^1 and R^3 are different. In some embodiments, the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol. In some embodiments, R^1 , R^2 , or R^3 is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0008] In another aspect a polymer is provided, the polymer represented by Formula III:



In Formula III, R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; A is hydrogen, alkyl, or —C(O)R^4 ; R^4 is hydrogen, alkyl, or phenyl; PG^{1a} is the polymerization product of a polymerization group PG^1 ; and PG^1 is acrylyl, methacrylyl, isocyanyl, styrenyl, epoxylyl, vinyl, oxetanyl, DL-lactidyl, or bicyclo[2.2.1]hept-2-enyl. In some embodiments, the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol; m is 1 to 1000; and q is 1 to 1000. In some embodiments, R^1 is $\text{C}_2\text{--C}_{10}$ alkylene; and R^2 is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

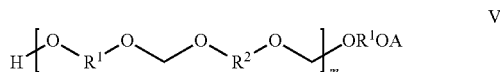
[0009] In another aspect a polymer is provided, where the polymer is represented by Formula IV:



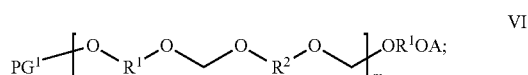
In Formula IV, R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; R^5 is hydrogen, CN, alkyl, or phenyl; A is hydrogen, alkyl, or —C(O)R^4 ; and R^4 is hydrogen, alkyl, or phenyl. In some embodiments, the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol; m is 1 to 1000; and q is 1 to 1000. In some embodiments, R^1 is $\text{C}_2\text{--C}_{10}$ alkylene; and R^2 is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0010] A method is provided for preparing polymer represented by Formula III. The method includes contacting

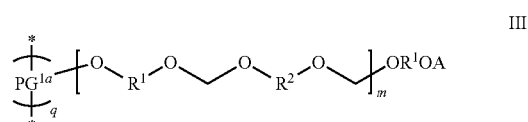
XCH₂OR²OCH₂X with HOR¹OH, HOR¹OA, and a base to form a polymer represented by Formula V



contacting the polymer represented by Formula V with a compound represented by PG¹-L and a base to form a polymer represented by Formula VI:

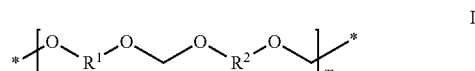


and polymerizing PG¹ of the polymer represented by Formula VI to form the polymer represented by Formula III:



In Formulae III, V, and VI, R¹ and R² are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; R⁴ is hydrogen, alkyl, or phenyl; A is hydrogen, alkyl, or —C(O)R⁴; X is a leaving group; PG¹ is a polymerizable group that is acrylyl, methacrylyl, isocycanyl, styrenyl, epoxy, vinyl, oxetanyl, DL-lactidyl, or bicyclo[2.2.1]hept-2-enyl; PG^{1a} is the polymerization product of the polymerizable group PG¹; L is a leaving group; m is 1 to 1000; and q is 1 to 1000. In some embodiments, R¹ is C₂-C₁₀ alkylene; and R² is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0011] In another aspect, a method is provided for degrading a polymer, where the method includes providing a polymer including a linker represented by Formula I, contacting the polymer with acid; and obtaining a composition including HOR¹OH and HOR²OH.



[0012] The foregoing summary is illustrative only and is not intended to be in any way limiting. In addition to the illustrative aspects, embodiments and features described above, further aspects, embodiments and features will become apparent by reference to the following drawings and the detailed description.

DETAILED DESCRIPTION

[0013] The illustrative embodiments described in the detailed description and claims are not meant to be limiting. Other embodiments may be utilized, and other changes may be made, without departing from the spirit or scope of the subject matter presented here.

[0014] The present technology is described herein using several definitions, as set forth throughout the specification.

[0015] As used herein, unless otherwise stated, the singular forms “a,” “an,” and “the” include plural reference. Thus, for example, a reference to “a cell” includes a plurality of cells, and a reference to “a molecule” is a reference to one or more molecules.

[0016] As used herein, “about” will be understood by persons of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to persons of ordinary skill in the art, given the context in which it is used, “about” will mean up to plus or minus 10% of the particular term.

[0017] Alkyl groups include straight chain, branched chain, or cyclic alkyl groups having 1 to 24 carbons or the number of carbons indicated herein. In some embodiments, an alkyl group has 1 to 16 carbon atoms, 1 to 12 carbons, 1 to 8 carbons or, in some embodiments, 1 to 6, or 1, 2, 3, 4 or 5 carbon atoms. Examples of straight chain alkyl groups include groups such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, isobutyl, sec-butyl, tert-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. In some embodiments, the alkyl groups may be substituted alkyl groups.

[0018] Heteroalkyl groups include alkyl groups, as defined herein, substituted by one or more O, N, or S atoms.

[0019] Cycloalkyl groups are cyclic alkyl groups having 3 to 10 carbon atoms. In some embodiments, the cycloalkyl group has 3 to 7 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 5, 3 to 6, or 5, 6 or 7. Cycloalkyl groups further include monocyclic, bicyclic and polycyclic ring systems. Monocyclic groups include, e.g., cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, and cycloheptyl groups. Bicyclic and polycyclic cycloalkyl groups include bridged or fused rings, such as, but not limited to, bicyclo[3.2.1]octane, decalanyl, and the like. Cycloalkyl groups include rings that are substituted with straight or branched chain alkyl groups as defined above. In some embodiments, the cycloalkyl groups are substituted cycloalkyl groups. Representative substituted alkenyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above. Representative substituted alkyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

[0020] Alkenyl groups include straight and branched chain alkyl groups as defined above, except that at least one double bond exists between two carbon atoms. Thus, alkenyl groups have 2 to 24 carbon atoms, and typically 2 to 10 carbons or, in some embodiments, 2 to 8, 2 to 6, or 2 to 4 carbon atoms. Examples include, but are not limited to vinyl, allyl, —CH=CH(CH₃), —CH=C(CH₃)₂, —C(CH₃)=CH₂, —C(CH₃)=CH(CH₃), —C(CH₂CH₃)=CH₂, among others. Representative substituted alkenyl groups may be mono-substituted or substituted more than once, such as, but not limited to, mono-, di- or tri-substituted with substituents such as those listed above.

[0021] The terms “alkylene,” “cycloalkylene,” “alkenylene,” “arylene,” “heteroarylene,” and “alkylarylalkylene” alone or as part of another substituent means a divalent radical derived from an alkyl, cycloalkyl, alkenyl, aryl, heteroaryl, or alkylarylalkyl group, respectively, as exemplified

by $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$. For alkylene, cycloalkylene, alkenylene, arylene, heteroarylene, and alkylarylalkylene linking groups, no orientation of the linking group is implied.

[0022] The term “amine” (or “amino”) as used herein refers to $-\text{NHR}$ and $-\text{NRR}'$ groups, where R, and R' are independently hydrogen, or a substituted or unsubstituted alkyl, alkenyl, alkynyl, cycloalkyl, aryl or aralkyl group as defined herein. Examples of amino groups include NH_2 , methylamino, dimethylamino, ethylamino, diethylamino, propylamino, isopropylamino, phenylamino, benzylamino, and the like.

[0023] The term “oxo” refers to a divalent oxygen group. While the term includes doubly bonded oxygen, such as that found in a carbonyl group, as used herein, the term oxo explicitly includes singly bonded oxygen of the form $-\text{O}-$ which is part of a polymer backbone. Thus, an oxo group may be part of an ether linkage ($-\text{O}-$), an ester linkage ($-\text{O}-\text{C}(\text{O})-$), a carbonate linkage ($-\text{O}-\text{C}(\text{O})\text{O}-$), a carbamate linkage ($-\text{O}-\text{C}(\text{O})\text{NH}-$ or $-\text{O}-\text{C}(\text{O})\text{NR}-$), and the like.

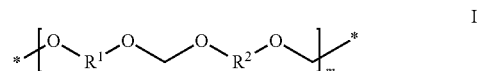
[0024] “Substituted” refers to a chemical group as described herein that further includes one or more substituents, such as lower alkyl (including substituted lower alkyl such as haloalkyl, hydroxyalkyl, aminoalkyl), aryl (including substituted aryl), acyl, halogen, hydroxy, amino, alkoxy, alkylamino, acylamino, thioamido, acyloxy, aryloxy, aryloxyalkyl, carboxy, thiol, sulfide, sulfonyl, oxo, both saturated and unsaturated cyclic hydrocarbons (e.g., cycloalkyl, cycloalkenyl), cycloheteroalkyls and the like. These groups may be attached to any carbon or substituent of the alkyl, alkenyl, alkynyl, aryl, cycloheteroalkyl, alkylene, alkenylene, alkynylene, arylene, heteroarylene, hetero moieties. Additionally, the substituents may be pendent from, or integral to, the carbon chain itself.

[0025] The present technology provides for polymers containing $-\text{OCH}_2\text{O}-$ linker moieties that render the polymers chemically stable during commercial use but easily cleaved upon exposure to conditions (e.g., acidic conditions) not typically encountered during commercial use. The $-\text{OCH}_2\text{O}-$ linker moieties can be combined with various monomers to tune the physical characteristics (e.g., flexibility, hardness, softness, etc.) of the polymer. The polymers described herein, having acid-sensitive $-\text{OCH}_2\text{O}-$ linkers, are more readily degraded with acid and recycled than polymers made from conventional polymers e.g., those made from PET, polyethylene, or polypropylene. The polymers can be incorporated in packaging materials that can be readily degraded to monomeric starting materials following commercial use. Further, the monomeric starting materials that can readily be resynthesized (i.e., recycled) into the polymers described herein. Packaging made from the polymers described herein is cost effective, convenient, and light weight.

[0026] The polymers described herein can be used to make packaging, containers, and plastic goods for any application. For example, the polymers described herein can be used in wide variety of plastics for any application such as food, beverage, or consumer packaging, sport drink bottles, freeze vacuum containers, shipping cartons, bags, optical lenses, utensils, plates, toys, furniture coatings, automobile plastic components, fiberglass, cookware, plastic utensils, computers (e.g., tablets, laptops, netbooks) computer components, medical implants, mobile electronics, phones, calculators, paneling, coatings, fibers, insulation, seats, tables, shelves,

table tops, counters, caulking and the like. The polymers described herein can also be used in aviation components.

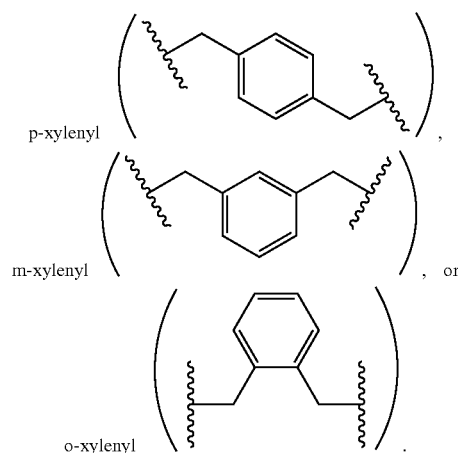
[0027] As noted above, the polymers include a $-\text{OCH}_2\text{O}-$ group. This group may be incorporated into a linker represented by Formula I:



In Formula I, R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol, and m is 1 to 1000.

[0028] In Formula I, R^1 and R^2 are groups that are joined by the $-\text{OCH}_2\text{O}-$ moieties. Each R^1 and R^2 group can be selected to tune the physical characteristics (e.g., flexibility, hardness, softness, etc.) of the polymer to accommodate the intended application (e.g., food packaging, consumer packaging, etc.) for the polymer. For example, flexible polymers generally include flexible alkyl groups at R^1 and/or R^2 , whereas the polymer can be made more rigid by incorporating inflexible aryl groups at R^1 and/or R^2 . Flexible groups impart “flexibility” and “softness” to the polymer, while rigid groups impart “rigidity” and “hardness.” Such terms, while relative, are widely used in the art and are well-understood terms of distinction.

[0029] For example, R^1 may be alkylene in Formula I. In some embodiments, R^1 is C_2 - C_{10} alkylene. In some embodiments, R^1 is $(\text{CH}_2)_2$; $(\text{CH}_2)_4$; $(\text{CH}_2)_6$; or $(\text{CH}_2)_8$. In some embodiments, R^1 is $(\text{CH}_2)_4$. R^1 may be alkenylene. In some embodiments, R^1 is C_2 - C_{10} alkenylene. In some embodiments, R^1 is vinylene or allylene. R^1 may be arylene. In some embodiments, R^1 is phenylene, biphenylene, anthracenylene, or naphthalenylene. R^1 may also be alkylarylalkylene. In some embodiments, R^1 is



[0030] Further, R^2 may be alkylene in Formula I. In some embodiments, R^2 is C_2 - C_{10} alkylene. In some embodiments, R^2 is $(\text{CH}_2)_2$; $(\text{CH}_2)_4$; $(\text{CH}_2)_6$; or $(\text{CH}_2)_8$. In some embodiments, R^2 is $(\text{CH}_2)_4$. R^2 may be alkenylene. In some embodiments, R^2 is C_2 - C_{10} alkenylene. In some embodiments, R^2 is vinylene or allylene. R^2 may be arylene. In some embodi-

ments, R² is phenylene, biphenylene, anthracenyene, or naphthalenyene. R² may also be alkylarylalkylene. In some embodiments, R² is p-xylenyl, m-xylenyl, or o-xylenyl.

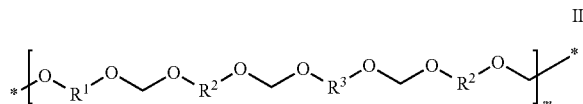
[0031] In Formula I, each R¹ and R² can independently be a mixture of groups. For example, each R¹ and R² can independently be a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl, where p-xylenyl groups, for example, can add rigidity to the polymer, whereas m-xylenyl groups, for example, can decrease the rigidity of the polymer.

[0032] In some embodiments, R¹ is C₂-C₁₀ alkylene; and R² is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl. In some embodiments, R² is a mixture of p-xylenyl and m-xylenyl having a p-xylenyl:m-xylenyl ratio of about 2:1 to about 20:1. In some embodiments, R² is a mixture of p-xylenyl and m-xylenyl having a p-xylenyl:m-xylenyl ratio of about 5:1, 10:1, or 15:1. In some embodiments, R² is a mixture of p-xylenyl and o-xylenyl having a p-xylenyl:o-xylenyl ratio of about 2:1 to about 20:1. In some embodiments, R² is a mixture of p-xylenyl and o-xylenyl having a p-xylenyl:o-xylenyl ratio of about 5:1, 10:1, or 15:1.

[0033] The polymers of Formula I have a weight average molecular weight (Mw) of about 500 g/mol to about 2,000,000 g/mol. This may include an Mw of about 500 g/mol to about 500,000 g/mol, about 500 g/mol to about 100,000 g/mol, about 500 g/mol to about 50,000 g/mol, or about 500 g/mol to about 10,000 g/mol. Specific examples of Mw include about 500 g/mol, about 1,000 g/mol, about 5,000 g/mol, about 10,000 g/mol, about 20,000 g/mol, about 30,000 g/mol, about 40,000 g/mol, about 50,000 g/mol, about 60,000 g/mol, about 70,000 g/mol, about 80,000 g/mol, about 90,000 g/mol, about 100,000 g/mol, about 200,000 g/mol, about 250,000 g/mol, about 500,000 g/mol, about 750,000 g/mol, about 1,000,000 g/mol, about 2,000,000 g/mol, and ranges between any two of these values.

[0034] In some embodiments, m in Formula I is 1 to 1,000, 1 to 500, 1 to 250, 1 to 100, 1 to 50, or 1 to 10. Specific examples of m include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 200, 250, 300, 400, 500, 750, 1,000, and ranges between any two of these values.

[0035] In accordance with another aspect a polymer is provided, where the polymer includes a linker represented by Formula II:



In Formula II, R¹, R², and R³ are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; R¹ and R³ are different; the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol, and m is 1 to 1000.

[0036] In Formula II, R¹ may be alkylene. In some embodiments, R¹ is C₂-C₁₀ alkylene. In some embodiments, R¹ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R¹ is (CH₂)₄. R¹ may be alkenylene. In some embodiments, R¹ is C₂-C₁₀ alkenylene. In some embodiments, R¹ is vinylene or allylene. R¹ may be arylene. In some embodiments, R¹ is phenylene, biphenylene, anthracenyene, or naphthalenyene. R¹ may also be alkylarylalkylene. In some embodiments, R¹ is p-xylenyl, m-xylenyl, or o-xylenyl. R² may be alkylene in Formula II. In some embodiments, R² is

C₂-C₁₀ alkylene. In some embodiments, R² is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R² is (CH₂)₄. R² may be alkenylene. In some embodiments, R² is C₂-C₁₀ alkenylene. In some embodiments, R² is vinylene or allylene. R² may be arylene. In some embodiments, R² is phenylene, biphenylene, anthracenyene, or naphthalenyene. R² may also be alkylarylalkylene. In some embodiments, R² is p-xylenyl, m-xylenyl, or o-xylenyl.

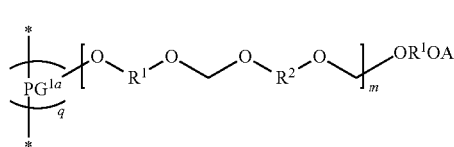
[0037] R³ may be alkylene in Formula II. In some embodiments, R³ is C₂-C₁₀ alkylene. In some embodiments, R³ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R³ is (CH₂)₄. R³ may be alkenylene. In some embodiments, R³ is C₂-C₁₀ alkenylene. In some embodiments, R³ is vinylene or allylene. R³ may be arylene. In some embodiments, R³ is phenylene, biphenylene, anthracenyene, or naphthalenyene. R³ may also be alkylarylalkylene. In some embodiments, R³ is p-xylenyl, m-xylenyl, or o-xylenyl. In some embodiments, R¹, R², or R³ is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0038] In some embodiments, the polymer has a weight average molecular weight (Mw) of about 500 g/mol to about 2,000,000, 500 g/mol to about 1,000,000 g/mol, about 500 g/mol to about 500,000 g/mol, about 500 g/mol to about 100,000 g/mol, about 500 g/mol to about 50,000 g/mol, or about 500 g/mol to about 10,000 g/mol. Specific examples of Mw include about 500 g/mol, about 1,000 g/mol, about 5,000 g/mol, about 10,000 g/mol, about 20,000 g/mol, about 30,000 g/mol, about 40,000 g/mol, about 50,000 g/mol, about 60,000 g/mol, about 70,000 g/mol, about 80,000 g/mol, about 90,000 g/mol, about 100,000 g/mol, about 200,000 g/mol, about 250,000 g/mol, about 500,000 g/mol, about 750,000 g/mol, about 1,000,000 g/mol, and ranges between any two of these values. In some embodiments, m is 1 to 500, 1 to 250, 1 to 100, 1 to 50, or 1 to 10. Specific examples of m include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 200, 300, 400, 500, and ranges between any two of these values.

[0039] In some embodiments, R¹ and R³ are alkylene; and R² is alkylarylalkylene. In some embodiments, R¹ and R³ are alkylarylalkylene; and R² is alkylene. In some embodiments, each alkylarylalkylene is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

[0040] In some embodiments, each alkylarylalkylene is, independently, a mixture of p-xylenyl and m-xylenyl having a p-xylenyl:m-xylenyl ratio of about 2:1 to about 20:1. In some embodiments, each alkylarylalkylene is, independently, a mixture of p-xylenyl and o-xylenyl having a p-xylenyl:o-xylenyl ratio of about 2:1 to about 20:1. In some embodiments, each alkylene is C₁-C₁₀ alkylene. In some embodiments, each alkylene is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈.

[0041] The linkers described above may be the entire, stand-alone polymer, or the linker may be incorporated into other polymers. For example, the polymer may be represented by Formula III:



III

In Formula III, R¹ and R² are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; A is hydrogen, alkyl, or —C(O)R⁴; R⁴ is hydrogen, alkyl, or phenyl; PG^{1a} is the polymerization product of a polymerization group PG¹; PG¹ is acrylyl, methacrylyl, isocycanyl, styrenyl, epoxy, vinyl, oxetanyl, DL-lactidyl, or bicyclo[2.2.1]hept-2-enyl; the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol; m is 1 to 1000; and q is 1 to 1000.

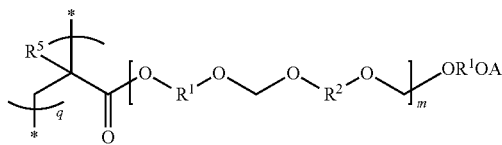
[0042] In Formula III, R¹ may be alkylene. In some embodiments, R¹ is C₂-C₁₀ alkylene. In some embodiments, R¹ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R¹ is (CH₂)₄. R¹ may be alkenylene. In some embodiments, R¹ is C₂-C₁₀ alkenylene. In some embodiments, R¹ is vinylene or allylene. R¹ may be arylene. In some embodiments, R¹ is phenylene, biphenylene, anthracenylene, or naphthalenylene. R¹ may also be alkylarylalkylene. In some embodiments, R¹ is p-xylenyl, m-xylenyl, or o-xylenyl.

[0043] R² may be alkylene in Formula III. In some embodiments, R² is C₂-C₁₀ alkylene. In some embodiments, R² is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R² is (CH₂)₄. R² may be alkenylene. In some embodiments, R² is C₂-C₁₀ alkenylene. In some embodiments, R² is vinylene or allylene. R² may be arylene. In some embodiments, R² is phenylene, biphenylene, anthracenylene, or naphthalenylene. R² may also be alkylarylalkylene. In some embodiments, R² is p-xylenyl, m-xylenyl, or o-xylenyl.

[0044] In some embodiments, the polymer has a Mw of about 500 g/mol to about 1,000,000. This may include an Mw of about 500 g/mol to about 500,000, about 500 g/mol to about 100,000, about 500 g/mol to about 50,000, or about 500 g/mol to about 10,000. Specific examples of Mw include about 500 g/mol, about 1,000 g/mol, about 5,000 g/mol, about 10,000 g/mol, about 20,000 g/mol, about 30,000 g/mol, about 40,000 g/mol, about 50,000 g/mol, about 60,000 g/mol, about 70,000 g/mol, about 80,000 g/mol, about 90,000 g/mol, about 100,000 g/mol, about 200,000 g/mol, about 250,000 g/mol, about 500,000 g/mol, about 750,000 g/mol, about 1,000,000 g/mol, about 2,000,000, and ranges between any two of these values. In some embodiments, m is 1 to 500, 1 to 250, 1 to 100, 1 to 50, or 1 to 10. Specific examples of m include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 200, 250, 300, 400, 500, 750, 1,000,000, and ranges between any two of these values. Specific examples of q include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, and ranges between any two of these values.

[0045] In accordance with another aspect a polymer is provided, where the polymer is represented by Formula IV:

IV



In Formula IV, R¹ and R² are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; R⁵ is hydrogen, CN, alkyl, or phenyl; A is hydrogen, alkyl, or —C(O)R⁴; R⁴ is hydrogen, alkyl, or phenyl; the polymer has

a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol; m is 1 to 1000; and q is 1 to 1000.

[0046] In Formula IV, R¹ may be alkylene. In some embodiments, R¹ is C₂-C₁₀ alkylene. In some embodiments, R¹ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R¹ is (CH₂)₄. R¹ may be alkenylene. In some embodiments, R¹ is C₂-C₁₀ alkenylene. In some embodiments, R¹ is vinylene or allylene. R¹ may be arylene. In some embodiments, R¹ is phenylene, biphenylene, anthracenylene, or naphthalenylene. R¹ may also be alkylarylalkylene. In some embodiments, R¹ is p-xylenyl, m-xylenyl, or o-xylenyl.

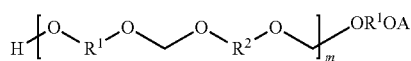
[0047] R² may be alkylene in Formula IV. In some embodiments, R² is C₂-C₁₀ alkylene. In some embodiments, R² is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R² is (CH₂)₄. R² may be alkenylene. In some embodiments, R² is C₂-C₁₀ alkenylene. In some embodiments, R² is vinylene or allylene. R² may be arylene. In some embodiments, R² is phenylene, biphenylene, anthracenylene, or naphthalenylene. R² may also be alkylarylalkylene. In some embodiments, R² is p-xylenyl, m-xylenyl, or o-xylenyl.

[0048] In some embodiments, the polymer has a weight average molecular weight (Mw) of about 500 g/mol to about 2,000,000, about 500 g/mol to about 1,000,000, about 500 g/mol to about 500,000, about 500 g/mol to about 100,000, about 500 g/mol to about 50,000, or about 500 g/mol to about 10,000. Specific examples of Mw include about 500 g/mol, about 1,000 g/mol, about 5,000 g/mol, about 10,000 g/mol, about 20,000 g/mol, about 30,000 g/mol, about 40,000 g/mol, about 50,000 g/mol, about 60,000 g/mol, about 70,000 g/mol, about 80,000 g/mol, about 90,000 g/mol, about 100,000 g/mol, about 200,000 g/mol, about 250,000 g/mol, about 500,000 g/mol, about 750,000 g/mol, about 1,000,000 g/mol, about 2,000,000, and ranges between any two of these values. In some embodiments, m is 1 to 50. In some embodiments, m is 1 to 40, 1 to 30, 1 to 20, 1 to 10, 1 to 5. Specific examples of m include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 200, 250, 300, 400, 500, 750, 1,000,000, and ranges between any two of these values. In some embodiments, q is 1 to 50. In some embodiments, q is 1 to 40, 1 to 30, 1 to 20, 1 to 10, or 1 to 5. Specific examples of q include 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, and ranges between any two of these values.

[0049] In some embodiments, R¹ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈; and R² is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

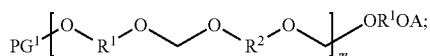
[0050] The above polymers are amenable to forming into a wide variety of articles as introduced above. The polymers may be formed into articles using techniques such as blowing, compaction molding, compression molding, injection molding, extrusion, rotomolding, vacuum molding, thermoforming, and the like as are known in the art.

[0051] In accordance with another aspect a method is provided of preparing polymer represented by Formula III where the method includes: contacting XCH₂OR²OCH₂X with HOR¹OH, HOR¹OA, and a base to form a polymer represented by Formula V



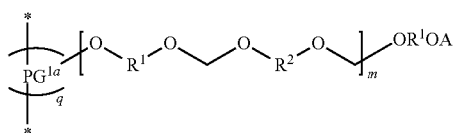
V

contacting the polymer represented by Formula V with a compound represented by PG¹-L and a base to form a polymer represented by Formula VI:



VI

and polymerizing PG¹ of the polymer represented by Formula VI to form the polymer represented by Formula III:



III

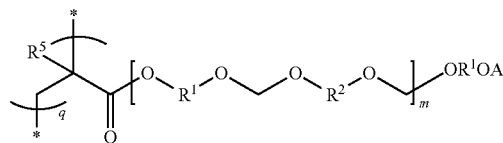
In Formulae III, V, and VI, R¹ and R² are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; A is hydrogen, alkyl, or C(O)R⁴; R⁴ is hydrogen, alkyl, or phenyl; X is a leaving group; PG¹ is a polymerizable group selected from the group consisting of acrylyl, methacrylyl, isocycanyl, styrenyl, epoxy, vinyl, oxetanyl, DL-lactidyl, and bicyclo[2.2.1]hept-2-enyl; PG^{1a} is the polymerization product of the polymerizable group PG¹; L is a leaving group; m is 1 to 1000; and q is 1 to 1000.

[0052] In Formula III, R¹ may be alkylene. In some embodiments, R¹ is C₂-C₁₀ alkylene. In some embodiments, R¹ is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R¹ is (CH₂)₄. R¹ may be alkenylene. In some embodiments, R¹ is C₂-C₁₀ alkenylene. In some embodiments, R¹ is vinylene or allylene. R¹ may be arylene. In some embodiments, R¹ is phenylene, biphenylene, anthracenylenylene, or naphthalenylenylene. R¹ may also be alkylarylalkylene. In some embodiments, R¹ is p-xylenyl, m-xylenyl, or o-xylenyl.

[0053] R² may be alkylene in Formula III. In some embodiments, R² is C₂-C₁₀ alkylene. In some embodiments, R² is (CH₂)₂; (CH₂)₄; (CH₂)₆; or (CH₂)₈. In some embodiments, R² is (CH₂)₄. R² may be alkenylene. In some embodiments, R² is C₂-C₁₀ alkenylene. In some embodiments, R² is vinylene or allylene. R² may be arylene. In some embodiments, R² is phenylene, biphenylene, anthracenylenylene, or naphthalenylenylene. R² may also be alkylarylalkylene. In some embodiments, R² is p-xylenyl, m-xylenyl, or o-xylenyl.

[0054] In some embodiments, the polymer has a weight average molecular weight (Mw) of about 500 g/mol to about 2,000,000 g/mol, about 500 g/mol to about 1,000,000 g/mol, about 500 g/mol to about 500,000 g/mol, about 500 g/mol to about 100,000 g/mol, about 500 g/mol to about 50,000 g/mol, or about 500 g/mol to about 10,000 g/mol. Specific examples of Mw include about 500 g/mol, about 1,000 g/mol, about 5,000 g/mol, about 10,000 g/mol, about 20,000 g/mol, about 30,000 g/mol, about 40,000 g/mol, about 50,000 g/mol, about 60,000 g/mol, about 70,000 g/mol, about 80,000 g/mol, about 90,000 g/mol, about 100,000 g/mol, about 200,000 g/mol, about 250,000 g/mol, about 500,000 g/mol, about 750,000 g/mol, about 1,000,000 g/mol, about 2,000,000, and ranges between any two of these values.

[0055] In some embodiments, the polymer represented by Formula III is a polymer represented by Formula IV:

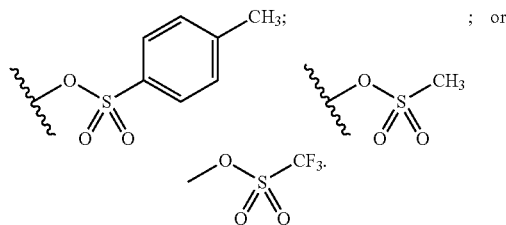


IV

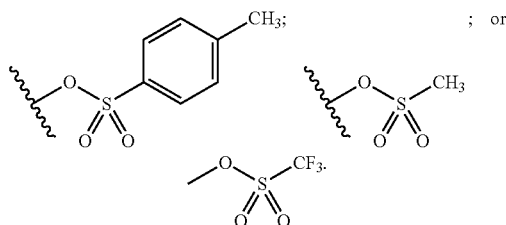
[0056] In Formula IV, R⁵ is hydrogen, CN, alkyl, or phenyl.

[0057] In some embodiments, the method further includes forming XCH₂OR²OCH₂X by contacting R⁶OCH₂OR²OCH₂OR⁶ with HX, where R⁶ is alkyl. In some embodiments, R⁶ is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, or octyl

[0058] In some embodiments, X is Cl, Br, I,



In some embodiments, L is Cl, Br, I,



In some embodiments, X and L are both Cl.

[0059] In some embodiments, the base is a tertiary amine, secondary amine, pyridine, or a carbonate salt. In some embodiments, the base is morpholine, N-methylmorpholine, piperidine, N-methylpiperidine, piperazine, N-methylpiperazine, N,N-dimethylpiperazine, triethylamine, diisopropylethylamine, or pyridine.

[0060] In another aspect, a method is provided for degrading any of the above polymers, the method including providing the polymer, contacting the polymer with acid, and obtaining a composition including alcohol degradation products. For example, where the polymer is that of Formula I, above, the alcohol degradation products will include HOR¹OH and HOR²OH. Where the polymer includes a further polymeric moiety or polymerizable group, such as those represented in Formulae III, IV, and VI, the degradation products will include the polymer fragments as well as the alcohol degradation products.

[0061] Because the polymers described above are originally prepared from alcohols such as HOR¹OH and HOR²OH, the acid degradation provides again the starting

materials for the polymerization. Thus, at least in the segments of the polymer which include R^1 and R^2 the regeneration of the starting materials is realized. These materials may then be used to make other polymers. Because the polymers are degraded into their original starting materials, the above polymers provide at least one advantage over other recycled plastics and polymers, that advantage being that the recycled (actually re-polymerized) polymers are the same as the original polymers. Other recycled plastics typically grinder the polymers into smaller fragments, then treat the terminal groups to link together the smaller fragments and oligomers. The present "recycled" polymers are to be completely reconstructed from the original starting materials that are recovered from the degradation process.

[0062] Illustrative acids for use in the methods of degrading include, but are not limited to, HCl, HBr, H_2SO_4 , acetic acid, trifluoroacetic acid, phosphoric acid, nitric acid, and combinations thereof. The acid may be added as the neat acid to the polymer or as a diluted solution such as an aqueous solution. Such an aqueous acid solution can have any pH of less than 7.0. Representative pH values for the acidic solution that is added to the polymer may be <6.0, <5.0, <4.0, <3.0, <2.0, or <1.0.

[0063] The temperature of the degradation will impact the rate at which the degradation occurs. Accordingly, a wide range of temperatures may be employed. For example, the contacting may be conducted at a temperature of about 20° C. to about 200° C. This will include temperatures of about 20° C. to about 150° C., or about 20° C. to about 100° C., or about 20° C. to about 50° C. In some embodiments, the contacting is conducted at room temperature.

[0064] The present technology, thus generally described, will be understood more readily by reference to the following Examples, which are provided by way of illustration and are not intended to be limiting of the present technology.

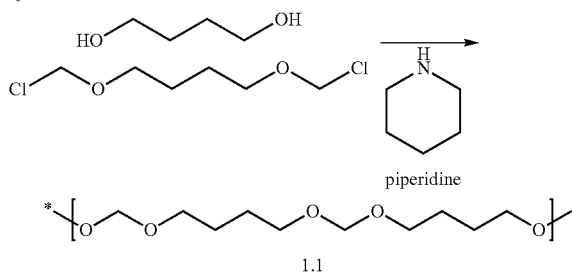
EXAMPLES

Example 1

Synthesis of Representative Polymers

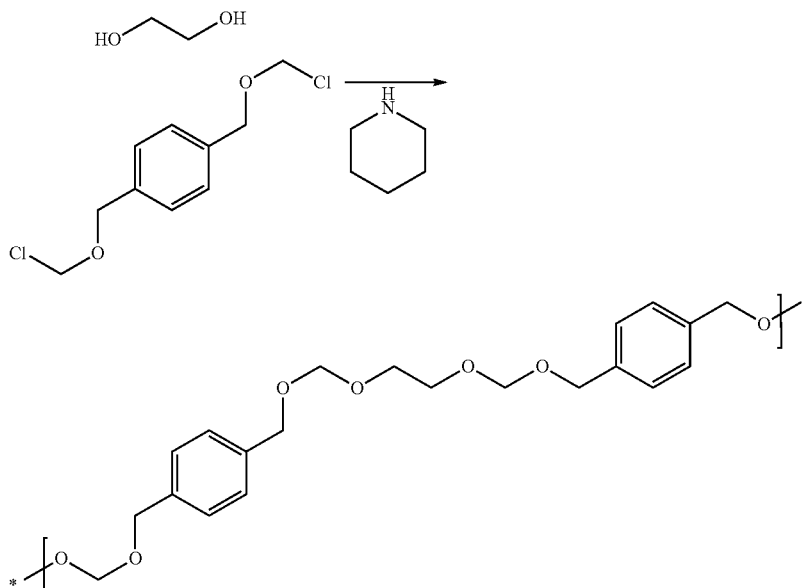
[0065] Polymer 1.1:

[0066] Butane-1,4-diol (1 mmol) and 1,4-bis(chloromethoxy)butane (1 mmol) are combined in DMF (10 mL) with piperidine (2.5 mmol) and stirred 1 hour at 60° C. Polymer 1.1 precipitates from solution and is washed with dilute aqueous HCl (0.1M), aqueous $NaHCO_3$, and water. Polymer 1.1 is expected to be softer and more flexible than polymers 1.2 and 1.3, described below. The softness, hardness, and flexibility of these polymers can be measured according to protocols known in the art, such as ASTM D4145-10 *Standard Test Method for Coating Flexibility of Prepainted Sheet*, ASTM D1004-09 *Standard Test Method for Tear Resistance (Graves Tear) of Plastic Film and Sheeting*, and ASTM D3892-93 (2009) *Standard Practice for Packaging/Packing of Plastics*.



[0067] Polymer 1.2:

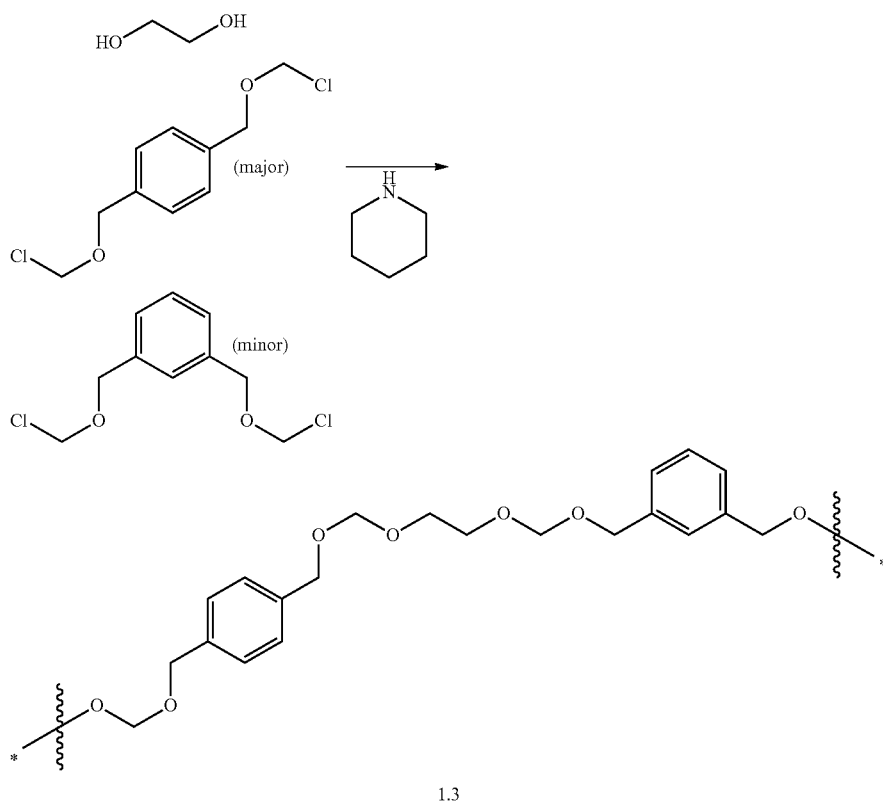
[0068] Ethane-1,2-diol (1 mmol) and 1,4-bis((chloromethoxy)methyl) benzene (1 mmol) are combined in DMF (10 mL) with piperidine (2.5 mmol) and stirred 1 hour at 60° C. Polymer 1.2 precipitates from solution and is washed with dilute aqueous HCl (0.1M), aqueous $NaHCO_3$, and water. Polymer 1.2 is expected to be harder and more rigid than polymers 1.1 and 1.3.



[0069] Polymer 1.3:

[0070] Ethane-1,2-diol (1 mmol), 1,3-bis((chloromethoxy)methyl)benzene (0.1 mmol), and 1,4-bis((chloromethoxy)methyl)benzene (1 mmol) are combined in DMF (10 mL) with piperidine (2.5 mmol) and stirred 1 hour at 60° C. Polymer 1.3 precipitates from solution and is washed with dilute aqueous HCl (0.1M), aqueous NaHCO₃, and water. Polymer 1.3 is expected to be harder and more rigid than polymers 1.1 but softer and more flexible than polymer 1.2.

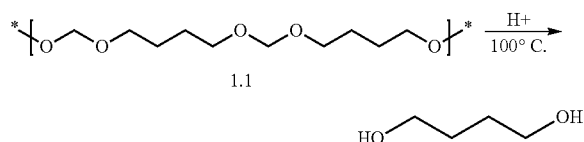
[0071] Synthetic methods substantially similar to those shown above can be used to make any of the polymers described herein.



Example 2

Degradation of Representative Polymers

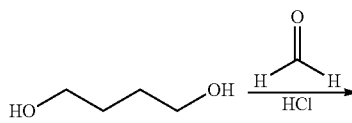
[0072] Polymer 1.1 is treated with CH₂Cl₂ and gaseous HCl and stirred 3 hours. The reaction mixture is concentrated and the crude butane-1,4-diol can be used directly in example 3 without further treatment or purification.



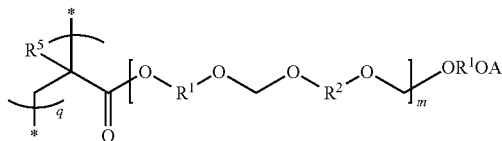
Example 3

Recycling of Representative Polymers

[0073] Polymer 1.1 is “recycled” by bubbling HCl gas into a mixture of crude butane-1,4-diol (1 mmol) and formaldehyde (2.5 mmol). The crude 1,4-bis(chloromethoxy)butane can be modified as shown in Example 1 to yield polymer 1.1.



10. A polymer represented by Formula IV:



wherein:

- A is hydrogen, alkyl, or $-\text{C}(\text{O})\text{R}^4$;
- R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene;
- R^4 is hydrogen, alkyl, or phenyl;
- R^5 is hydrogen, CN, alkyl, or phenyl;
- the polymer has a weight average molecular weight of about 500 g/mol to about 2,000,000 g/mol;
- m is 1 to 1000; and
- q is 1 to 1000.

11. The polymer of claim 10, wherein:

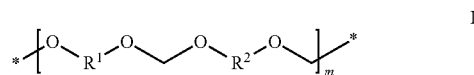
- R^1 is $(\text{CH}_2)_2$; $(\text{CH}_2)_4$; $(\text{CH}_2)_6$; or $(\text{CH}_2)_8$; and
- R^2 is a mixture of at least two of p-xylenyl, m-xylenyl, and o-xylenyl.

12. The polymer of claim 10, wherein m is 1 to 50.

13. The polymer of claim 10, wherein q is 1 to 50.

14. A method of degrading a polymer, the method comprising:

providing a polymer comprising a linker represented by Formula I;
 contacting the polymer with an acid; and
 obtaining a composition including HOR^1OH and HOR^2OH ;
 wherein:



- R^1 and R^2 are, independently, alkylene, alkenylene, arylene, heteroarylene, or alkylarylalkylene; and
- m is 1 to 1000.

15. The method of claim 14, further comprising converting the composition including HOR^1OH and HOR^2OH to a recycled polymer comprising the linker represented by Formula I.

16. The method of claim 14, wherein the acid is selected from the group consisting of HCl, HBr, H_2SO_4 , acetic acid, trifluoroacetic acid, phosphoric acid, and nitric acid.

17. The method of claim 14, wherein the contacting further comprises contacting at a temperature of from about 20°C . to about 120°C .

18. The method of claim 14, wherein the providing the polymer includes the linker having a value of m from about 1 to about 50, inclusive.

* * * * *