GLYCEROL ETHER POLYMERS

FIELD OF THE INVENTION

The present invention relates to polymers made from glycerol ethers such as glycerol monoethers and glycerol diethers.

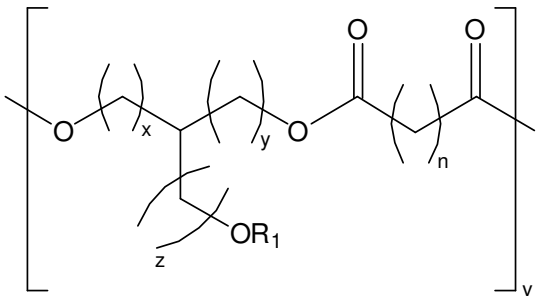
BACKGROUND OF THE INVENTION

Bottlebrush polymers (BBPs) are a special class of polymers with relatively short pendant chains attached onto a polymer backbone. The development of novel bottlebrush polymers made from polyesters is of high interest as they could be sustainable alternatives to traditional petroleum-based polymers. Currently, BBPs have found suitable use as material platforms for ultrasoft interfaces, sensing, lubricants and delivery applications due to their unique entanglement-free rheology. However, currently most existing BBPs do not exhibit entanglement-free rheology at the low temperature range. Moreover, the currently existing polyester based BBPs are highly crosslinked polymers that do not readily allow for finetuning of the thermomechanical and viscoelastic properties. In addition, known polyester BBPs are generally hydrophilic in nature, and does not allow precise finetuning of the hydrophobicity/hydrophilicity ratio. Moreover, conventional polyester BBPs are prone to transesterification, limiting their applications.

There is therefore a pressing need to develop a polymer, that overcomes or at least ameliorates, one or more of the disadvantages described above.

SUMMARY

In an aspect, there is provided a polymer having the following general structure (I):



(I),

wherein

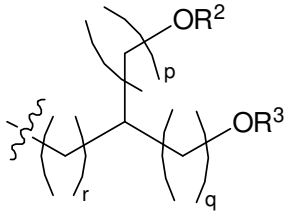
x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24;

v is an integer of 1 to 2000; and

R^1 is H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl;

or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer or 1 to 5;

R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and ~~~ is where the substituent of general structure (II) attaches to the polymer of general structure (I).

Advantageously, monoglyceryl ethers (MGEs) or diglyceryl ethers (DGEs), that have an aliphatic chain attached onto a glycerol backbone via an ether linkage, may be suitable bio-based monomers for the synthesis of highly tunable polyester polymers, such as bottle brush polymers (BBPs).

Advantageously, the polymer may comprise various aliphatic chains in various parts of the polymer, and increasing the chain length within the repetitive unit of aliphatic polyesters may facilitate tuning of the thermo-mechanical properties of the BBPs towards the softer and elastomeric end of the spectrum. In an example, the introduction of longer alkyl chains may increase the overall hydrophobicity of the polymer, and the presence of poly(ethylene glycol) side chains may effectively increase the overall hydrophobicity of the polymer. By virtue of the design of the polymer, dual functional groups may be introduced into the side chains of the polymer, allowing for versatile incorporation of various functionalities to the polymer. Further advantageously, ether groups on the pendant chain of BBPs may allow for greater thermostability of the polymer.

Further advantageously, unlike conventional BBPs which are highly crosslinked and hydrophilic in nature, the hydrophobicity/hydrophilicity ratio and the viscoelastic nature of the polymers of the present disclosure may be easily fine-tuned to prepare softer elastomeric polymers.

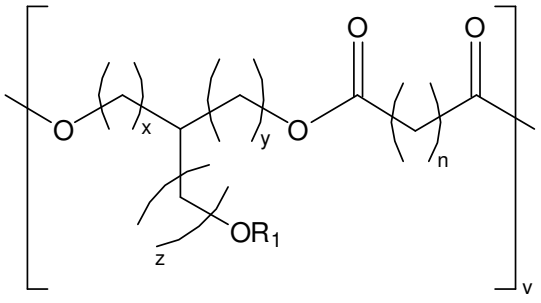
In view of the above, the BBPs as disclosed herein may advantageously have an enhanced chemical stability. The enhanced chemical stability may ensure that the BBPs form well-defined structures that are not prone to transesterification.

Further advantageously, the polymers of the present disclosure may be biodegradable due to the biocompatibility and biodegradable nature of the constituent monomers. The polymers of the present disclosure may be degraded through enzymatic and hydrolytic degradation reactions while demonstrating proper physico-mechanical properties for a wide range of applications. Advantageously, the polymers of the present disclosure may have properties comparable to non-biodegradable commodity plastics such as

polypropylene or polyethylene, while being biodegradable and having significantly lower environmental impact.

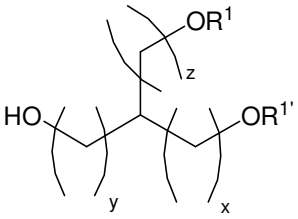
In another aspect, there is provided a foam, gel, thermoplastic or elastomer comprising the polymer as defined above.

In another aspect, there is provided a method for preparing a polymer having the following general structure (I):



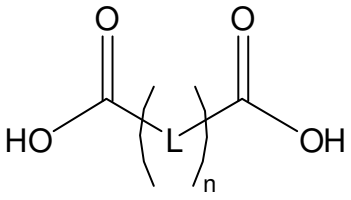
(I),

comprising the step of providing a glyceryl ether having the following general structure (III):

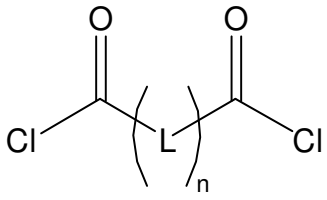


(III)

and contacting the glyceryl ether having general structure (III) with a dicarboxylic acid having the following general structure (IVa) or a diacyl chloride having the following structure (IVb):



(IVa),



(IVb)

wherein L is -CH_2- or aryl;

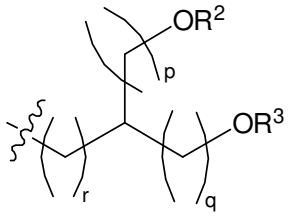
under polymer reaction conditions,

wherein

x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24; and

R^1 and $R^{1'}$ are each independently H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl; or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer from 1 to 5;

R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and

~~~ is where the substituent of general structure (II) attaches to the glyceryl ether of general structure (III),

wherein R^1 or $R^{1'}$ in the glyceryl ether having general structure (III) is H but R^1 and $R^{1'}$ are not both H.

The method as defined above may involve straightforward polycondensation reactions followed by a curing step, making the preparation of the polymer efficient. The method further allows for the synthesis of a large variety of BBPs and to fine-tune their properties by changing the alkyl chain length on the 1) monoglycerol ether/diglycerol ether (MGE/DGE), the 2) diacid and 3) the position of alkyl chain on MGE/DGE diol.

In another aspect, there is provided a use of the polymer as defined above or the foam, gel, thermoplastic or elastomer as defined above as a soft-tissue alternative, lubricant, surface coating, motion control grease, ultrasoft surfaces, in nanocapsules, in sensing and in delivery applications.

The polymers of the present disclosure may be suitable for use in biological systems, for example as soft tissue replacement alternatives, due to the biocompatibility and biodegradable nature of constituent monomers.

DEFINITIONS

The following words and terms used herein shall have the meaning indicated:

"Acyl" means an R-C(=O)- group in which the R group may be an optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted heterocycloalkyl, optionally substituted aryl or optionally substituted heteroaryl group as defined herein. Examples of acyl include acetyl, benzoyl and amino acid derived aminoacyl. The group may be a terminal group or a bridging group. If the group is a terminal group it is bonded to the remainder of the molecule through the carbonyl carbon.

"Alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, most preferably 2-10 carbon atoms, in the normal chain. The group
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may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

"Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C_1–C_{30} alkyl, more preferably a C_1-C_{20} alkyl, most preferably C_1-C_{10} unless otherwise noted. Examples of suitable straight and branched C_1-C_6 alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

"Alkynyl" as a group or part of a group means an aliphatic hydrocarbon group containing a carbon-carbon triple bond and which may be straight or branched preferably having from 2-30 carbon atoms, more preferably 2-20 carbon atoms, more preferably 2-19 carbon atoms in the normal chain. Exemplary structures include, but are not limited to, ethynyl and propynyl. The group may be a terminal group or a bridging group.

"Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C_{5-7} cycloalkyl or C_{5-7} cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C_6-C_{18} aryl group.

“Bio-based” in the context of this application means that the material is wholly or partly driven from materials of biological origin, such as plants, animals, enzymes, and microorganisms including bacteria, fungi and yeast.

The word “substantially” does not exclude “completely” e.g. a composition which is “substantially free” from Y may be completely free from Y. Where necessary, the word “substantially” may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from

1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

[Fig. 1]

Fig. 1 refers to a set of images showing: (a) a graphical representation of branched bottle brush polyesters formed from monoglycerol ethers with the pendant ether side chains (1002) and polyester backbone (1004). (a') a graphical representation of branched bottle brush polyesters formed from diglycerol ethers with the R_1 and R_2 pendant ether side chains (1006) and polyester backbone (1004), wherein R_1 and R_2 independently refer to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups. (b) a chemical scheme showing the synthesis of MGE. (c) a chemical scheme showing A2+B2 polymerisation of 1-O-MGE with a diacid. The R group is variable and allows large permutations of various polymers to be formed with different thermomechanical and viscoelastic properties. (d) a chemical scheme showing A2+B2 polymerisation of 2-O-MGE with a diacid. The R group is variable and allows large permutations of various polymers to be formed with different thermomechanical and viscoelastic properties. (e) a graphical representation of an MGE-based polyester with varied alkyl chain lengths in the backbone *n* and the chain *m*.

[Fig. 2]

Fig. 2 refers to a set of schemes showing the detailed synthesis of (a) 1-O-MGE, (b) 2-O-MGE, (c) 1,2-O-DGE 1',2' diol, (d) 1,3-O-DGE 1',2' diol and (e) 1,2-O-DGE 1',3' diol via Williamson ether synthesis and acid catalysed hydrolysis.

[Fig. 3]

Fig. 3 shows some schematic representations of the monomers prepared in the present disclosure showing monoglycerol ethers (MGE) (3002) and diglycerol ethers (DGE) (3004). R_1 and R_2 independently refer to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups.

[Fig. 4]

Fig. 4 is (a) a schematic representation of BBPs formed from monoglycerol ether monomers from commercially available solketal and 2-phenyl-1,3-dioxan-5-ol, in 3 steps. R independently refers to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups. (b) a schematic representation of BBPs formed from diglycerol ether monomers prepared in the present disclosure. R_1 and R_2 independently refers to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups.

[Fig. 5]

Fig. 5 shows some schematic representations of BBPs prepared in the present disclosure showing monoglycerol polyesters (6002) and diglycerol polyesters (6004). R, R_1 and R_2 independently refer to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups.

[Fig. 6]

Fig. 6 shows plots of reaction extent vs time and plots of M_n and Đ vs reaction extent for the *m*=9, 1-O-MGE/*n*=10, diacid/Sn (1/1/0.1), *m*=10, 1-O-MGE/*n*=10, diacid/Sn (1/1/0.1), *m*=11,1-O-MGE/*n*=10, diacid/Sn (1/1/0.1), *m*=12, 1-O-MGE/*n*=10, diacid/Sn (1/1/0.1), *m*=13, 1-O-MGE/*n*=10, diacid/Sn (1/1/0.1) *m*=14, 1-O-MGE/*n*=10, diacid/Sn (1/1/0.1) systems (Table 1 (entries 1-6). (a) Plots of reaction extent vs time, (b) Plots of *Mw*/*Mn* vs. extent of reaction p (%) and (c) *Mn* vs extent of reaction p (%) (bottom) for the 1-O-MGE/diacid/Sn (1/1/0.1) system (180°C) (Table 1, entry 3). The solvent was diphenyl ether (30 wt.%) for all systems. The symbols are as indicated in the figures.

[Fig. 7]

Fig. 7 is a set of ^{1}H NMR spectra of (a) 1-O MGE (*m* = 18) /diacid (*n*= 9) BBP and its starting materials; (b) 2-O MGE (*m* = 18) /diacid (*n*= 9) BBP and its starting materials; (c) 1-O MAG (*m* = 18) /diacid (*n*= 9) BBP and its starting materials ; (d) polymerization of monomer with branched chain; (e) polymerization of monomer with branched chain (zoomed in); (f) polymerization of 1-O-MGE diol with saturated side chain; (g) polymerization of 1-O-MGE diol with unsaturated side chain; (h) comparing 1-O-MGE, 1-O-MAG and 2-O-MGE monomers and polymers; (i) 1,2-O-DGE 1',2' diol (m=4)/diacid (n=10); and (j) 1,2-O-DGE 1',3' diol (m=4)/diacid (n=10).

[Fig. 8]

Fig. 8 is a graph showing the T_m values for 1-O-MGE BBPs with m = 9-14 and 18 and n = 10 (Table 2 (entries 1-6 and 16)).

[Fig. 9]

Fig. 9 is a set of graphs showing (a) the T_m values for ethylene glycol, 1-O-MGE BBPs with m = 12, 16 and 18 and *n* = 7-12, (b) the T_m values 2-O-MGE BBPs with m = 3 and n = 4-12, and (c) the T_m values 1-O-MGE BBPs with m = 16 and n = 4-14, 18 and 22.

[Fig. 10]

Fig. 10 is a schematic illustration of the arrangements of the MGE BBPs with (a) even and (b) odd number of carbons between the ester groups. The arrows indicate the direction of polarization.

[Fig. 11]

Fig. 11 is a set of diagrams showing the influence of the ester bond vs. ether bond. (a) shows the structure of 1-O-MGEBBP and 1-O-MAG BBP, (b) is a graph showing the T_m values for 1-O-MGE BBPs (circle) and 1-O-MAG BBPs (square) with m = 18 and n =7-12 (Table 2 (entries 13-18)), and (c) is a schematic diagram showing1-O-MGE BBP (side chain is ether bond) and 1-O-MAG BBP (side-chain is ester bond).

The arrows underneath each diagram indicate that different alkyl chain length MGEs and α,ω diacids lead to BBPs with variable thermomechanical and viscoelastic properties.

[Fig. 12]

Fig. 12 is a graph comparing the T_m values of 1-O-MGE BBPs (circle) and 2-O-MGE BBPs (square) with m = 18 and n =7-12 (Table 2 (entries 13-24)).

[Fig. 13]

Fig. 13 is a graph showing the influence of a double bond on the diacid, and compares the T_m values for 1-O-MGE BBPs (m = 16, n = 4) ,that are made from saturated diacids such as succinic acid and unsaturated diacids such as fumaric acid and itaconic acid. C16 diol succinic acid (square) showed the highest T_m at 42.7°C. The introduction of double bonds in C16 diol fumaric acid (circle) within the chain lead to a lower T_m at 34.2°C and the introduction of double bonds in C16 diol fumaric acid (circle) out of the chain lead to an even lower T_m at 27.7°C .

[Fig. 14]

Fig. 14 is a graph showing the TGA curves of (a) 1-O-MGE BBP with m =9-14, n = 10, and (b) 1-O-MGE BBP with m =18, n = 7-12.

[Fig. 15]

Fig. 15 is a set of TGA graphs that (a) compares the values for 1-O-MGE BBP and 1-O-MAG BBP, and (b) compares the values of 1-O-MGE BBP and 2-O-MGE BBP. Fig. 15a shows that the introduction of ester linkages (1-*O*-MAG BBPs) into the side chains of the BBPs typically lowers the T_m-at large m values compared to 1-*O*-MGE BBPs. Fig 15b shows that a 1-*O*-MGE BBP typically have higher T_m compared to 2-*O*-MGE BBPs.

[Fig. 16]

Fig. 16 is a schematic diagram showing gel permeation chromatograms indicating that MGE BBPs can undergo hydrolytic degradation to form MGE and *α,ω* diacids, then subsequently undergo polycondensation to reform MGE BBPs. (a) is the chromatogram of 1-O-MGE BBP (Mn =20291, D =1.32) being subjected to hydrolytic conditions (60% THF/40% NaOH (aq)), (b) is a chromatogram that shows that after 1 hour, the polyesters had efficiently degraded to form 1-O-MGE diol and diacid monomers, and (c) and (d) are chromatograms that show that polymers can be reformed under repolymerization with (c) Mn = 1521, D =2.11 after 6 hours and (d) Mn = 8089, D = 1.72 after 18 hours.

[Fig. 17]

Fig. 17 is a schematic diagram showing the scalability of preparing the 1-O-MGE monomer from epichlorohydrin in a 10 L reactor.

[Fig. 18]

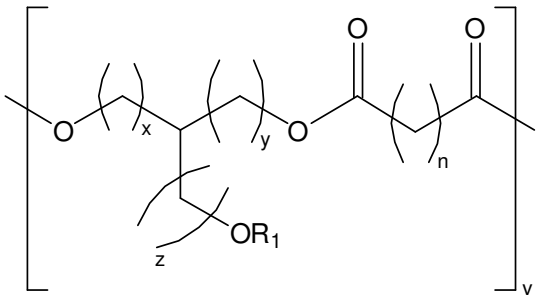
Fig. 18 shows a series of graphs showing the reaction monitoring of the formation of 1-O-MGE BBP from 1-O-MGE diol *m* =18 and *n* =12 diacid using ^{1}H NMR from t = 0 to t = 24 hours. Proton signals from species (a), (b), (c) and (d), were detected from ^{1}H NMR.

[Fig. 19]

Fig. 19 is a graph showing the ratio of species (A), (B), (C), (D) with respect to time. The A axis shows the time in minutes and the B axis shows the relative %.

DETAILED DESCRIPTION OF OPTIONAL EMBODIMENTS

There is provided a polymer having the following general structure (I):



(I),

wherein

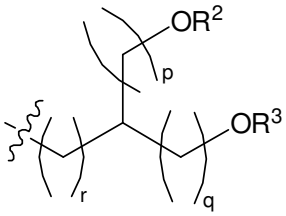
x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24;

v is an integer of 1 to 2000; and

R^1 is H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl;

or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer or 1 to 5;

R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and ~~~ is where the substituent of general structure (II) attaches to the polymer of general structure (I).

x, y and z may each independently be 0 or an integer of 1 to 5, or an integer of 1, 2, 3, 4 or 5. x may be 0 or 1. y may be 1. z may be 0 or 1.

n may be an integer of 1 to 24, 1 to 4, 1 to 8, 1 to 12, 1 to 16, 1 to 20, 4 to 8, 4 to 12, 4 to 16, 4 to 20, 4 to 24, 8 to 12, 8 to 16, 8 to 20, 8 to 24, 12 to 16, 12 to 20, 12 to 24, 16 to 20, 16 to 24 or 20 to 24.

v may be an integer of 1 to 2000, 1 to 100, 1 to 200, 1 to 500, 1 to 1000, 100 to 200, 100 to 500, 100 to 1000, 100 to 2000, 200 to 500, 200 to 1000, 200 to 2000, 500 to 1000, 500 to 2000 or 1000 to 2000.

R^1 may be H.

R^1 may be linear or branched C_1-C_{30} alkyl. The linear or branched C_1-C_{30} alkyl may comprise 1 to 30, 1 to 5, 1 to 10, 1 to 15, 1 to 20, 1 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

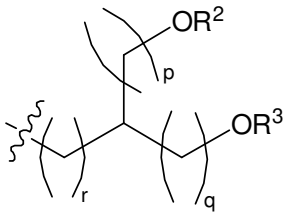
The linear or branched C_1-C_{30} alkyl may comprise n-propyl , n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl, n-octadecyl, n-tetraeicosyl and any combination thereof.

R^1 may be linear or branched C_2-C_{30} alkenyl. The linear or branched C_2-C_{30} alkenyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^1 may be linear or branched C_2-C_{30} alkynyl. The linear or branched C_2-C_{30} alkynyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^1 may be selected from the group consisting of 2-ethylhexyl, 3,7-dimethyloctan-1-yl, geranyl, neryl, citronellyl, phytyl, farnesyl, and any combination thereof. R^1 may comprise a monoterpene.

R^1 may be a substituent having the following general structure (II):



(II)

p, q and r may each independently be 0 or an integer or 1 to 5, or an integer of 1, 2, 3, 4 or 5. p may be 0 or 1. q may be 0 or 1. R may be 0 or 1.

R^2 and R^3 may each independently be H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

R^2 and R^3 may each independently be H.

R^2 and R^3 may each independently be linear or branched C_1-C_{30} alkyl. The linear or branched C_1-C_{30} alkyl may comprise 1 to 30, 1 to 5, 1 to 10, 1 to 15, 1 to 20, 1 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^2 and R^3 may each independently be linear or branched C_2-C_{30} alkenyl. The linear or branched C_2-C_{30} alkenyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^2 and R^3 may each independently be linear or branched C_2-C_{30} alkynyl. The linear or branched C_2-C_{30} alkynyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^2 and R^3 may independently be selected from the group consisting of 2-ethylhexyl, 3,7-dimethyloctan-1-yl, geranyl, neryl, citronellyl, phytyl, farnesyl, and any combination thereof. R^2 and R^3 may independently comprise a monoterpene.

 may be where the substituent of general structure (II) attaches to the polymer of general structure (I).

x may be 0 or 1, y may be 1, z may be 0 or 1, p may be 0 or 1, q may be 0 or 1, or r may be 0 or 1.

x may be 0 or 1, y may be 1, z may be 0 or 1, p may be 0 or 1, q may be 0 or 1, and r may be 0 or 1.

x may be 0, y may be 1, z may be 1 and R^1 may be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

x may be 1, y may be 1, z may be 0 and R^1 may be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

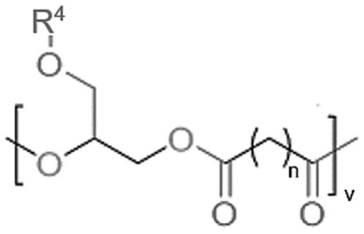
x may be 0, y may be 1, z may be 1, R^1 may be the substituent of general structure (II), r may be 0, p may be 1 and q may be 1.

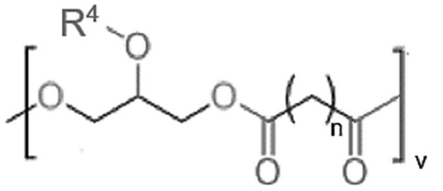
x may be 0, y may be 1, z may be 1, R^1 may be the substituent of general structure (II), r may be 1, p may be 1 and q may be 0.

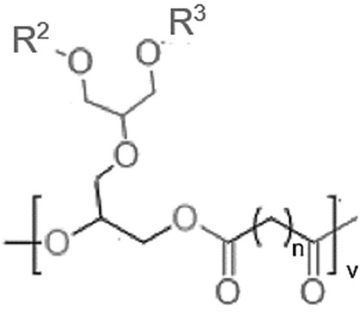
x may be 1, y may be 1, z may be 0, R^1 may be the substituent of general structure (II), r may be 1, p may be 1 and q may be 0.

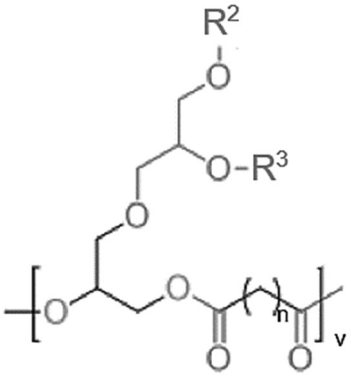
When x is 1, y is 1, and z is 0, R^1 may not be a linear or branched C_1-C_6 alkyl.

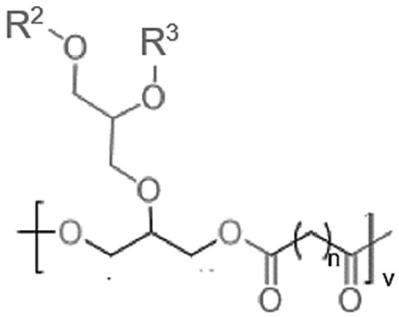
The polymer may have the following structure:

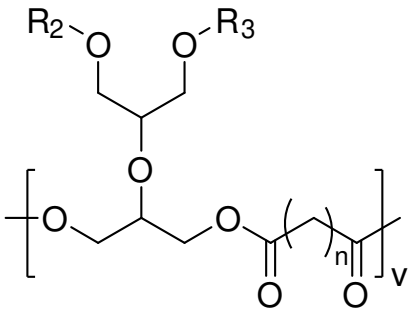


,


,


,




, or


,

wherein R^2, R^3 and R^4 may each independently be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

R^2 and R^3 may each independently be as defined above.

R^4 may be H.

R^4 may be linear or branched C_1-C_{30} alkyl. The linear or branched C_1-C_{30} alkyl may comprise 1 to 30, 1 to 5, 1 to 10, 1 to 15, 1 to 20, 1 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^4 may be linear or branched C_2-C_{30} alkenyl. The linear or branched C_2-C_{30} alkenyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^4 may be linear or branched C_2-C_{30} alkynyl. The linear or branched C_2-C_{30} alkynyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

R^4 may be selected from the group consisting of 2-ethylhexyl, 3,7-dimethyloctan-1-yl, geranyl, neryl, citronellyl, phytyl, farnesyl, and any combination thereof. R^4 may comprise a monoterpene.

The polymer may be a bottle brush polyester.

The bottle brush polyester may be a branched bottle brush polyester.

The polymer may be a biodegradable polymer.

The polymer may have a molecular weight in the range of about 7,000 to about 100,000, about 7,000 to about 8,000, about 7,000 to about 9,000, about 7,000 to about 10,000, about 7,000 to about 20,000, about 7,000 to about 50,000, about 8,000 to about 9,000, about 8,000 to about 10,000, about 8,000 to about 20,000, about 8,000 to about 50,000, about 8,000 to about 100,000, about 9,000 to about 10,000, about 9,000 to about 20,000, about 9,000 to about 50,000, about 9,000 to about 100,000, about 10,000 to about 20,000, about 10,000 to about 50,000, about 10,000 to about 100,1000, about 20,000 to about 50,000, about 20,000 to about 100,000 or about 50,000 to about 100,000

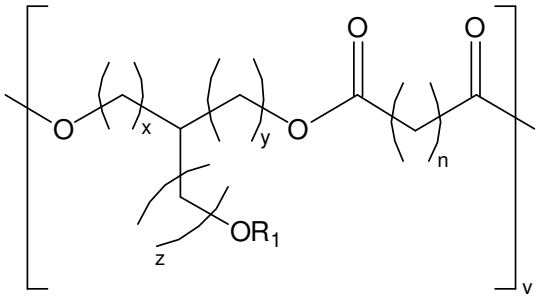
The polymer may have an intrinsic viscosity in the range of about 0.2 dL/g to about 2.5 dL/g, about 0.2 dL/g to about 0.5 dL/g, about 0.2 dL/g to about 1 dL/g, about 0.2 dL/g to about 1.5 dL/g, about 0.2 dL/g to about 2 dL/g, about 0.5 dL/g to about 1 dL/g, about 0.5 dL/g to about 1.5 dL/g, about 0.5 dL/g to about 2 dL/g, about 0.5 dL/g to about 2.5 dL/g, about 1 dL/g to about 1.5 dL/g, about 1 dL/g to about 2 dL/g, about 1 dL/g to about 2.5 dL/g, about 1.5 dL/g to about 2 dL/g, about 1.5 dL/g to about 2.5 dL/g, or about 2 dL/g to about 2.5 dL/g.

The polymer may have a melting temperature in the range of about -40 °C to about 100 °C, about -40 °C to about -20 °C, about -40 °C to about 0 °C, about -40 °C to about 20 °C, about -40 °C to about 40 °C, about – 40 °C to about 60 °C, about -40 °C to about 80 °C, about -20 °C to about 0 °C, about -20 °C to about 20 °C, about – 20 °C to about 40 °C, about -40 °C to about 60 °C, about – 40 °C to about 80 °C, about -40 °C to about 100 °C, about 0 °C to about 20 °C, about 0 °C to about 40 °C, about 0 °C to about 60 °C, about 0 °C to about 80 °C, about 0 °C to about 100 °C, about 20 °C to about 40 °C, about 20 °C to about 60 °C, about 20 °C to about 80 °C, about 20 °C to about 100 °C, about 40 °C to about 60 °C, about 40 °C to about 80 °C, about 40 °C to about 100 °C, about 60 °C to about 80 °C, about 60 °C to about 100 °C or about 80 °C to about 100 °C.

The polymer may have a degradation temperature of above 300 °C. The polymer may have a degradation temperature in the range of about 300 °C to about 500 °C, about 300 °C to about 350 °C, about 300 °C to about 400 °C, about 300 °C to about 450 °C, about 350 °C to about 400 °C, about 350 °C to about 450 °C, about 350 °C to about 500 °C, about 400 °C to about 450 °C, about 400 °C to about 500 °C or about 450 °C to about 500 °C.

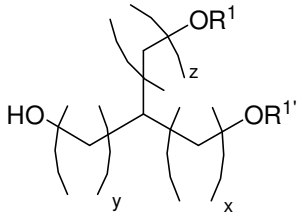
There is also provided a foam, gel, thermoplastic or elastomer comprising the polymer as defined above.

There is also provided a method for preparing a polymer having the following general structure (I):



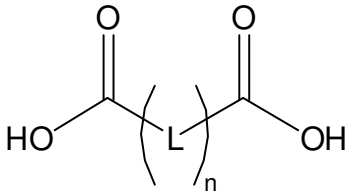
(I),

comprising the step of providing a glyceryl ether having the following general structure (III):

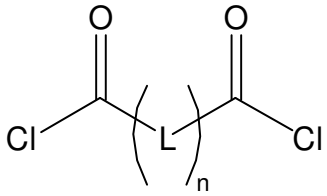


(III)

and contacting the glyceryl ether having general structure (III) with a dicarboxylic acid having the following general structure (IVa) or a diacyl chloride having the following structure (IVb):



(IVa),



(IVb)

wherein L is -CH_2- or aryl;

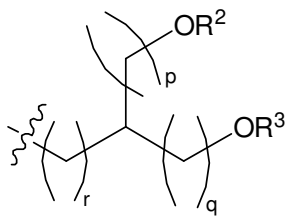
under polymer reaction conditions,

wherein

x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24; and

R^1 and $R^{1'}$ are each independently H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl; or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer from 1 to 5;

R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and

~~~ is where the substituent of general structure (II) attaches to the glyceryl ether of general structure (III),

wherein R^1 or $R^{1'}$ in the glyceryl ether having general structure (III) is H but R^1 and $R^{1'}$ are not both H.

R^1, R^2, R^3, x, y, z, n, p, q, r may be as defined above.

L may be -CH_2- or aryl. The aryl may be furanyl, phenyl, naphthyl or any combination thereof.

$R^{1'}$ may be H.

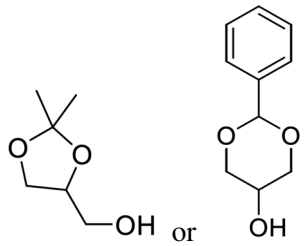
$R^{1'}$ may be linear or branched C_1-C_{30} alkyl. The linear or branched C_1-C_{30} alkyl may comprise 1 to 30, 1 to 5, 1 to 10, 1 to 15, 1 to 20, 1 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

$R^{1'}$ may be linear or branched C_2-C_{30} alkenyl. The linear or branched C_2-C_{30} alkenyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

$R^{1'}$ may be linear or branched C_2-C_{30} alkynyl. The linear or branched C_2-C_{30} alkynyl may comprise 2 to 30, 2 to 5, 2 to 10, 2 to 15, 2 to 20, 2 to 25, 5 to 10, 5 to 15, 5 to 20, 5 to 25, 5 to 30, 10 to 15, 10 to 20, 10 to 25, 10 to 30, 15 to 20, 15 to 25, 15 to 30, 20 to 25, 20 to 30 or 25 to 30 carbon atoms.

$R^{1'}$ may be selected from the group consisting of 2-ethylhexyl, 3,7-dimethyloctan-1-yl, geranyl, neryl, citronellyl, phytyl, farnesyl, and any combination thereof. $R^{1'}$ may comprise a monoterpene.

The providing step may comprise reacting a compound of the following structure:

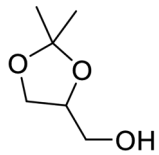


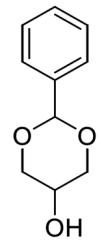
with a linear or branched C_1-C_{30} alkyl halide, linear or branched C_2-C_{30} alkenyl halide, or linear or branched C_2-C_{30} alkynyl halide, under glyceryl ether reaction conditions.

The halide may be a bromide, chloride, iodide or fluoride.
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The alkyl halide may be alkyl bromide, alkyl chloride, alkyl iodide or alkyl fluoride. The alkyl halide may be alkyl bromide.

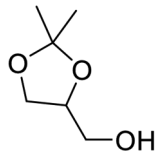
The glyceryl ether reaction condition may comprise Williamson Ether Synthesis, comprising contacting the compound of the following structure:

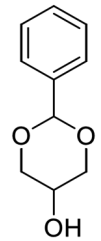


or


with an alkali metal or an alkali metal hydride at a temperature in the range of -4 °C to 4 °C in a solvent, adding the linear or branched C_1-C_{30} alkyl halide, linear or branched C_2-C_{30} alkenyl halide, or linear or branched C_2-C_{30} alkynyl halide to form a mixture and stirring the mixture at a temperature in the range of 60 °C to 80 °C for a duration in the range of 3 hours to 24 hours.

The compound of the following structure:



or


may be contacted with an alkali metal or an alkali metal hydride at a temperature in the range of about -4 °C to about 4 °C, about -4 °C to about -2 °C, about -4 °C to about 0 °C, about -4 °C to about 2 °C, about -2 °C to about 0 °C, about -2 °C to about 2 °C, about -2 °C to about 4 °C, about 0 °C to about 2 °C, about 0 °C to about 4 °C, or about 2 °C to about 4 °C.

The alkali metal may be sodium metal.

The alkali metal hydride may be NaH or KH.

The solvent may be toluene, tetrahydrofuran, acetonitrile, N,N-dimethylformamide, diethyl ether, or a polar aprotic solvent such as dimethylsulfoxide (DMSO).

The mixture may be stirred at a temperature in the range of about 60 °C to about 80 °C, about 60 °C to about 70 °C, or about 70 °C to about 80 °C.

The mixture may be stirred for a duration in the range of about 3 hours to about 24 hours, about 3 hours to about 9 hours, about 3 hours to about 15 hours, about 3 hours to about 21 hours, about 9 hours to about 15 hours, about 9 hours to about 21 hours, about 9 hours to about 24 hours, about 15 hours to about 21 hours, about 15 hours to about 24 hours or about 21 hours to about 24 hours.

The contacting step of the Williamson Ether Synthesis may be followed by acidification, wherein the acidification step may be performed in a solvent comprising 1M aqueous HCl and ethanol at a volume ratio

in the range of about 5:1 to about 2:1, about 5:1 to about 4:1, about 5:1 to about 3:1, about 4:1 to about 3:1, about 4:1 to about 2:1, or about 3:1 to about 2:1.

R^1 or $R^{1'}$ in the glyceryl ether having general structure (III) may be H but R^1 and $R^{1'}$ may not both be H.

x may be 0, y may be 1, z may be 1, R^1 may be linear or branched C_1-C_{30} alkyl and $R^{1'}$ may be H.

x may be 0, y may be 1, z may be 1, $R^{1'}$ may be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl and R^1 may be H.

x may be 1, y may be 1, z may be 0, R^1 may be linear or branched C_1-C_{30} alkyl and $R^{1'}$ may be H.

x may be 1, y may be 1, z may be 0, $R^{1'}$ may be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl and R^1 may be H.

x may be 0, y may be 1, z may be 1, R^1 may be the substituent of general structure (II), r may be 0, p may be 1, q may be 1 and $R^{1'}$ may be H.

x may be 0, y may be 1, z may be 1, $R^{1'}$ may be the substituent of general structure (II), r may be 0, p may be 1, q may be 1 and R^1 may be H.

x may be 0, y may be 1, z may be 1, R^1 may be the substituent of general structure (II), r may be 1, p may be 1, q may be 0 and $R^{1'}$ may be H.

x may be 0, y may be 1, z may be 1, $R^{1'}$ may be the substituent of general structure (II), r may be 1, p may be 1, q may be 0 and R^1 may be H.

x may be 1, y may be 1, z may be 0, R^1 may be the substituent of general structure (II), r may be 1, p may be 1, q may be 0 and $R^{1'}$ may be H.

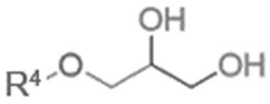
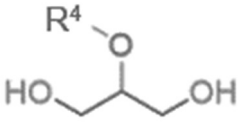
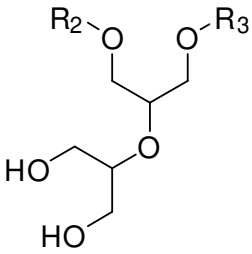
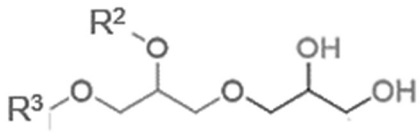
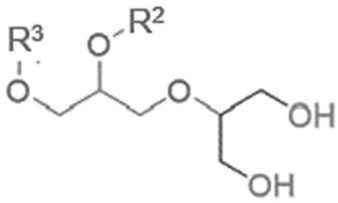
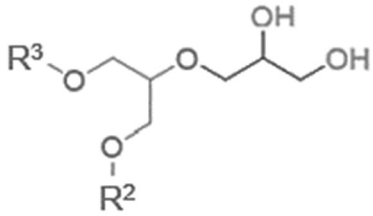
x may be 1, y may be 1, z may be 0, $R^{1'}$ may be the substituent of general structure (II), r may be 1, p may be 1, q may be 0 and R^1 may be H.

x may be 0, y may be 1, z may be 1, R^1 may be the substituent of general structure (II), r may be 0, p may be 1, q may be 1 and $R^{1'}$ may be H.

x may be 0, y may be 1, z may be 1, $R^{1'}$ is the substituent of general structure (II), r may be 0, p may be 1, q may be 1 and R^1 may be H.

When x is 1, y is 1, and z is 0, R^1 may not be a linear or branched C_1-C_6 alkyl and $R^{1'}$ may be H.

The glyceryl ether having general structure (III) may have the following structure:


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,

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or

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wherein R^2, R^3 and R^4 may each independently be linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

R^2, R^3 and R^4 may be as defined above.

The dicarboxylic acid having general structure (IVa) may be selected from the group consisting of 1,3-propanedioic acid, 1,4-butanedioic acid, 1,5-pentanedioic acid, 1,6-hexanedioic acid, 1,7-heptanedioic acid, 1,8-octanedioic, 1,9-nonanedioic acid, 1,10-decanedioic acid, 1,11-undecanedioic acid, 1,12-dodecanedioic acid, 1,13-tridecanedioic acid, 1,14-tetradecanedioic acid, 1,15-pentadecanedioic acid, 1,16-hexadecanedioic acid, 1,17-heptadecanedioic acid, 1,18-octadecanedioic acid, 1,19-nonadecanedioic acid, 1,20-icosanedioic acid, 1,21-heneicosanedioic acid, 1,22-docosanedioic acid, 1,23-tricosanedioic acid, 1,24-tetracosanedioic acid, furan-2,5-dicarboxylic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid and any mixture thereof.

The diacyl chloride having general structure (IVb) may be selected from the group consisting of 1,3-propanedioyl dichloride, 1,4-butanedioyl dichloride, 1,5-pentanedioyl dichloride, 1,6-hexanedioyl dichloride, 1,7-heptanedioyl dichloride, 1,8-octanedioyl dichloride, 1,9-nonanedioyl dichloride, 1,10-decanedioyl dichloride, 1,11-undecanedioyl dichloride, 1,12-dodecanedioyl dichloride, 1,13-tridecanedioyl dichloride, 1,14-tetradecanedioyl dichloride, 1,15-pentadecanedioyl dichloride, 1,16-hexadecanedioyl dichloride, 1,17-heptadecanedioyl dichloride, 1,18-octadecanedioyl dichloride, 1,19-nonadecanedioyl dichloride, 1,20-icosanedioyl dichloride, 1,21-heneicosanedioyl dichloride, 1,22-docosanedioyl dichloride, 1,23-tricosanedioyl dichloride, 1,24-tetracosanedioyl dichloride, furan-2,5-dicarbonyl dichloride, terephthaloyl chloride, naphthalene-2,6-dicarbonyl dichloride and any mixture thereof.

The polymer reaction conditions may be any condition that may allow the glyceryl ether having general structure (III) to react with the dicarboxylic acid having general structure (IVa) or diacyl chloride having general structure (IVb).

The glyceryl ether having general structure (III) may be contacted with the dicarboxylic acid having general structure (IVa) or diacyl chloride having general structure (IVb) at a molar ratio in the range of about 3:1 to about 1:2, about 3:1 to about 2:1, about 3:1 to about 1:1, about 2:1 to about 1:1, about 2:1 to about 1:2 or about 1:1 to about 2:1.

The contacting step of the polymer reaction conditions may comprise a first heating step performed at a temperature in the range of about 150 °C to about 220 °C, about 150 °C to about 170 °C, about 150 °C to about 200 °C, about 170 °C to about 200 °C, about 170 °C to about 220 °C, or about 200 °C to about 220 °C.

The contacting step of the polymer reaction conditions may comprise a first heating step performed under an inert atmosphere. The inert atmosphere may consist of nitrogen gas, argon gas, and any mixture thereof.

The first heating step may further comprises a catalyst.

The catalyst may be selected from a group consisting of chromium, manganese, iron, cobalt, nickel, copper, zinc, tin, p-toluene sulfonic acid monohydrate and any mixture thereof.

The catalyst may comprise tin. The catalyst may be elemental tin.

The molar ratio of the catalyst to the glyceryl ether having general structure (III) may be in the range of about 1:8 to about 1:100, about 1:8 to about 1:10, about 1:8 to about 1:20, about 1:8 to about 1:50, about 1:10 to about 1:20, about 1:10 to about 1:50, about 1:10 to about 1:100, about 1:20 to about 1:50, about 1:20 to about 1:100 or about 1:50 to about 1:100.

The contacting step of the polymer reaction conditions may further comprise a second heating step performed at a temperature in the range of about 150 °C to about 250 °C, about 150 °C to about 170 °C, about 150 °C to about 200 °C, about 150 °C to about 220 °C, about 170 °C to about 200 °C, about 170 °C to about 220 °C, about 170 °C to about 250 °C, about 200 °C to about 220 °C, about 200 °C to about 250 °C or about 220 °C to about 250 °C.

The contacting step of the polymer reaction conditions may further comprises a second heating step performed for a duration in the range of about 12 hours to about 36 hours, about 12 hours to about 18 hours, about 12 hours to about 24 hours, about 12 hours to about 30 hours, about 18 hours to about 24 hours, about 18 hours to about 30 hours, about 18 hours to about 36 hours, about 24 hours to about 30 hours, about 24 hours to about 36 hours or about 30 hours to about 36 hours.

The contacting step of the polymer reaction conditions may further comprises a second heating step performed under an inert atmosphere. The inert atmosphere may be as defined above.

There is also provided the use of the polymer as defined above or the foam, gel, thermoplastic or elastomer as defined above as a soft-tissue alternative, lubricant, surface coating, motion control grease, ultrasoft surfaces, in nanocapsules, in sensing and in delivery applications.

In an example, ultra soft surfaces may be surfaces with ultra-soft conformability and low outgassing. They may be used to provide an effective thermal interface between heat sinks and electronic devices. They may be used on uneven surfaces, air gaps or rough surface textures and may help to provide superior thermal

performance and long-term stability as compared to conventional thermal pads. Commonly they may be used for telecommunications equipment, PC boards, chassis applications, thermally enhanced Ball Grid Arrays (BGAs), memory modules, graphics processing unit (GPU)/central processing unit (CPU) applications and a host of other industrial devices. Typically, increasing the alkyl chain length of the backbone of the polyesters may increase the flexibility of the polyester chains. This may causes the polymer to become softer.

In another example, the delivery application may refer to the delivery of molecular cargo. Polyester BBPs may have distinct hydrophilic/hydrophobic ratios and may exhibit various shape-changing behaviors depending on the type of solvents they are present in. This may allow the entrapment of molecular cargo and its subsequent site-activated release under suitable conditions.

EXAMPLES

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Monoglycerol ethers (MGEs) that have an aliphatic chain attached onto a glycerol backbone via an ether linkage, may exist as diols and may have variable alkyl chain lengths. MGEs may be broadly classified as 1-*O*-monoglyceryl ether (1-O-MGE) or 2-*O*-monoglyceryl ether (2-O-MGE) depending on whether the alkyl chain is present on the *sn-1* or *sn-2* position. 1-O-MGE and 2-O-MGE may be obtained via Williamson ether synthesis of commercially available alkyl bromides together with solketal and 2-phenyl-1,3-dioxan-5-ol, respectively, followed by an acidification step (Fig. 1b).

In nature, hyperthermophilic archea have membranes with increased thermal stability due to the ether linkage as compared to the ester linked membranes of nonthermophilic eukaryotes and bacteria. Though it might seem like a small difference based on chemical structure, replacing ester groups with ether groups on the pendant chain of BBPs have demonstrated greater thermostability as compared to its fatty acyl counterparts.

In the present disclosure, a series of 1-O-MGE and 2-O-MGE diols with varied alkyl chain lengths (number of carbon (*m)* = 3, 8–14, 16 and 18 in the etheric R group (Fig. 1b) were prepared. These were combined with a series of commercially available diacids with various alkyl chain lengths (number of carbon (*n)* = 7-16, 18 and 22.and a range of MGE-based BBPs that have polyester backbones and pendant ether chains (branches) with varied *m* and *n* values and different ether positions in MGE (1- or 2-positions) were synthesized (Fig. 1a, Fig. 1c, Fig. 1d an Fig. 1e) for seeking large diversities of MGE-based BBPs with varied polymer properties.

The synthesised MGE-based polyester-backbone BBPs were characterised, and the thermal, mechanical, and hydrolytic degradation properties were investigated. The BBPs generally had a molecular weight of more than 10,000, melting points between -20°C to 40°C and degradation temperatures above 350°C, making them suitable lubricants for low temperature applications. The polymers could be broken down under physiological environments through macromolecular cleavage reactions into shorter chains, which ultimately formed non-toxic by-products.

The synthesised DGE-based polyester-backbone BBPs were characterised, and the thermal properties were investigated. The BBPs generally had a molecular weight of more than 6000. The DGE diols differ from the MGE diols with an additional glycerol moiety. The introduction of an additional glycerol moiety typically increased the hydrophilicity of the DGE BBP polymers. DGE BBP polymers offered synthetic advantages of dual tunability across its dual aliphatic arms whereby R^2 and R^3 could be attached from different glycidyl ethers and alkyl bromides. The polymers could be broken down under physiological environments through macromolecular cleavage reactions into shorter chains, which ultimately formed non-toxic by-products.

Hyperbranched polyethers (not polyesters) with ether-linked branch chains have been previously reported. However, there are currently no reports on the synthesis of polyesters using 1-O-MGE and 2-O-MGE or other diglycerol ethers (DGEs) as monomers.

Materials

All the chemicals used were either synthesised or commercially available. Silica gel column chromatography was performed with 230-400 nm mesh, from Merck (Rahway, New Jersey, USA), Alkyl bromides (97% - 99%, Sigma Aldrich (St. Louis, Minnesota, USA)), Glycidyl ethers (97% - 99%, Sigma Aldrich (St. Louis, Minnesota, USA)), C_4 Diacid Succinic Acid (99%, Sigma Aldrich (St. Louis, Minnesota, USA)), C_5 Diacid Glutaric Acid (99%, Sigma Aldrich (St. Louis, Minnesota, USA)), C_6 Diacid adipic acid (99%, Sigma Aldrich (St. Louis, Minnesota, USA)), C_7 Diacid pimelic acid (98%, Sigma Aldrich (St. Louis, Minnesota, USA)), C_8 Diacid subaric acid (98% Sigma Aldrich (St. Louis, Minnesota, USA)), C_9 Diacid azelaic acid (98% Sigma Aldrich (St. Louis, Minnesota, USA)), C_{10} Diacid sebacic acid (99 %, Wilmar International (Singapore)), C_{11} Diacid undecanedioic acid (99% Sigma Aldrich (St. Louis, Minnesota, USA)), C_{12} Diacid dodecanedioc acid (99% Sigma Aldrich (St. Louis, Minnesota, USA)) α,ω-diacids with 10-16 carbon atoms (99 %, Wilmar International (Singapore)), high density polyethylene (HDPE, Sinopec Qilu Petrochem.Co. (Shandong, China)), poly(butylene adipate-co-terephthalate) (PBAT, Yifan Pharm. Co. (Hangzhou, Zhejiang, China) and chloroform (AR grade, Sinopharm Chem. Reagent Co. (Shanghai, China)) were all used as received.

Methods

Characterization

^{1}H NMR spectra were recorded with a JEOL ECA400 UltraShield 400MHz (Tokyo, Japan). $CDCl_3$ was used as solvent and tetramethylsilane as internal reference. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane (TMS δ = 0.00 ppm). ^{13}C NMR were recorded with a JEOL ECA400 UltraShield 70 MHz (Tokyo, Japan). $CDCl_3$ was used as solvent and tetramethylsilane as internal reference. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane. (TMS δ = 0.00 ppm).

The GPC analysis was performed on a Shodex GPC-101 liquid chromatograph (Tokyo, Japan) equipped with a Shodex KD-806M mixed gel column (300 × 8.0 mm; particle size = 10 μm) (THF). The eluent was THF at a flow rate of 0.6 mL/min (40 °C). Sample detection was conducted using a Shodex differential refractometer RI-101. The column system was calibrated with standard poly(methyl methacrylate)s and polystyrenes.

The thermal analysis of the cocrystals was performed with QSeries differential scanning calorimetry (DSC) Q50 and thermal gravimetric analysis (TGA) Q500 (TA instrument, New Castle, US). The DSC analysis was conducted using an aluminum sample pan under flowing nitrogen at a flow rate of 50 mL/min. The samples were cooled down to -80 °C and heated up to 70-100 °C (depending on the samples) with a heating rate of 10 °C/min. The TGA analysis was carried out in platinum pans under flowing air at a flow rate of 60 mL/min with a heating rate of 10 °C/min at a temperature range of 26-600 °C.

Thermal transition behavior were recorded with differential scanning calorimetry (DSC, Q200, TA Instrument (New Castle, Delaware, USA)) under nitrogen flow. Approximately 8-10 mg of sample was tested under a standard heat-cool-heat cycle, both heating and cooling rates were 10°C/min.

Thermogravimetric (TG) measurements were carried out under nitrogen atmosphere by a thermal analyzer (TGA, Q500, TA Instrument (New Castle, Delaware, USA)) from 30 °C to 550 °C with a heating rate of 10 °C/min.

Synthesis of 1-O-MGE

As shown in Fig. 2a, to a stirred solution of solketal (1a, 5g, 0.0378 mol) (1 equiv.) in anhydrous toluene, was added at 0°C, NaH (60% dispersion in mineral oil, 3.02 g, 0.0756 mol (2 equiv.) for 30 minutes. Alkyl bromide (0.0378 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 6 to 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of solketal was observed. Upon completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride solution, toluene was removed in vacuo and crude reaction mass extracted with ethyl acetate (2 x 20 ml) and washed with deionized water (1 x 20 ml). The organic layer was removed in vacuo and the resulting intermediate (2a) was acidified to form (3a). Generally, purification was performed by flash column chromatography for C_3, C_8, C_9 1-O-MGE and vacuum distillation or recrystallization for C_{10} to C_{14}, C_{16} and C_{18} 1-O-MGE. Typical yields were 60 to 80 mol%.

Synthesis of 2-O-MGE

As shown in Fig. 2b, to a stirred solution of 2-phenyl-1,3-dioxan-5-ol (1b, 5g, 0.0278mol) (1 equiv.) in anhydrous toluene, was added at 0°C, NaH (60% dispersion in mineral oil, 2.22g, 0.0556 mol (2 equiv.) for 30 minutes. Alkyl bromide (0.0278 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 6 to 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of 2-phenyl-1,3-dioxan-5-ol was observed. Upon completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride solution, toluene was removed in vacuo and crude reaction mass extracted with ethyl acetate (2 x 20 ml) and washed with deionized water (1 x 20 ml). The organic layer was removed in vacuo and the resulting intermediate (2b) was acidified to form (3b). Generally, purification was performed by flash column chromatography for C_3, C_8, C_9 2-O-MGE and vacuum distillation or recrystallization for C_{10} to C_{14}, C_{16} and C_{18} 2-O-MGE. Typical yields were 60 to 80 mol%.

Synthesis of 1-O-MGE BBPs

To a mixture of 1-O-MGE diol (1 equiv.) and diacid (1 equiv.), was added tin powder (catalyst) (0.1 equiv.). The reaction mixture was heated at 180 °C for 24 hours with magnetic stirring. The monomers melted at

the studied temperatures of 180 °C, and the polymerization was melt polycondensation. The tin powder (approximately 150 μm diameter) was not fully dissolved in the reaction mixture, and the surfaces of the powder particles would catalyze the esterification (polymerization). The reactor was not capped with a stopcock, and the water generated during the polymerization was evaporated from the reaction mixture at the polymerization temperature of 180 °C so that the equilibrium of the esterification was shifted from the reactants (alcohols and carboxylic acids) to the product (esters). The reaction extent was determined from the consumption of CH proton of glycerol backbone using ^{1}H NMR. M_n and $Đ$ values were PMMA-calibrated gel permeation chromatography (GPC) values, where PMMA is poly(methyl methacrylate). The DP value was calculated from the M_n value of the polymer and the molecular weights of the diol and diacid. The M_n value was not an absolute value but a PMMA-calibrated value, and hence the DP value was viewed as an estimate. For 1-O-MGEs, relatively high molecular weight polymer (M_n > 10,000) with a relatively high reaction extent (>90%) was achieved after 24 hours of stirring.

Synthesis of 2-O-MGE BBPs

To a mixture of 2-O-MGE diol (1 equiv.) and diacid (1 equiv.), was added tin powder (catalyst) (0.1 equiv.). The reaction mixture was heated at 180 °C for 24 hours with magnetic stirring. The monomers melted at the studied temperatures of 180 °C, and the polymerization was melt polycondensation. The tin powder (approximately 150 μm diameter) was not fully dissolved in the reaction mixture, and the surfaces of the powder particles catalyzed the esterification (polymerization). The reactor was not capped with a stopcock, and the water generated during the polymerization was evaporated from the reaction mixture at the polymerization temperature of 180 °C so that the equilibrium of the esterification is shifted from the reactants (alcohols and carboxylic acids) to the product (esters). The reaction extent was determined from the consumption of CH group of glycerol backbone using ^{1}H NMR. M_n and $Đ$ values were PMMA-calibrated gel permeation chromatography (GPC) values, where PMMA is poly(methyl methacrylate). The DP value was calculated from the M_n value of the polymer and the molecular weights of the diol and diacid. The M_n value was not an absolute value but a PMMA-calibrated value, and hence the DP value was viewed as an estimate. For 2-O-MGEs, relatively high molecular weight polymer (M_n > 15,000) with a relatively high reaction extent (>95%) was achieved after 6 hours of stirring.

Synthesis of 1,2-O-DGE 1',2' diol

As shown in Fig. 2c, to a stirred solution of solketal (1a, 5g, 0.0378 mol) (1 equiv.) in anhydrous toluene, was added at 0°C, NaH (60% dispersion in mineral oil, 3.02g, 0.0756 mol (2 equiv.)) for 30 minutes. Glycidyl Ether (0.0378 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of solketal or glycidyl ether was observed. Upon completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride solution, toluene was removed in vacuo and crude reaction mass extracted with ethyl acetate (2 x 20 ml) and washed with deionized water (1 x 20 ml). The organic layer was removed in vacuo and the resulting intermediate (4a) was obtained. Generally, purification can be performed by flash column chromatography at this stage to prevent complicated mixtures from arising in subsequent steps. Intermediate 4a was reconstituted in anhydrous toluene and NaH (60% dispersion in mineral oil, 3.02g, 0.0756 mol (approximately 2 equiv.)) was added. The mixture was left stirring for 30 minutes. Alkylated bromide (0.0378 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of

intermediate 4a was observed. Generally, purification was performed by flash column chromatography to afford 1,2-O-DEG 1',2' diol.

Synthesis of 1,2-O-DGE 1',3' diol

As shown in Fig. 2d, to a stirred solution of 2-phenyl-1,3-dioxan-5-ol (1b, 5g, 0.0278mol) (1 equiv.) in anhydrous toluene, was added at 0°C, NaH (60% dispersion in mineral oil, 2.22g, 0.0556 mol (2 equiv.) for 30 minutes. Glycidyl Ether (0.0278 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 72 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of 2-phenyl-1,3-dioxan-5-ol or glycidyl ether was observed. Upon completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride solution, toluene was removed in vacuo and crude reaction mass extracted with ethyl acetate (2 x 20 ml) and washed with deionized water (1 x 20 ml). The organic layer was removed in vacuo and the resulting intermediate (4b) was obtained. Generally, purification can be performed by flash column chromatography at this stage to prevent complicated mixtures from arising in subsequent steps. Intermediate 4b was reconstituted in anhydrous toluene and NaH (60% dispersion in mineral oil, 2.22g, 0.0556 mol (approximately 2 equiv.) was added. The mixture was left stirring for 30 mins. Alkylated bromide (0.0378 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 6 to 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of intermediate 4b was observed. Generally, purification was performed by flash column chromatography to afford 1,2-O-DEG 1', 3' diol.

Synthesis of 1,3-O-DGE 1',2' diol

As shown in Fig. 2e, to a stirred solution of aliphatic alcohol (0.0378 mol) (1 equiv.) in anhydrous toluene, was added at 0°C, NaH (60% dispersion in mineral oil, 3.02g, 0.0756 mol (2 equiv.) for 30 minutes. Epichlorohydrin (0.0189 mol) (0.5 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction mass was stirred at reflux for 6 to 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of aliphatic alcohol was observed. Upon completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride solution, toluene was removed in vacuo and crude reaction mass extracted with ethyl acetate (2 x 20 ml) and washed with deionized water (1 x 20 ml). The organic layer was removed in vacuo and the resulting intermediate (4c) was obtained. To resulting intermediate 4c was added NaH (60% dispersion in mineral oil, 3.02g, 0.0756 mol (approximately 2 equiv) for 30 minutes. 3-chloropropane-1,2-diol (0.0378 mol) (1 equiv.) was added into the reaction mixture in a dropwise fashion. Reaction maixture was stirred at reflux for 6 to 20 hours. The reaction was monitored using gas chromatography mass spectrometry (GCMS) until the consumption of intermediate 4c was observed. Generally, purification was performed by flash column chromatography to afford 1,3-O-DEG 1',2' diol.

Synthesis of 1,2-O-DGE 1',2' BBP 1,2-O-DGE 1',3' BBP, 1,3-O-DGE 1',2' BBPs

To a mixture of DGE diol (1 equiv.) and diacid (1 equiv.), was added tin powder (catalyst) (0.1 equiv.). The reaction mixture was heated at 180 °C for 24 hours with magnetic stirring. The monomers melted at the studied temperatures of 180 °C, and the polymerization was by melt polycondensation. The tin powder (approximately 150 µm diameter) was not fully dissolved in the reaction mixture, and the surfaces of the powder particles catalyzed the esterification (polymerization). The reactor was not capped with a stopcock,

and the water generated during the polymerization was evaporated from the reaction mixture at the polymerization temperature of 180 °C so that the equilibrium of the esterification was shifted from the reactants (alcohols and carboxylic acids) to the product (esters). The reaction extent was determined from the consumption of CH group in the DGE unit using ^{1}H NMR. M_n and $Đ$ values were PMMA-calibrated gel permeation chromatography (GPC) values, where PMMA is poly(methyl methacrylate). The DP value was calculated from the M_n value of the polymer and the molecular weights of the diol and diacid. The M_n value was not an absolute value but a PMMA-calibrated value, and hence the DP value was viewed as an estimate. For 1,2-O-DEG 1',2' BBP 1,2-O-DEG 1',3' BBP, 1,3-O-DEG 1',2' BBP, typical molecular weights of (M_n > 6,000) with a relatively modest reaction extent (>80%) was achieved after 24 hours of stirring.

Example 1: Synthesis of the Monomers

1-O-MGE diol monomers and 2-O-MGE diol monomers

Ten 1-O-MGE diol monomers and ten 2-O-MGE diol monomers were synthesised with varied alkyl chain lengths (m = 3, 8−14, 16 and 18) (Fig. 2). 1-O-MGE and 2-O-MGE were synthesized via Williamson ether synthesis of commercially available solketal and 2-phenyl-1,3-dioxan-5-ol (1 equiv.) using NaH (60% dispersion in mineral oil, 2 equiv.) in anhydrous toluene (30 mL). After stirring at 0 °C for 30 minutes, the alkyl bromide (R = C_3, C_8-C_{14}, C_{16} and C_{18}) in anhydrous toluene (1 mL) was added dropwise. The reaction was monitored using Gas Chromatography Mass Spectrometry (GCMS), and the reaction conversion was typically 70−80%. After quenching the reaction with a saturated ammonium chloride solution, the resulting mixture containing an intermediate **2a** or **2b** (Fig. 2) was extracted twice with ethyl acetate, combined and concentrated to dryness. Subsequent acid catalysed hydrolysis (3:1 solution of 1M HCl/EtOH) led to the desired compound 1-O-MGE (**3a)** or 2-O-MGE (**3b)** (Fig. 2), which was purified by flash column chromatography (short-alkyl chained, R = C_3, C_8-C_9) or recrystallisation (mid-alkyl chained, R = $C_{10\text{-}14}$, C_{16} and C_{18}). Some examples of the synthesized monomers are shown in Fig. 3. R_1 and R_2 independently refer to C_3, $C_{8\text{-}14}$, C_{16} or C_{18} alkyl groups.

1,2-O-DGE 1',2' diol monomer and 1,2-O-DGE 1',3' diol monomer

1,2-O-DGE 1',2' diol monomer and 1,2-O-DEG 1',3' diol monomer were synthesised with alkyl chain lengths (m =4) as shown in Fig. 2c and Fig. 2d. 1,2-O-DGE 1',2' diol and 1,2-O-DEG 1',3' diol monomer were synthesized via Williamson ether synthesis of commercially available starting materials solketal and 2-phenyl-1,3-dioxan-5-ol (1 equiv) respectively using NaH (60% dispersion in mineral oil, 2 equiv.) in anhydrous toluene (30 mL). After stirring at 0 °C for 30 minutes, the glycidyl ether (R = C_4) in anhydrous toluene (1 mL) was added dropwise. The reaction was monitored using Gas Chromatography Mass Spectrometry (GCMS), and the reaction conversion was typically 70−80%. After quenching the reaction with a saturated ammonium chloride solution, the resulting mixture containing an intermediate 4a (Fig. 2c) or 4b (Fig. 2d) was extracted twice with ethyl acetate, combined and concentrated to dryness. Generally, purification was performed by flash column chromatography at this stage to prevent complicated mixtures from arising in subsequent steps. Intermediate 4a and 4b were reconstituted in anhydrous toluene and NaH (60% (approximately 2 equiv.) was added. After stirring at 0 °C for 30 minutes, the alkyl bromide (R = C_4) in anhydrous toluene (1 mL) was added dropwise. The reaction was monitored using Gas Chromatography Mass Spectrometry (GCMS), and the reaction conversion was typically 70%. After quenching the reaction with a saturated ammonium chloride solution, the resulting mixture was extracted twice with ethyl acetate,

combined and concentrated to dryness. Subsequent acid catalysed hydrolysis (3:1 solution of 1M HCl/EtOH) led to the desired compound 1,2-O-DGE 1',2' diol or 1,2-O-DEG 1',3' diol , which was purified by flash column chromatography.

Synthesis of 1,3-O-DEG 1',2' diol monomer

An example of 1,3-O-DEG 1',2' diol monomer was synthesized via Williamson ether synthesis of commercially available aliphatic alcohols (1 equiv) using NaH (60% dispersion in mineral oil, 2 equiv.) in anhydrous toluene (30 mL). After stirring at 0 °C for 30 minutes, epichlorohydrin (0.5 equiv.) in anhydrous toluene (1 mL) was added dropwise. The reaction was monitored using Gas Chromatography Mass Spectrometry (GCMS), and the reaction conversion was typically >85%. After quenching the reaction with a saturated ammonium chloride solution, the resulting mixture containing an intermediate 4c (Fig. 2e) was extracted twice with ethyl acetate, combined and concentrated to dryness. Generally, purification can be performed by flash column chromatography at this stage to prevent complicated mixtures from arising in subsequent steps. Intermediate 4c was reconstituted in anhydrous toluene and NaH (60% (approximately 2 equiv.) was added. After stirring at 0 °C for 30 minutes, 3-chloropropane-1,2-diol in anhydrous toluene (1 mL) was added dropwise. The reaction was monitored using Gas Chromatography Mass Spectrometry (GCMS), and the reaction conversion was typically 60 %. After quenching the reaction with a saturated ammonium chloride solution, the resulting mixture was extracted twice with ethyl acetate, combined and concentrated to dryness and was which was purified by flash column chromatography to afford 1,3-O-DEG 1',2' diol monomer.

Example 2: Synthesis of the Polymers

30 BBPs were synthesized using a series of 1-O-MGE and 2-O-MGE with m = 3, 8-14, 16 and 18 (in all integers) and a series of diacids with n = 4-14, 18 and 22 (in all integers), as shown in Fig. 4. As shown in Fig. 4a, a mixture of MGE diol (1 equiv.), diacid (1 equiv.), diphenyl ether (DPE, 30%wt) and tin powder (catalyst) (0.1 equiv.) were heated at 180 °C for 24 hours with magnetic stirring. The monomers melted at the studied temperatures of 180 °C, and the polymerization was melt polycondensation. The tin powder (approximately 150 µm diameter) was not fully dissolved in the reaction mixture, and the surfaces of the powder particles would catalyze the esterification (polymerization). The reactor was not capped with a stopcock, and the water generated during the polymerization was evaporated from the reaction mixture at the polymerization temperature of 180 °C so that the equilibrium of the esterification is shifted from the reactants (alcohols and carboxylic acids) to the product (esters).

Fig. 4b shows how some BBPs were synthesized from diglycerol ethers (DGEs). A graphical representation of the DGE polymer is shown in Fig. 1a'.

Some examples of the synthesized BBP polymers are shown in Fig. 5. R, R_1 and R_2 independently refer to C_3, C_{8-14}, C_{16} or C_{18} alkyl groups.

DGE BBPs were synthesized using a series of 1,2-O-DGE 1',2' diol monomer and 1,2-O DGE 1',3' diol monomer with m = 4 (in all integers) and diacid n = 10 (in all integers), as shown in Fig. 4b. As shown in Fig. 4b, a mixture of DGE diol (1 equiv.), diacid (1 equiv.), diphenyl ether (DPE, 30%wt) and tin powder (catalyst) (0.1 equiv.) were heated at 180 °C for 24 hours with magnetic stirring. The monomers melted at the studied temperatures of 180 °C, and the polymerization was melt polycondensation. The tin powder

(approximately 150 μm diameter) was not fully dissolved in the reaction mixture, and the surfaces of the powder particles would catalyze the esterification (polymerization). The reactor was not capped with a stopcock, and the water generated during the polymerization was evaporated from the reaction mixture at the polymerization temperature of 180 °C so that the equilibrium of the esterification is shifted from the reactants (alcohols and carboxylic acids) to the product (esters).

Table 1 shows the polymerization results for 30 representative BBPs prepared from 1-O-MGE.

Table 1. Synthesis of BBPs from 1-O-MGE

Entry	MGE(diol)	*m* value in diol	*n* value in diacid	$[diol]_0/[diacid]_0/[tin]_0$ (equiv.)	T (°C)	t (h)	Reaction extent (*p*) (%)[a]	Mn[b]	Đ[b]	DP[c]
1	1-*O*-MGE	9	10	1/1/0.1	180	24	95	12000	1.16	29
2	1-*O*-MGE	10	10	1/1/0.1	180	24	94	15000	1.29	34
3	1-*O*-MGE	11	10	1/1/0.1	180	24	95	13000	1.17	29
4	1-*O*-MGE	12	10	1/1/0.1	180	24	93	18000 10000	1.59 1.17	38 22
5	1-*O*-MGE	13	10	1/1/0.1	180	24	94	12000	1.38	25
6	1-*O*-MGE	14	10	1/1/0.1	180	24	93	11000	1.36	23
7	1-*O*-MGE	12	7	1/1/0.1	180	24	93	16000	1.19	39
8	1-*O*-MGE	12	8	1/1/0.1	180	24	96	15000	1.40	35
9	1-*O*-MGE	12	9	1/1/0.1	180	24	95	17000	1.15	38
10	1-*O*-MGE	12	10	1/1/0.1	180	24	93	10000	1.17	22
11	1-*O*-MGE	12	11	1/1/0.1	180	24	93	16000	1.09	33
12	1-*O*-MGE	12	12	1/1/0.1	180	24	92	12000	1.38	32
13	1-*O*-MGE	18	7	1/1/0.1	180	24	91	12000	1.17	24
14	1-*O*-MGE	18	8	1/1/0.1	180	24	93	15000	1.16	29
15	1-*O*-MGE	18	9	1/1/0.1	180	24	93	17000	1.15	32
16	1-*O*-MGE	18	10	1/1/0.1	180	24	94	12000	1.13	19
17	1-*O*-MGE	18	11	1/1/0.1	180	24	93	15000	1.15	26
18	1-*O*-MGE	18	12	1/1/0.1	180	24	90	12000	1.16	21
19	2-*O*-MGE	18	7	1/1/0.1	180	6	99	12000	1.13	24
20	2-*O*-MGE	18	8	1/1/0.1	180	6	99	14000	1.17	26
21	2-*O*-MGE	18	9	1/1/0.1	180	6	99	15000	1.10	27
22	2-*O*-MGE	18	10	1/1/0.1	180	6	99	14000	1.14	14
23	2-*O*-MGE	18	11	1/1/0.1	180	6	99	10000	1.14	17
24	2-*O*-MGE	18	12	1/1/0.1	180	6	99	15000	1.16	27
25	2-*O*-MGE	3	7	1/1/0.1	150	8	99	15000	1.18	51
26	2-*O*-MGE	3	8	1/1/0.1	150	8	99	18000	1.34	58
27	2-*O*-MGE	3	9	1/1/0.1	150	8	99	17000	1.28	53
28	2-*O*-MGE	3	10	1/1/0.1	150	8	99	15000	1.16	45
29	2-*O*-MGE	3	11	1/1/0.1	150	8	99	15000	1.33	43
30	2-*O*-MGE	3	12	1/1/0.1	150	8	99	14000	1.24	38

a. Consumption of CH proton of glycerol backbone with ^{1}H NMR

b. M_n and $Đ$ values of purified polymers determined by PMMA-calibrated GPC using THF as an eluent

c. Degree of polymerization (DP) calculated from the M_n value of the polymer and the molecular weights of the monomers (diol and diacid), where one DP (one repeating unit) consists of a combination of one diol and one diacid.

For example, the polymerization of 1-O-MGE with m = 9 and a diacid with n = 10 (Table 1 (entry 1)) reached a 95% reaction extent (consumption of CH proton of glycerol backbone with ^{1}H NMR) after 24 hours and yielded a BBP with M_n = 12000 (DP = 29) and $Đ$ (= M_w/M_n) = 1.16 (after purification via precipitation in ethanol), where M_n and M_w are the number- and weight-average molecular weight, respectively. DP is the degree of polymerization, and $Đ$ is the dispersity. The reaction extent (p) was determined from consumption of CH proton of glycerol backbone with ^{1}H NMR. The Mn and $Đ$ values are PMMA-calibrated gel permeation chromatography (GPC) values, where PMMA is poly(methyl methacrylate). The DP value was calculated from the M_n value of the polymer and the molecular weights of the diol and diacid. The M_n value is not an absolute value but a PMMA-calibrated value, and hence the DP value was viewed as an estimate. Thus, a relatively high molecular weight polymer (M_n = 12000 (DP = 29)) was successfully obtained with a relatively high reaction extent (95%).

Fig. 6 and Table 1 (entries 1-6) show the polymerization results for the combinations of 1-O-MGE diols with varied m values of 9-14 with a diacid with a fixed n value of 10. Table 1 (entries 7-12) shows the results for the combinations of a 1-O-MGE diol with a fixed m value of 12 with diacids with varied n values of 7-12. Table 1 (entries 13-18) shows the results for the combinations of a 1-O-MGE diol with a fixed m value of 18 with diacids with varied n values of 7-12.

A different MGE, i.e., 2-O-MGE, was also studied instead of 1-O-MGE. Table 1 (entries 19-24) shows the results for the combinations of a 2-O-MGE diol with a fixed m value of 18 with diacids having varied n values of 7-12. Because of the structural difference of 2-O-MGE and 1-O-MGE, the M_n reached 10,000 after 6 hours for 2-O-MGE (m = 18) in most cases (n = 7-12), while it reached 10,000 only after 24 hours for 1-O-MGE (m = 18) in all studied cases (n = 7-12). This could be due to the increased reactivity of 2-O-MGEs having two primary alcohols as compared to the 1-O-MGEs having both a primary and secondary alcohol.

Fig. 7 shows the ^{1}H NMR spectra of some of the synthesized monomers and their respective BBPs.

Fig. 7a shows the ^{1}H NMR spectra of the mixture of 1-O-MGE (m = 18) diol and diacid (n = 9) before (top spectrum) and after (bottom spectrum) the polymerization. The CH proton (proton c) and CH_2 protons adjacent to OH (protons b) in 1-O-MGE appeared at 3.89-3.84 ppm and 3.74 ppm, respectively. The CH_2 protons adjacent to COOH in the diacid (protons j) appeared at 2.37 ppm. After the polymerization, these peaks shifted to 5.22-5.17 ppm (CH proton (proton c')), 4.33-4.16 ppm (CH_2 protons adjacent to −OC(=O) linkage (proton b')), and 2.31−2.38 ppm (CH_2 protons adjacent to −(C=O)O linkage (proton j')) for the polymer backbone. From the decay in the peaks of the monomers (peak at 3.89-3.84 ppm) and the increase in the peaks of the polymer (sum of integration ratios of peaks at 5.22-5.17, 5.01-4.99, 4.02-3.98 ppm) the p value was determined. Simultaneously, the peaks *b'* (CH*), c'* ($HOCH_2CH$) and *f'* (CH_2COO*)* for the corresponding protons in the polymer converted from the monomers newly appeared 5.17, 4.11-4.34, and 2.31-2.38ppm, respectively, confirming the formation of the polymer.

Fig. 7b shows the ^{1}H NMR spectra of the mixture of 2-O-MGE (m = 18) diol and diacid (n = 9) before (top spectrum) and after (bottom spectrum) the polymerization.. The CH proton (proton c) in 2-O-MGE appeared at 3.49-3.44 ppm. Fig. 7b shows the ^{1}H NMR spectra of the mixture of 2-O-MGE (m = 18) diol

and diacid (n = 9) before (top spectrum) and after (bottom spectrum) the polymerization. After the polymerization, the peaks at 3.49-3.44 ppm for the CH proton (proton c) and 3.79–3.66 ppm for the CH_2 protons adjacent to OH (protons b) in 2-O-MGE and the peak at 2.37–2.33 ppm for the CH_2 protons adjacent to COOH in the diacid (protons h) shifted to 3.70–3.65 ppm for the CH proton (proton c'), 4.20–4.09 ppm for the CH_2 protons adjacent to −OC(=O) linkage (protons b'), and 2.34–2.30 ppm for the CH_2 protons adjacent to −(C=O)O linkage (protons h') for the polymer backbone, confirming the formation of the polymer. From the decay in the peaks of the monomers (peak at 3.49-3.44 ppm) and the increase in the peaks of the polymer (3.79–3.66 ppm) the *p* value was determined.

Fig. 7c shows the ^{1}H NMR spectra of the mixture of 1-O-MAG (m = 18) diol and diacid (n = 9) before (top spectrum) and after (bottom spectrum) the polymerization, whereby MAG stands for monoacyl glycerol. The CH proton (proton c) and CH_2 protons adjacent to OH (protons b) in 1-O-MGE appeared at 3.94-3.89 ppm3.79–3.66 and 3.64 ppm, respectively. The CH_2 protons adjacent to COOH in the diacid (protons j) appeared at 2.37 ppm. After the polymerization, these peaks shifted to 5.28-5.24 ppm (CH proton (proton c')), 4.31-4.08 ppm (CH_2 protons adjacent to −OC(=O) linkage (proton b')), and 2.36–2.29 ppm (CH_2 protons adjacent to –(C=O)O linkage (proton j')) for the polymer backbone confirming the formation of the polymer. From the decay in the peaks of the monomers (peak at 3.94-3.89 ppm) and the increase in the peaks of the polymer (5.28-5.24 ppm) the *p* value was determined.

Fig. 7d shows the formation of 2-ethylhexyl 1-O-MGE diol from 2-(((2-ethylhexyl)oxy)methyl)oxirane. This was a representative example of a BBP with branched alkyl side chain being formed. The BBP could be formed in one pot synthesis from the glycidyl ether 2-(((2-ethylhexyl)oxy)methyl)oxirane.

Fig. 7e shows the zoomed in ^{1}H NMR spectra of Fig. 7d indicating the transformation of 2-ethylhexyl glycidyl ether (bottom spectrum) to 2-ethylhexyl 1-O-MGE diol (middle spectrum) and then to 2-ethylhexyl 1-O-MGE BBP (top spectrum, *n* = 9). The CH proton (proton c, bottom spectrum) in 2-ethylhexyl glycidyl appeared at 3.14-3.10 ppm. After hot water-promoted ring opening of the epoxide ring, the CH proton (proton c, middle spectrum) appeared at 3.89-3.84 ppm indicating the formation of 2-ethylhexyl 1-*O*-MGE. After applying the polymerization conditions, the CH proton shifted to 5.22-5.17 ppm (proton c', top spectrum)), indicating the successful polymerisation.

Fig. 7f shows the ^{1}H NMR spectra of the mixture of 1-O-MGE (*m* = 18) diol and diacid (n = 9) monitored from 1 hour to 24 hour. The zoomed in spectra from 6.0 ppm to 3.0 ppm showing the comparison of ^{1}H'NMR spectra of 1-O-MGE BBP before polymerisation and after polymerisation. This example indicated a successful example of BBPs with saturated side chain being formed.

Fig. 7g shows the ^{1}H NMR spectra of the mixture of 1-O-MGE (*m* = 18, with a cis double bond) diol and diacid (n = 9) monitored from 1 hour to 24 hours. Zoomed in spectra from 6.0 ppm to 3.0 ppm showing the comparison of ^{1}H'NMR spectra of 1-O-MGE BBP before polymerisation and after polymerisation. The double bond signals are shown at 5.3 ppm. This example indicated a successful example of BBPs with unsaturated side chain being formed.

Fig. 7h shows the ^{1}H NMR spectra of the mixture of 1-O-MGE (m = 18) diol and diacid (n = 9) before (top spectrum) and after (bottom spectrum) the polymerization. The CH proton (proton c) and CH_2 protons adjacent to OH (protons b) in 1-O-MGE appeared at 3.89-3.84 ppm and 3.74 ppm, respectively. The CH_2 protons adjacent to COOH in the diacid (protons j) appeared at 2.37 ppm. After the polymerization, these peaks shifted to 5.22-5.17 ppm (CH proton (proton c')), 4.33-4.16 ppm (CH2 protons adjacent to −OC(=O) linkage (proton b')), and 2.31−2.38 ppm (CH2 protons adjacent to −(C=O)O linkage (proton j')) for the polymer backbone. From the decay in the peaks of the monomers (peak at 3.89-3.84 ppm) and the increase in the peaks of the polymer (sum of integration ratios of peaks at 5.22-5.17, 5.01-4.99, 4.02-3.98 ppm) the p value was determined. Simultaneously, the peaks *b'* (CH*), c'* ($HOCH_2CH$) and *f'* (CH_2COO*)* for the corresponding protons in the polymer converted from the monomers newly appeared 5.17, 4.11-4.34, and 2.31-2.38ppm, respectively, confirming the formation of the polymer. The zoomed in spectra show the comparison of H'NMR spectra of 1-O-MGE BBP before polymerisation and after polymerisation. This example indicated a successful example of BBPs with branched side chain being formed in a one pot synthesis from 2-(((2-ethylhexyl)oxy)methyl)oxirane.

Fig. 7i shows the ^{1}H NMR spectra of the mixture of 1,2-O-DGE 1',2' diol (m = 4) and diacid (n = 10) before (top spectrum) and after (bottom spectrum) the polymerization. The CH proton (proton c) in 1,2-O-DGE 1',2' appeared at 3.87-3.84 ppm. The CH_2 protons adjacent to COOH in the diacid (protons l) appeared at 2.36-2.32 ppm. After the polymerization, these peaks shifted to 5.21 ppm (CH proton (proton c'), and 2.34−2.28 ppm (CH_2 protons adjacent to −(C=O)O linkage (proton j')) for the polymer backbone. From the decay in the peaks of the monomers (peak at 3.87-3.84 ppm) and the increase in the peaks of the polymer (sum of integration ratios of peaks at 5.21 ppm) the p value was determined. This example indicated a successful example of DGE BBPs.

Fig. 7j shows the ^{1}H NMR spectra of the mixture of and 1,2-O- DGE 1',3' diol (m = 4) and diacid (n = 10) before (top spectrum) and after (bottom spectrum) the polymerization. The CH proton (proton c) in 1,2-O-DGE 1',3' diol appeared overlapped with other glycerol protons in 3.82-3.44 ppm. The CH_2 protons adjacent to COOH in the diacid (protons k) appeared at 2.35-2.32 ppm. After the polymerization, the CH peak was distinguishable at shifted to 3.79-3.75 ppm (CH proton (proton c')), and (CH_2 protons adjacent to −(C=O)O linkage (proton k')) became pronounced at 2.34-2.30 ppm. Simultaneously, the peaks *c'* (CH*),* and *k'* (CH_2COO*)* for the corresponding protons in the polymer converted from the monomers newly confirms the formation of the polymer. This example indicated a successful example of DGE BBPs.

Example 3: Melting Temperature

The melting temperatures (T_m) using Differential Scanning Calorimetry (DSC) were determined (Fig. 8, Fig. 9 and Table 2).

Fig. 8 shows the effect of varying alkyl chain length of diols on the T_m. with a fixed *n* value of 10 (backbone alkyl chain length derived from the diacid), the T_m values increased with an increase in the *m* value (branched alkyl chain length) from 9 to 14 (Fig. 8). A difference of 94.7 °C was observed between m = 0 (linear polyester) and m = 9 (bottle brush polyester).

Table 2. Thermal properties of BBPs.

Entry[a]	MGE (diol)	*m/n* in polymer	M_n	T_m[c](°C)
1	1-O-MGE	9/10	12000	–21.7
2	1-O-MGE	10/10	15000	–9.0
3	1-O-MGE	11/10	13000	–15.9
4	1-O-MGE	12/10	10000	3.6
5	1-O-MGE	13/10	12000	6.8
6	1-O-MGE	14/10	11000	8.1
7	1-O-MGE	12/7	16000	-14.0
8	1-O-MGE	12/8	15000	-24.5
9	1-O-MGE	12/9	17000	-21.3
10	1-O-MGE	12/10	10000	3.6
11	1-O-MGE	12/11	16000	19.8
12	1-O-MGE	12/12	12000	12.7
13	1-O-MGE	18/7	12000	30.8
14	1-O-MGE	18/8	15000	33.4
15	1-O-MGE	18/9	17000	28.3
16	1-O-MGE	18/10	12000	30.0
17	1-O-MGE	18/11	15000	31.9
18	1-O-MGE	18/12	12000	22.8
19	2-O-MGE	18/7	12000	17.9
20	2-O-MGE	18/8	14000	20.0
21	2-O-MGE	18/9	15000	14.9
22	2-O-MGE	18/10	14000	11.6
23	2-O-MGE	18/11	10000	21.9
24	2-O-MGE	18/12	15000	17.9

a. Esterification conditions: diol/diacid 1:1 mol/mol, Tin powder (10 mol% based on diol), temperature/time (T/t): 180 °C/6 to 24 hours

b. Temperature of melting (second scan). The entries in Table 2 correspond to those in Table 1.

Interestingly, "odd-even" effects of the *m* and *n* values on the T_m values (Fig. 8) were observed. The T_m values of an "odd-even" (odd *m* and even *n)* polyester are lower than those of adjacent "even-even" (even *m* and even *n)* polyesters. Fig. 8 shows an example of polyesters formed when *m*= 9 and 11, whereby the T_m values are -21.7°C and -15.9°C, respectively, which are lower than the T_m of -9.0°C for *m*=10 polyester. Previous reports have only shown "odd-even" effects caused by changes made in the backbone of the polyester, and reports of "odd-even" effects caused by the pendant chains of bottle brush polymers has not been previously reported.

Fig. 9a shows that linear polymers have very high melting temperatures compared to the BBPs, suggesting that side chains from the BBPs disrupt the packing of chains and lead to lower melting points. A comparison of ethylene glycol and 1-O-MGE when *m* = 12 show an average drop of about 50 °C across *n* = 7-12. Fig. 9a also shows that as the alkyl chain length of the side chain increases, the melting points of the polymers tend to increase.

For completeness, Fig. 9b shows the T_m of 2-O-MGE BBP when *m* = 3 and *n* = 4-12.. This represents a case whereby the alkyl side chains are short (*m* = 3), where odd-even effects are still prevalent in the T_m of the BBPs. Fig. 9c shows the T_m of 1-O-MGE BBP with m = 16 and n = 4-14, 18 and 22, showing that when

the n values are changed from 4 to 14, and m = 16, a U-shaped trend for the T_m could be observed. Further, when m = 16 and n = 4, 18 or 22, the BBPs may be good candidates for automobile greases.

Typically, polyesters derived from dicarboxylic acids containing even numbers of carbon atoms melt at higher temperatures than those derived from diacids containing odd numbers of carbon atoms. This observation was ascribed to the fact that the crystalline phase of an aliphatic polyester with an even number of carbon atoms between ester groups contains close layers of dipoles of opposite direction (effectively cancelling the local polarization), whereas close carbonyl layers of identical direction are present in the crystal of polyesters derived from dicarboxylic acids having odd numbers of carbon atoms (Fig. 10). As the local polarization of the stacked polyester chains are cancelled out, greater hydrophobic interactions between the aliphatic segment chains can occur, and a higher T_m results.

Fig. 11 shows the graphs of T_m of BBPs made from 1-O-MGE BBPs (circle) and 1-O-MAG BBPs (square) (m = 18 and n = 7-12) and indicates that generally, the T_m of 1-O-MGE BBPs are lower than 1-O-MAG BBPs at low values of n ($n < 7$), and higher than 1-O-MAG BBPs at higher values of n (typically $n > 7$). This showed that different alkyl chain length MGEs and α,ω diacid lead to BBPs with variable thermomechanical and viscoelastic properties.

Fig. 12 is a graph showing how the position of the ether linkage affects melting point, and is a graph of T_m of BBPs made from 1-O-MGE BBPs (circle) and 2-O-MGE BBPs (square) (m = 18 and n = 7-12) which indicates that generally, the T_m of 1-O-MGE BBPs are higher than 2-O-MGE BBPs across all n values. 1-O-MGE BBPs has a 2 carbon diol backbone that is more rigid than the 3 carbon diol backbone found in 2-O-MGE BBPs and have higher T_m.

Fig. 13 shows the graphs of T_m of 1-O-MGE BBPs made from 1-O-MGE diol (m =16) various (n =4) diacids. C16 diol succinic acid (square) shows the highest T_m at 42.7°C. The introduction of double bonds in C16 diol fumaric acid (circle) within the chain leads to a lower T_m at 34.2°C and the introduction of double bonds in C16 diol fumaric acid (circle) out of the chain leads to an even lower T_m at 27.7°C . This showed that the introduction of double bonds into the main chain, typically lead to a reduction in the T_m.

Example 4: Decomposition Temperature

Table 3 show the 5%-decomposition temperature ($T_{d,5}$) and 50%-decomposition temperature ($T_{d,50}$) of 1-O-MGE BBPs with m = 9-14 and n=10 using thermogravimetric analysis (TGA). Generally, the $T_{d,50}$ values were above 350 °C for all studied BBPs. The current set of data does not show significant changes of $T_{d,5}$ and $T_{d,50}$ with respect to the m values of the 1-O-MGE.

Table 3. Thermal degradation properties of 1-O-MGE BBPs with m = 9-14 and n=10

Entry[a]	MGE (diol)	*m/n* in polymer	Mn	$T_{d,5}$ [b] (°C)	$T_{d,50}$ [c] (°C)
1	1-O-MGE	9/10	12000	327	378
2	1-O-MGE	10/10	15000	333	380
3	1-O-MGE	11/10	13000	295	378
4	1-O-MGE	12/10	10000	324	375
5	1-O-MGE	13/10	12000	324	380
6	1-O-MGE	14/10	11000	329	381

a. Esterification conditions: diol/diacid 1:1 mol/mol, Tin powder (10 mol% based on diol), temperature/time (T/t): 180 °C/18 to 24 hours
b. $T_{d,5}$ is the temperature when the sample reaches 5% weight loss.
c. $T_{d,50}$ is the temperature when the sample reaches 50% weight loss.

Fig. 14a and Table 4 show the % weight loss against temperature of 1-O-MGE BBP with m =9-14, n = 10. The results indicate that the effect of varying the alkyl chain length on the side chains of BBPs does not have significant effects on the decomposition temperatures of the polymers.

Fig. 14b and Table 5 show the % weight loss against the temperature of 1-O-MGE BBP with m = 18, n = 7-11. The results indicate that the effect of varying the alkyl chain length on the diacid main chains of BBPs typically does not lead to significant effects on the decomposition temperatures of the polymers.

Table 4. Thermal degradation properties of 1-O-MGE BBPs with m = 9-14 and n=10

Entry[a]	**MGE (diol)**	***m/n* in polymer**	**Mn**	**$T_{d,5}$ [b] (°C)**	**$T_{d,50}$ [c] (°C)**
1	1-O-MGE	9/10	12000	327	378
2	1-O-MGE	10/10	15000	333	380
3	1-O-MGE	11/10	13000	295	378
4	1-O-MGE	12/10	10000	324	375
5	1-O-MGE	13/10	12000	324	380
6	1-O-MGE	14/10	11000	329	381

a. Esterification conditions: diol/diacid 1:1 mol/mol, Tin powder (10 mol% based on diol), temperature/time (T/t): 180 °C/18 to 24 hours
b. $T_{d,5}$ is the temperature when the sample reaches 5% weight loss.
c. $T_{d,50}$ is the temperature when the sample reaches 50% weight loss.

Table 5. Thermal degradation properties of 1-O-MGE BBPs with m = 18 and n=7-11

Entry[a]	**MGE (diol)**	***m/n* in polymer**	**Mn**	**$T_{d,5}$** [b] **(°C)**	**$T_{d,50}$** [c] **(°C)**
1	1-O-MGE	18/7	12000	307	376
2	1-O-MGE	18/8	15000	313	387
3	1-O-MGE	18/9	17000	313	385
4	1-O-MGE	18/10	12000	333	380
5	1-O-MGE	18/11	15000	266	386

a. Esterification conditions: diol/diacid 1:1 mol/mol, Tin powder (10 mol% based on diol), temperature/time (T/t): 180 °C/18 to 24 hours
b. $T_{d,5}$ is the temperature when the sample reaches 5% weight loss.
c. $T_{d,50}$ is the temperature when the sample reaches 50% weight loss.

Fig. 15a and Table 6 compare the % weight loss against the temperature of for 1-O-MGE BBP and 1-O-MAG BBP with m = 18, n = 7-11. The results indicate that introducing ether groups into the side chains of the BBPs as compared to ester groups tends to increase the $T_{d,5}$ and the $T_{d,50}$ of the polymers and as such increases the thermostability of the polymers.

Fig. 15b and Table 7 compare the % weight loss against the temperature of for 1-O-MGE BBP and 2-O-MGE BBP with m = 18, n = 7-11. The results indicate that 1-O-MGE BBP tend to have higher $T_{d,5}$ values compared to 2-O-MGE BBP while $T_{d,50}$ values are relatively similar across the two classes of polymers.

Table 6. Thermal degradation properties of 1-O-MGE BBP and 1-O-MAG BBP

Entry[a]	MGE (diol)	m/n in polymer	M_n	$T_{d,5}$[b] (°C)	$T_{d,50}$[b] (°C)
1	1-*O*-MGE	18/7	12000	306.7	376.4
2	1-*O*-MGE	18/8	15000	313.2	386.7
3	1-*O*-MGE	18/9	17000	312.8	384.5
4	1-*O*-MGE	18/10	12000	332.5	380.2
5	1-*O*-MGE	18/11	15000	265.5	385.5
6	1-*O*-MAG(Ester)	18/7	15000	313.4	360.2
7	1-*O*-MAG(Ester)	18/8	14000	198.5	376.8
8	1-*O*-MAG(Ester)	18/9	12000	247.1	375.4
9	1-*O*-MAG(Ester)	18/10	20000	176.6	375.8
10	1-*O*-MAG(Ester)	18/11	19000	172.9	372.8

Table 7. Thermal degradation properties of 1-O-MGE BBP and 2-O-MGE BBP

Entry[a]	MGE (diol)	m/n in polymer	M_n	$T_{d,5}$[b] (°C)	$T_{d,50}$[b] (°C)
1	1-*O*-MGE	18/7	12000	306.7	376.4
2	1-*O*-MGE	18/8	15000	313.2	386.7
3	1-*O*-MGE	18/9	17000	312.8	384.5
4	1-*O*-MGE	18/10	12000	332.5	380.2
5	1-*O*-MGE	18/11	15000	265.5	385.5
6	2-*O*-MGE	18/7	12000	192.7	388.7
7	2-*O*-MGE	18/8	14000	232.5	367.7
8	2-*O*-MGE	18/9	15000	297.3	389.1
9	2-*O*-MGE	18/10	14000	188.9	390.0
10	2-*O*-MGE	18/11	10000	211.3	399.2

Fig. 16 shows the gel permeation chromatograms of 1-O-MGE BBP subjected to hydrolytic degradation. Fig. 16a shows the chromatogram of 1-O-MGE BBP (Mn =20291, D =1.32) being subjected to hydrolytic conditions (60% THF/40% NaOH (aq)). Fig. 16b shows that after 1 hour, the polyesters had efficiently degraded to form 1-O-MGE diol and diacid monomers. Fig 16c and 16d show that polymers can be reformed under repolymerization with Mn = 1521, D =2.11 after 6 hours and Mn = 8089, D = 1.72 after 18 hours.

Fig. 17 shows the key steps required to synthesise 1-O-MGE diols from epichlorohydrin. This reaction was performed in a 10 L reactor and achieved an overall reaction yield of 87%.

Fig. 18 shows the ^{1}HNMR spectra of the mixture of 1-O-MGE (*m* = 18) diol and diacid (n = 9) monitored from 0 minutes to 24 hours. The spectra is zoomed in from 6.0 ppm to 3.0 ppm to observe the appearance and disappearance of species A, B, C and D through the polymerisation process.

Fig. 19 and Table 8 show that intermediate B typically exist in solution more greatly than intermediate C. It is likely that intermediate C exists as a more transient intermediate and forms the product D more quickly due to the presence of a primary alcohol that is known to have higher reactivities.

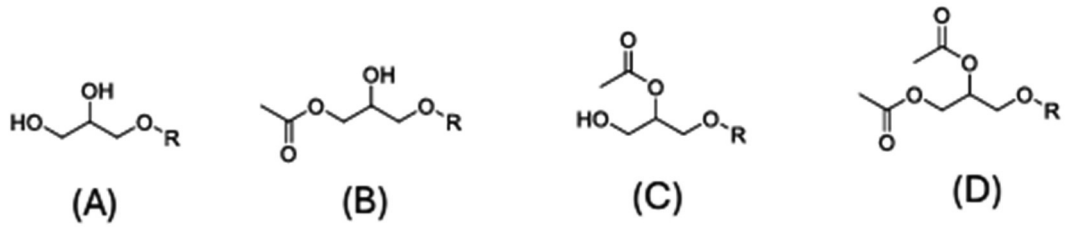


Table 8. Ratio of species (A), (B), (C) and (D) with respect to time.

Time (min)	(A) %	(B) %	(C) %	(D) %
0	100	0	0	0
10	81.81	13.29	4.91	0
20	61.46	30.33	8.21	0
30	40.78	40.24	10.75	8.23
40	28.58	45.27	12.76	13.4
50	21.54	46.95	12.69	18.82
60	17.37	45.37	11.99	25.27
70	14.73	44.90	11.06	29.32
80	14.44	42.54	10.39	32.63
90	13.57	41.71	11.33	33.39
100	12.17	41.41	11.27	35.15
110	12.38	41.06	11.56	35
120	11.95	41.02	11.30	35.73
130	11.61	40.65	11.50	36.25
140	11.68	39.86	11.38	37.07
150	10.04	40.44	11.43	38.10
160	10.43	40.78	10.80	37.99
170	9.42	39.55	11.82	39.21
180	10.49	39.61	10.87	39.03
240	6.41	38.41	9.71	45.47

300	0	35.47	11.38	53.15
360	0	33.83	8.89	57.29
420	0	30.66	9.72	59.62
480	0	29.35	8.72	61.93
1440	0	0	7.41	92.6

INDUSTRIAL APPLICABILITY

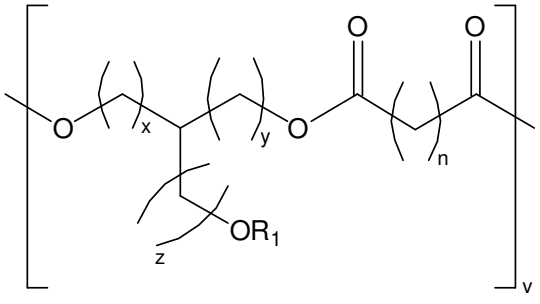
The polymer as defined herein may be useful as an alternative to petroleum-based polymers. The polymer as defined herein may be useful as a soft-tissue alternative, lubricant, surface coating, motion control grease, ultrasoft surfaces, in nanocapsules, in sensing and in delivery applications. The polymer as defined herein may also be useful as thermoplastic vulcanizates that may be used for 3D printing, packaging materials, fibre technology, self-cleaning surfaces, self-healing surfaces, shape memory polymers and anti-fouling polyester membranes.

The method for preparing the polymer as defined herein may be useful in preparing the polymer as defined above.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

CLAIMS

1. A polymer having the following general structure (I):



(I),

wherein

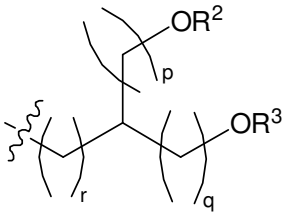
x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24;

v is an integer of 1 to 2000; and

R^1 is H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl;

or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer or 1 to 5;

R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and ~~~ is where the substituent of general structure (II) attaches to the polymer of general structure (I).

2. The polymer of claim 1, wherein:

x is 0 or 1;

y is 1;

z is 0 or 1;

p is 0 or 1;

q is 0 or 1; or

r is 0 or 1.

3. The polymer of claim 1 or 2, wherein:

i) x is 0, y is 1, z is 1 and R^1 is linear or branchedC_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

ii) x is 1, y is 1, z is 0 and R^1 is linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

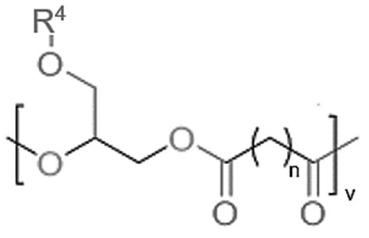
iii) x is 0, y is 1, z is 1, R^1 is the substituent of general structure (II), r is 0, p is 1 and q is 1;

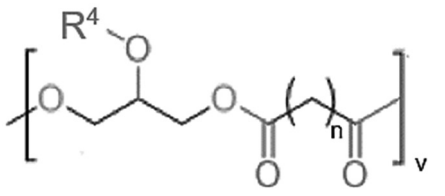
iv) x is 0, y is 1, z is 1, R^1 is the substituent of general structure (II), r is 1, p is 1 and q is 0; or

v) x is 1, y is 1, z is 0, R^1 is the substituent of general structure (II), r is 1, p is 1 and q is 0.

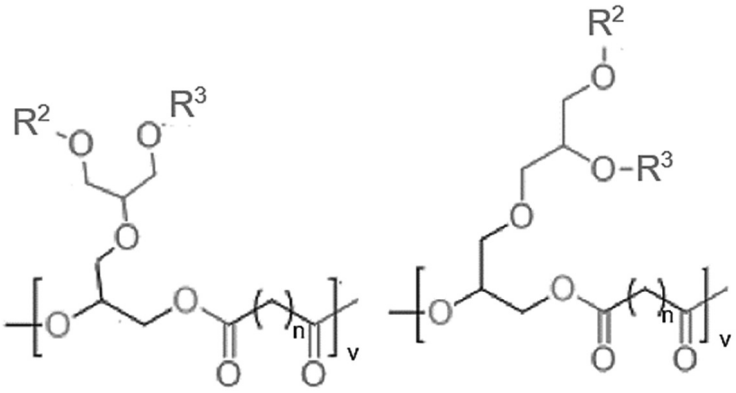
4. The polymer of claim 3, wherein when x is 1, y is 1, and z is 0, R^1 is not a linear or branched C_1-C_6 alkyl.

5. The polymer of any one of the preceding claims, wherein the polymer has the following structure:

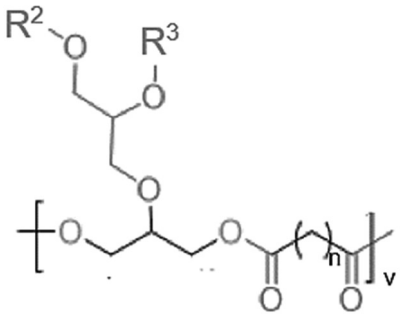


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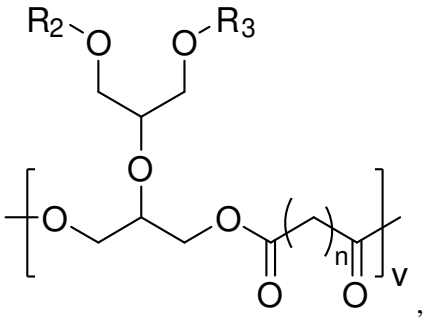
,



,



, or



,

wherein R^2, R^3 and R^4 are each independently linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

6. The polymer according to any one of the preceding claims, wherein the polymer is a bottle brush polyester.

7. The polymer according to claim 6, wherein the bottle brush polyester is a branched bottle brush polyester.

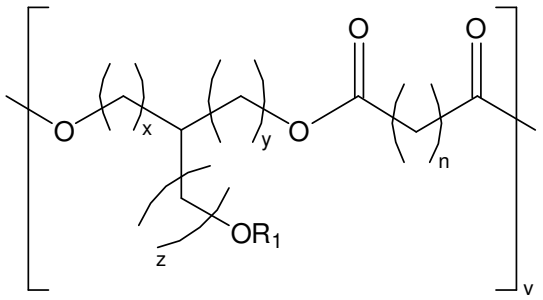
8. The polymer according to any one of the preceding claims, wherein the polymer is a biodegradable polymer.

9. The polymer according to any one of the preceding claims, wherein the polymer has a molecular weight in the range of 7,000 to 100,000.

10. The polymer according to any one of the preceding claims, wherein the polymer has an intrinsic viscosity in the range of 0.2 dL/g to 2.5 dL/g, or a melting temperature in the range of -40 °C to 100 °C, or a degradation temperature of above 300 °C.

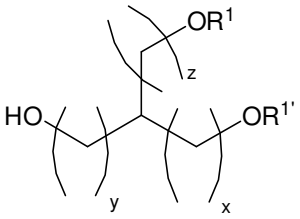
11. A foam, gel, thermoplastic or elastomer comprising the polymer according to any one of the preceding claims.

12. A method for preparing a polymer having the following general structure (I):



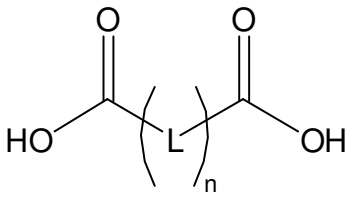
(I),

comprising the step of providing a glyceryl ether having the following general structure (III):

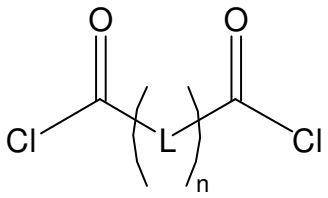


(III)

and contacting the glyceryl ether having general structure (III) with a dicarboxylic acid having the following general structure (IVa) or a diacyl chloride having the following structure (IVb):



(IVa),



(IVb)

wherein L is $-CH_2-$ or aryl;

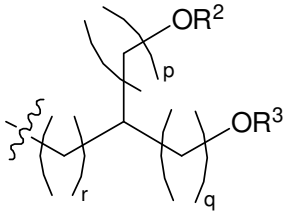
under polymer reaction conditions,

wherein

x, y and z are each independently 0 or an integer of 1 to 5;

n is an integer of 1 to 24; and

R^1 and $R^{1'}$ are each independently H, linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, linear or branched C_2-C_{30} alkynyl; or a substituent having the following general structure (II):



(II)

wherein

p, q and r are each independently 0 or an integer from 1 to 5;

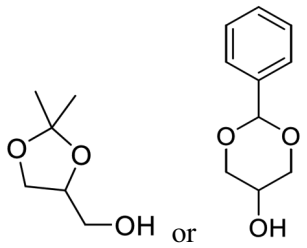
R^2 and R^3 are each independently H or linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl;

and

~~~ is where the substituent of general structure (II) attaches to the glyceryl ether of general structure (III),

wherein R^1 or $R^{1'}$ in the glyceryl ether having general structure (III) is H but R^1 and $R^{1'}$ are not both H.

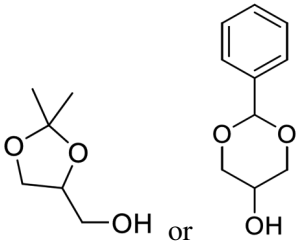
13. The method according to claim 12, wherein the providing step comprises reacting a compound of the following structure:



with a linear or branched C_1-C_{30} alkyl halide, linear or branched C_2-C_{30} alkenyl halide, or linear or branched C_2-C_{30} alkynyl halide, under glyceryl ether reaction conditions.

14. The method according to claim 13, wherein the halide is a bromide.

15. The method according to claim 13 or 14, wherein the glyceryl ether reaction condition comprises Williamson Ether Synthesis, comprising contacting the compound of the following structure:
~~~

 or with an alkali metal or an an alkali metal hydride at a temperature in the range of -4 °C to 4 °C in a solvent, wherein the solvent is preferably toluene, adding the linear or branched C_1-C_{30} alkyl halide, linear or branched C_2-C_{30} alkenyl halide, or linear or branched C_2-C_{30} alkynyl halide to form a mixture and stirring the mixture at a temperature in the range of 60 °C to 80 °C for a duration in the range of 3 hours to 24 hours.

16. The method according to claim 15, wherein the method is followed by acidification, wherein the acidification step is performed in a solvent comprising 1M aqueous HCl and ethanol at a volume ratio in the range of 5:1 to 2:1.

17. The method according to any one of claims 12 to 16, wherein

i) x is 0, y is 1, z is 1, R^1 is linear or branched C_1-C_{30} alkyl and $R^{1'}$ is H;

ii) x is 0, y is 1, z is 1, $R^{1'}$ is linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl and R^1 is H;

iii) x is 1, y is 1, z is 0, R^1 is linear or branched C_1-C_{30} alkyl and $R^{1'}$ is H;

iv) x is 1, y is 1, z is 0, $R^{1'}$ is linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl and R^1 is H;

v) x is 0, y is 1, z is 1, R^1 is the substituent of general structure (II), r is 0, p is 1, q is 1 and $R^{1'}$ is H;

vi) x is 0, y is 1, z is 1, $R^{1'}$ is the substituent of general structure (II), r is 0, p is 1, q is 1 and R^1 is H;

vii) x is 0, y is 1, z is 1, R^1 is the substituent of general structure (II), r is 1, p is 1, q is 0 and $R^{1'}$ is H;

viii) x is 0, y is 1, z is 1, $R^{1'}$ is the substituent of general structure (II), r is 1, p is 1, q is 0 and R^1 is H;

ix) x is 1, y is 1, z is 0, R^1 is the substituent of general structure (II), r is 1, p is 1, q is 0 and $R^{1'}$ is H;

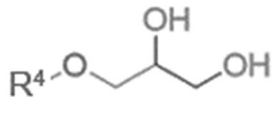
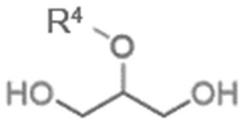
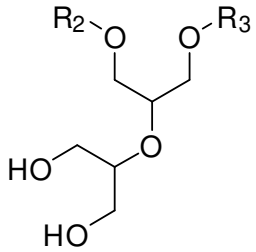
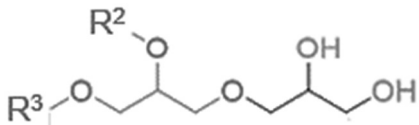
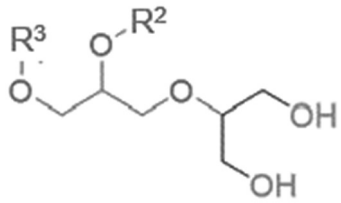
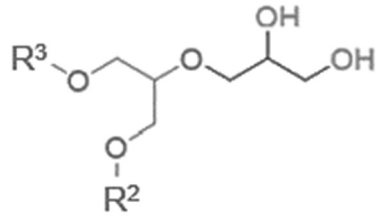
x) x is 1, y is 1, z is 0, $R^{1'}$ is the substituent of general structure (II), r is 1, p is 1, q is 0 and R^1 is H;

xi) x is 0, y is 1, z is 1, R^1 is the substituent of general structure (II), r is 0, p is 1, q is 1 and $R^{1'}$ is H; or

xii) x is 0, y is 1, z is 1, $R^{1'}$ is the substituent of general structure (II), r is 0, p is 1, q is 1 and R^1 is H.

18. The method of claim 17, wherein when x is 1, y is 1, and z is 0, R^1 is not a linear or branched C_1-C_6 alkyl and $R^{1'}$ is H.

19. The method according to any one of claims 12 to 18, wherein the glyceryl ether having general structure (III) has the following structure:


,

,

,

,

,
or

,

wherein R^2, R^3 and R^4 are each independently linear or branched C_1-C_{30} alkyl, linear or branched C_2-C_{30} alkenyl, or linear or branched C_2-C_{30} alkynyl.

20. The method according to any one of claims 12 to 19, wherein the dicarboxylic acid having general structure (IVa) is selected from the group consisting of 1,3-propanedioic acid, 1,4-butanedioic acid, 1,5-pentanedioic acid, 1,6-hexanedioic acid, 1,7-heptanedioic acid, 1,8-octanedioic, 1,9-nonanedioic acid, 1,10-decanedioic acid, 1,11-undecanedioic acid, 1,12-dodecanedioic acid, 1,13-tridecanedioic acid, 1,14-tetradecanedioic acid, 1,15-pentadecanedioic acid, 1,16-hexadecanedioic acid, 1,17-heptadecanedioic acid, 1,18-octadecanedioic acid, 1,19-nonadecanedioic acid, 1,20-icosanedioic acid, 1,21-heneicosanedioic acid, 1,22-docosanedioic acid, 1,23-tricosanedioic acid, 1,24-tetracosanedioic acid, furan-2,5-dicarboxylic acid, terephthalic acid, naphthalene-2,6-dicarboxylic acid and any mixture thereof, or the diacyl chloride having general structure (IVb) is selected from the group consisting of 1,3-propanedioyl dichloride, 1,4-butanedioyl dichloride, 1,5-

pentanedioyl dichloride, 1,6-hexanedioyl dichloride, 1,7-heptanedioyl dichloride, 1,8-octanedioyl dichloride, 1,9-nonanedioyl dichloride, 1,10-decanedioyl dichloride, 1,11-undecanedioyl dichloride, 1,12-dodecanedioyl dichloride, 1,13-tridecanedioyl dichloride, 1,14-tetradecanedioyl dichloride, 1,15-pentadecanedioyl dichloride, 1,16-hexadecanedioyl dichloride, 1,17-heptadecanedioyl dichloride, 1,18-octadecanedioyl dichloride, 1,19-nonadecanedioyl dichloride, 1,20-icosanedioyl dichloride, 1,21-heneicosanedioyl dichloride, 1,22-docosanedioyl dichloride, 1,23-tricosanedioyl dichloride, 1,24-tetracosanedioyl dichloride, furan-2,5-dicarbonyl dichloride, terephthaloyl chloride, naphthalene-2,6-dicarbonyl dichloride and any mixture thereof.

21. The method according to any one of claims 12 to 20, wherein the glyceryl ether having general structure (III) is contacted with the dicarboxylic acid having general structure (IVa) or diacyl chloride having general structure (IVb) at a molar ratio in the range of 3:1 to 1:2.

22. The method according to any one of claims 12 to 21, wherein the contacting step comprises a first heating step performed at a temperature in the range of 150 °C to 220 °C or under an inert atmosphere.

23. The method according to claim 22, wherein the first heating step further comprises a catalyst.

24. The method according to claim 23, wherein the catalyst is selected from a group consisting of chromium, manganese, iron, cobalt, nickel, copper, zinc, tin, p-toluene sulfonic acid monohydrate and any mixture thereof.

25. The method according to claim 23 or 24, wherein the molar ratio of the catalyst to the glyceryl ether having general structure (III) is in the range of 1:8 to 1:100.

26. The method according to any one of claims 23 to 25, wherein the contacting step further comprises a second heating step performed at a temperature in the range of 150 °C to 250 °C or for a duration in the range of 12 hours to 36 hours or under an inert atmosphere.

27. Use of the polymer according to any one of claims 1 to 10 or the foam, gel, thermoplastic or elastomer according to claim 11 as a soft-tissue alternative, lubricant, surface coating, motion control grease, ultrasoft surfaces, in nanocapsules, in sensing and in delivery applications.