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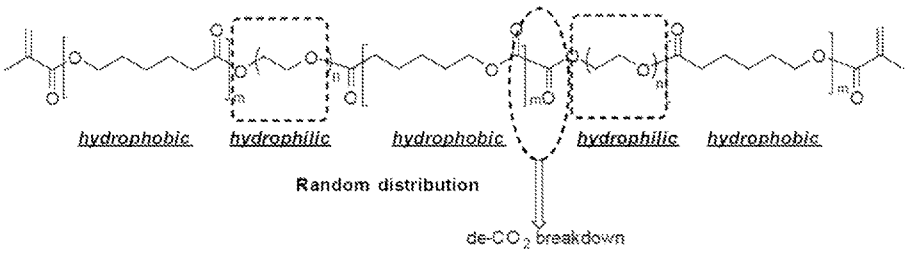


FIG. 1

(57) Abstract: Provided herein is a copolymeric material comprising one or more random copolymers having have a number average molecular weight of from 800 to 10,000 Daltons, where each of the one or more copolymers comprises each of a constitutional unit derived from caprolactone, a constitutional unit derived from polyethylene glycol and a constitutional unit derived from oxalic acid, where each of the constitutional units are connected via an ester linkage. The copolymers may comprise acrylate capping units, and such copolymers may be useful as an additive in a gel nail polish formulation, whereby a gel nail polish prepared using said formulation may be removed from a user's nail by ultrasonic irradiation.

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# PHOTO-CROSSLINKABLE ACRYLATES FOR NAIL COSMETIC APPLICATIONS

## Field of the Invention

The invention relates to a copolymeric material useful in gel nail polish formulations, and to a gel nail polish formulation comprising the copolymeric material. The invention also relates to a method of removing a cured gel nail polish from a nail.

## Background

Ultraviolet (UV) gel nails, Shellac and Polygels are used by millions of people worldwide. These nail cosmetic formulations (nail polish formulations) rely on a fast curing process of acrylate or methacrylate mixtures under UV irradiation to form long lasting and chip-resistant coatings on top of the natural nail plates. However, a significant drawback of these types of nail polish is that the removal of the cured coatings is painful to users because it requires human fingers to be soaked in acetone for a long period of time, followed by painful scraping and filing. It is well documented that this removal process would cause physical damages to human nail plates and may lead to traumatic onycholysis (*J. Cosmet. Dermatol.* **2012**, *11*, 27–29; *Clin. Exp. Dermatol.* **2019**, *44*, 599–605). In addition, the use of acetone in the removal process is a long standing problem of the nail cosmetic industry.

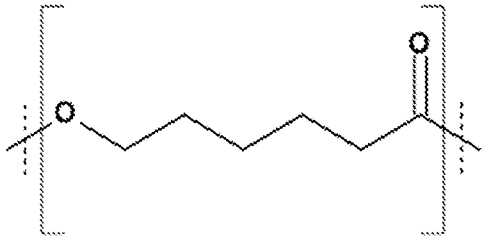
Therefore, there is a need for new photocrosslinkable nail polish formulations which may be easily removed without causing pain or harm to a user.

## Summary of the Invention

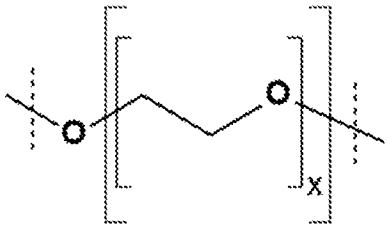
The current inventors have surprisingly found that a copolymeric material as defined herein may function as an additive to a nail polish formulation, enabling the cured nail polish to be easily removed using ultrasound irradiation in water. Thus, a nail polish formulation comprising the copolymeric material of the invention may be easier to remove than existing gel nail polish formulations, whilst providing the same high stability, scratch resistance and glossiness of existing gel nail polish formulations.

The invention therefore provides the following numbered clauses.

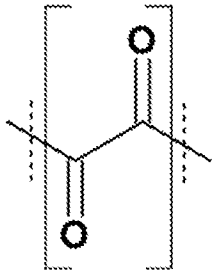
1. A copolymeric material comprising one or more random copolymers, where each of the one or more copolymers comprises each of the constitutional units of formulae (Ia), (Ib) and (Ic):



(Ia)



(Ib)



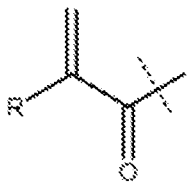
(Ic),

where each of the dotted lines represents a point of attachment of each constitutional unit to a further constitutional unit *via* an ester linkage; and

x is an integer for from 2 to 15, wherein

each of the copolymers in the copolymeric material have a number average molecular weight of from 800 to 10,000 Daltons.

2. The copolymeric material according to Clause 1, wherein each of the one or more copolymers further comprises two capping units of formula (Id):



(Id)

wherein R represents H or a $C_{1-6}$ alkyl group; and

the dashed line represents the point of attachment to the rest of the copolymer *via* an ester linkage.

3. The copolymeric material according to Clause 2, wherein R represents H or methyl, optionally wherein R represents methyl.

4. The copolymeric material according to any one of the preceding clauses, wherein each of the one or more copolymers is a random copolymer or a random block copolymer.

5. The polymer according to any one of the preceding clauses, wherein each of the one or more copolymers comprises from 1 to 5 constitutional units of formula (Ic), such as from 1 to 4 constitutional units of formula (Ic), such as from 2 to 3 constitutional units of formula (Ic).

6. The copolymeric material according to any one of the preceding clauses, wherein in formula (Ib), x is an integer of from 4 to 12, such as from 5 to 8.

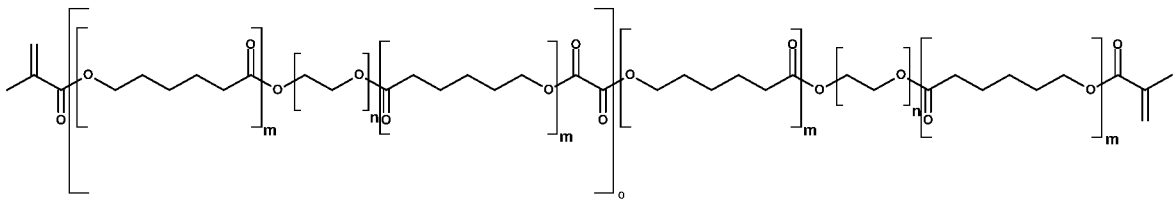
7. The copolymeric material according to any one of the preceding clauses, wherein each of the one or more copolymers have a number average molecular weight of from 1,000 to 2,500 Daltons.

8. The copolymeric material according to any one of the preceding clauses, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 15:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 15:1,
optionally wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 10:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 10:1.

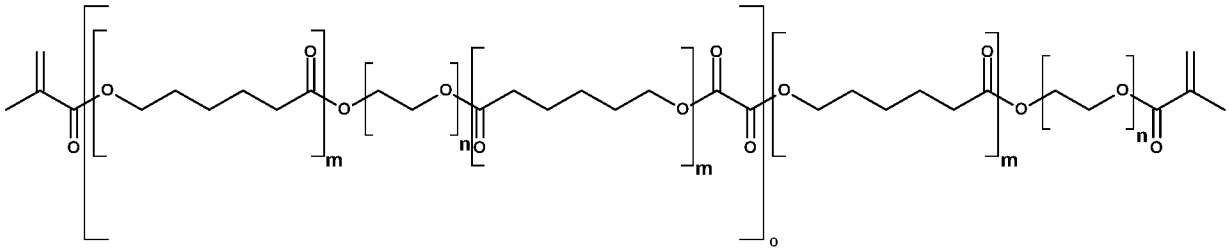
9. The copolymeric material according to any one of the preceding clauses, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 6:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 6:1.

10. The copolymeric material according to any one of the preceding clauses, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 5.5:1;
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 5.5:1; and
the molar ratio of constitutional units of formula (Ib) to (Ic) is from 0.8:1 to 1.2:1.

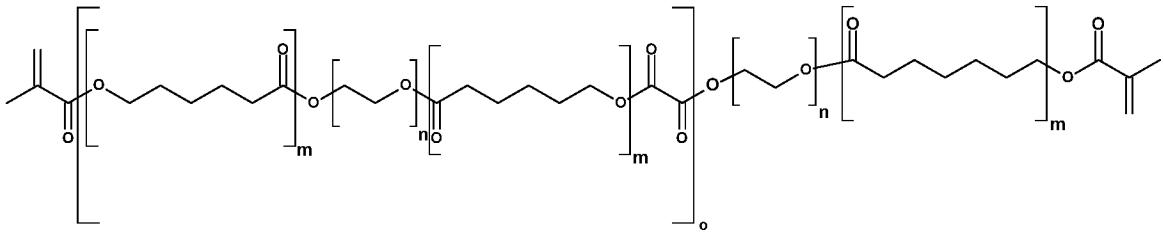
11. The copolymeric material according to any one of the preceding clauses, wherein the one or more copolymers is selected from one or more of the formula (IIa), (IIb), (IIc) and (IId):



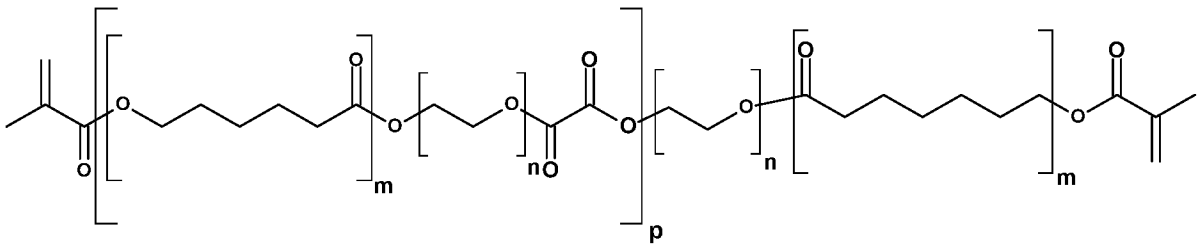
(IIa);



(IIb);



(IIc); and



(IId),

where m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 15:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 15:1; and

o and p are integers selected from 1 to 5.

12. The copolymeric material according to Clause 11, wherein m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 6:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 6:1.

13. The copolymeric material according to Clause 11, wherein m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 5.5:1;

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 5.5:1; and

the molar ratio of constitutional units of formula (Ib) to (Ic) is from 0.8:1 to 1.2:1.

14. The copolymeric material according to any one of Clauses 11 to 13, wherein the one or more copolymers includes the copolymer according to formula (IIa).

15. A gel nail polish formulation comprising a copolymeric material according to any one of Clauses 1 to 14.

16. A method of removing from a nail a gel nail polish formed by curing a gel nail polish formulation according to Clause 15, said method comprising the steps of:

(i) providing a nail coated with a gel nail polish formed by curing a gel nail polish formulation according to Clause 15; and

(ii) subjecting the nail to pulsed ultrasonic irradiation at a frequency of from 750 kHz to 1.5 MHz over a period of time until full or partial delamination of the gel nail polish from the nail is achieved.

17. The method according to Clause 16, wherein step (ii) comprises subjecting the nail to regular or intermittent bursts of ultrasonic irradiation over the period of time.

18. The method according to Clause 16 or 17, wherein the cumulative ultrasound pulse time is from about 6 to about 30 seconds, and the total irradiation period is from about 1 to about 10 minutes.

19. The method according to any one of Clauses 16 to 18, wherein the ultrasound is applied at a peak negative pressure sufficient to generate inertial cavitation events at an interface of the gel nail polish,

optionally wherein the peak negative pressure is from about 0.25 MPa to 5.0 MPa,

more optionally wherein the peak negative pressure is from about 2.0 MPa to about 5.0 MPa.

20. The method according to any one of Clauses 16 to 18, wherein the ultrasound has a spatial peak intensity of from 1 to 5 W $cm^{-2}$.

21. Use of a polymer according to Clause 2, or according to any one of Clauses 3 to 14 as dependent on Clause 2, as a crosslinking agent.

22. A method of preparing a copolymeric material according to any one of Clauses 1 and Clauses 4 to 14, as dependent upon Clause 1, where the one or more copolymers are not capped with capping units of formula (Id), said method comprising the steps of:

(a) providing a mixture comprising caprolactone, oxalic acid and polyethylene glycol in the presence of a catalyst; and

(b) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the polymeric material.

23. A method of preparing a copolymeric material according to any one of Clauses 1 and Clauses 4 to 14, as dependent upon Clause 1, where the one or more copolymers are not capped with capping units of formula (Id), said method comprising the steps of:

(a) providing an intermediate mixture comprising a catalyst and the reaction product of the reaction of oxalic acid with polyethylene glycol; and

(b) reacting the mixture with caprolactone to form the copolymeric material.

24. The method according to Clause 23, wherein the mixture in step (a) of Clause 22 is obtained by the steps of:

(i) providing a mixture comprising oxalic acid, polyethylene glycol and a catalyst; and

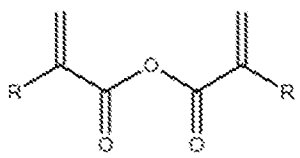
(ii) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the intermediate mixture.

25. The method according to any one of Clauses 23 to 24, wherein the catalyst is $Ti(BuO)_4$ or *para*-toluenesulfonic acid, provided that when the catalyst is *para*-toluenesulfonic acid a solvent is part of the mixture and water is removed from the reaction as it progresses, optionally wherein the solvent is toluene.

26. A method of preparing a copolymeric material according to any one of Clauses 2 and Clauses 3 to 14, as dependent upon Clause 2, said method comprising the steps of:

(A) providing a copolymeric material according to any one of Clauses 1 and Clauses 4 to 14, as dependent upon Clause 1, where the one or more copolymers are not capped with capping units of formula (Id); and

(B) reacting the copolymeric material according to any one of Clauses 1 and Clauses 4 to 14, as dependent upon Clause 1, where the one or more copolymers are not capped with capping units of formula (Id) with a compound of formula (III) to provide a copolymeric material according to Clause 2 or any one of Clauses 3 to 13 as dependent on Clause 2,



(III),

where R is as defined in Clause 2 or 3.

**Brief Description of the Figures**

**FIG. 1** depicts the structural design of new photo-crosslinkers responsible for ultrasound responsiveness breakdown of the UV-cured coatings.

**FIG. 2** depicts the (A) UV curing property of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates (**1**), and (B) mechanical strength of UV cured films with formulations made of Gellyfit topcoat (GT) and photocrosslinkers **1a-c** at 1 g/mL concentrations in butyl acetate.

**FIG. 3** depicts the commercial UV gels in Singapore market.

**FIG. 4** depicts the comparison of the mechanical strength of the UV cured films with no addition of solvent during curing time.

**FIG. 5** depicts (A) a schematic of an ultrasound setup for irradiating nail chamber, and (B) representative image of clip-based nail holders for fixing coated acrylic nails into the reaction chamber for ultrasonic irradiation.

**FIG. 6** depicts the comparative performance of YE02-025R5 series additives with GellyFit commercial coat. With ultrasound at a 5% duty cycle and 5 minutes (min) irradiation period, complete removal of the additive-containing films was observed. The control coating (GellyFit_ctrl) comparatively exhibited no remarkable change after ultrasound.

**FIG. 7** depicts the no full-delamination of coatings using conventional low frequency ultrasound on acrylic nails.

**FIG. 8** depicts the structures of products formed in the one-pot condensation step to prepare **5**.

**FIG. 9** depicts the structures of photocrosslinkers in the comparative study of mechanical strengths of UV-cured films.

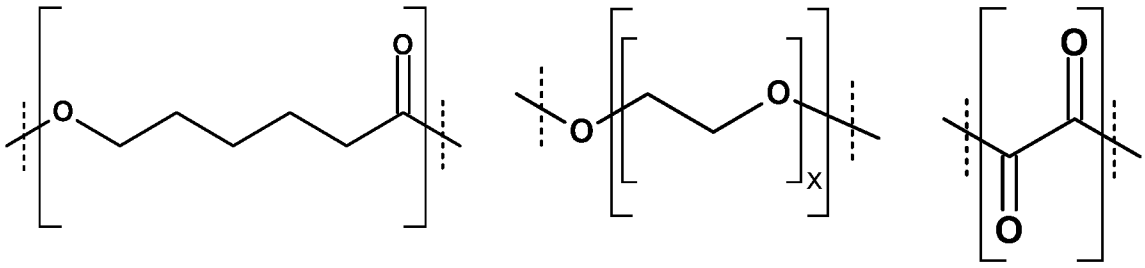
**FIG. 10** depicts the $H_2O_2$-induced film breakdown experiments.

**FIG. 11** depicts the $H_2O_2$-induced degradation of UV-cured films.

**FIG. 12** depicts the summary of structure-properties relationship.

**Detailed Description of the Invention**

It has been surprisingly found that a new copolymeric material may be useful in gel nail polish formulations because it enables the formulation to be removed through the use of ultrasound, rather than through the use of solvents. This, in a first aspect of the invention, there is provided a copolymeric material comprising one or more random copolymers, where each of the one or more copolymers comprises each of the constitutional units of formulae (Ia), (Ib) and (Ic):




(Ia) (Ib) (Ic),

where each of the dotted lines represents a point of attachment of each constitutional unit to a further constitutional unit *via* an ester linkage; and
x is an integer for from 2 to 15, wherein
each of the copolymers in the copolymeric material have a number average molecular weight of from 800 to 10,000 Daltons.

In embodiments herein, the word "comprising" may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word "comprising" may also relate to the situation where only the components/features listed are intended to be present (e.g. the word "comprising" may be replaced by the phrases "consists of" or "consists essentially of"). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word "comprising" and synonyms thereof may be replaced by the phrase "consisting of" or the phrase "consists essentially of" or synonyms thereof and *vice versa*.

The phrase, "consists essentially of" and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure,

such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

As used herein, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a copolymer” includes mixtures of two or more such copolymers, reference to “an interface” includes two or more such interfaces, reference to “the catalyst” includes mixtures of two or more such catalysts, and the like.

As used herein, a “copolymeric material” refers to a material comprising one or more copolymers. Thus, the copolymeric material of the invention comprises one or more random copolymers where each of the one or more copolymers comprises each of the constitutional units of formulae (Ia), (Ib) and (Ic).

The random copolymer(s) present in the copolymeric material may be random copolymers, or more particularly, may be random block copolymers, i.e. a polymer formed from a random arrangement of blocks. Blocks present in a random block copolymer may themselves comprise a random or non-random arrangement of the relevant constitutional units. In some embodiments of the invention that may be mentioned herein, a random block copolymer may generally comprise hydrophilic and hydrophobic blocks. In some embodiments of the invention that may be mentioned herein, a random block copolymer may comprise blocks formed from a single constitutional unit, i.e. blocks formed from a polymeric or oligomeric chain comprising a single constitutional unit, such as hydrophobic blocks comprising (poly)caprolactone or hydrophilic blocks comprising polyethylene glycol.

Without being bound by theory, it is believed that each copolymeric chain comprises from 1 to 5 oxalate moieties, i.e. from 1 to 5 constitutional units of formula (Ic). It is further believed that each copolymeric typically comprises from 1 to 3 constitutional units of formula (Ic). The remainder of each copolymeric chain is believed to be formed from constitutional units of formula (Ia) and (Ib), e.g. from blocks comprising constitutional units of formula (Ia) and (Ib), whether alone or mixed.

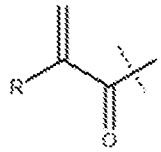
In the constitutional units of formula (Ia), (Ib) and (Ic), each of the dotted lines represents a point of attachment of each constitutional unit to a further constitutional unit *via* an ester linkage. As will be appreciated by a person skilled in the art, a constitutional unit of formula (Ib) is only able to form an ether linkage to a constitutional unit of formula (Ia) or (Ic), and cannot form an ether linkage to another constitutional unit of formula (Ib). As a result, the

length of polyethylene glycol blocks within the copolymeric material will broadly correspond to the length of a polyethylene glycol used to prepare the copolymeric material.

Within constitutional units of formula (Ib), x is an integer of from 2 to 15. In some embodiments of the invention that may be mentioned herein, x may be an integer of from 4 to 12, such as 5 to 10, for example 5 to 8, e.g. 8. In some embodiments of the invention that may be mentioned herein, the constitutional unit of formula (Ib) may be derived from a commercially available polyethylene glycol having a number average molecular weight of 400 (e.g. PEG400).

In the copolymeric material of the invention, each of the copolymers in the copolymeric material have a number average molecular weight of from 800 to 10,000 Daltons. This is believed to be advantageous because copolymers having higher molecular weights may have disadvantageously low solubility in common solvents for nail polish formulations (e.g. n-butyl acetate and ethyl acetate), which reduces their effectiveness as additives for a nail polish formulation. In some embodiments of the invention that may be mentioned herein, each of the one or more copolymers may have a number average molecular weight of from 1,000 to 2,500 Daltons. This molecular weight range is believed to provide copolymers having excellent solubility and compatibility with a gel nail polish formulation.

In some embodiments of the invention that may be mentioned herein, each of the one or more copolymers further comprises two capping units of formula (Id):




(Id)

wherein R represents H or a $C_{1-6}$ alkyl group; and
the dashed line represents the point of attachment to the rest of the copolymer *via* an ester linkage.

In some embodiments of the invention that may be mentioned herein, R may represents H or methyl, such as methyl.

Capping units of formula (Id) allow the copolymers to act as acrylate crosslinking agents. Since gel nail polish formulations generally comprise acrylate (or methacrylate) crosslinkable groups, the copolymeric material of the invention may be used as a crosslinking agent within gel nail polish formulations. As will be understood by a person skilled in the art, references herein to

crosslinking involving the copolymeric material of the invention will be understood to be references to crosslinking involving the copolymeric material of the invention in which the copolymers comprise capping units of formula (Id).

As mentioned above, the copolymeric material of the invention may be used as a crosslinking agent in a nail polish formulation (i.e. the copolymeric material of the invention in which the copolymers comprise capping units of formula (Id) may be used as a crosslinking agent in a nail polish formulation). The presence of oxalate esters within the copolymeric material of the invention means that polymers that incorporate the copolymeric material according to the invention are susceptible to decomposition under ultrasonic irradiation in water. Without being bound by theory, this decomposition is believed to be caused by decarboxylation of the oxalate ester bonds and resulting cleavage of the crosslinking moiety. This means that cured gel nail polish formulations incorporating the copolymeric material according to the invention may be easily removed by exposing the cured gel nail polish to ultrasound irradiation in water.

As mentioned above, each of the one or more copolymers are believed to comprise from 1 to 5 constitutional units of formula (Ic). Thus, in some embodiments of the invention that may be mentioned herein, each of the one or more copolymers may comprise from 1 to 4 constitutional units of formula (Ic), such as from 2 to 3 constitutional units of formula (Ic).

For the avoidance of doubt, it is herein explicitly contemplated that any end point of any range may be combined with any other end point for any range associated with the same variable. Thus, from the ranges disclosed above in relation to the number of constitutional units of formula (Ic) in each of the one or more copolymers, the following ranges are herein explicitly contemplated:
from 1 to 5; from 1 to 4; from 1 to 3; from 1 to 2;
from 2 to 5; from 2 to 4; from 2 to 3;
from 3 to 5; from 3 to 4; and
from 4 to 5.

As will be appreciated by a person skilled in the art, the molar ratio of constitutional units of formula (Ia), (Ib) and (Ic) is not particularly limited, provided the resulting copolymeric chains have at least one constitutional unit of formula (Ic) and are compatible with a gel nail polish formulation.

In some embodiments of the invention that may be mentioned herein:

the molar ratio of constitutional units of formula (Ia) to (Ib) may be from 3:1 to 15:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) may be from 3:1 to 15:1.

In some embodiments of the invention that may be mentioned herein:

the molar ratio of constitutional units of formula (Ia) to (Ib) may be from 3:1 to 10:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) may be from 3:1 to 10:1.

In some embodiments of the invention that may be mentioned herein:

the molar ratio of constitutional units of formula (Ia) to (Ib) may be from 4.5:1 to 6:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) may be from 4.5:1 to 6:1.

In some embodiments of the invention that may be mentioned herein:

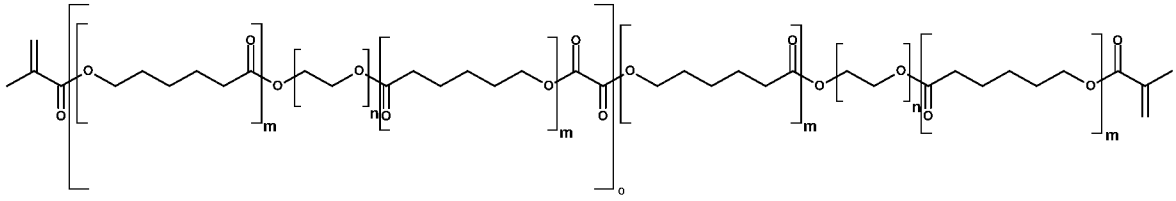
the molar ratio of constitutional units of formula (Ia) to (Ib) may be from 4.5:1 to 5.5:1;

the molar ratio of constitutional units of formula (Ia) to (Ic) may be from 4.5:1 to 5.5:1; and

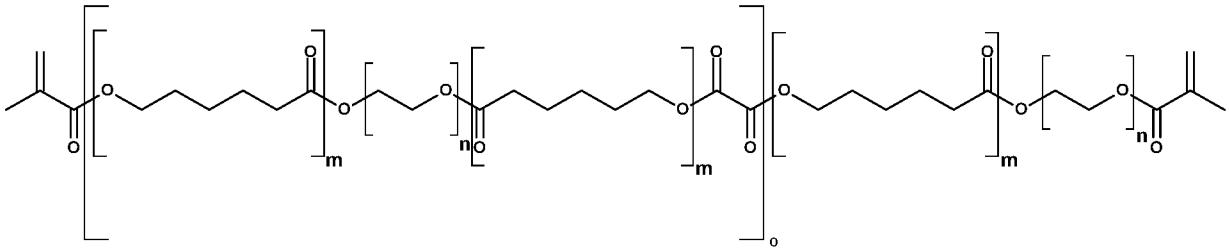
the molar ratio of constitutional units of formula (Ib) to (Ic) may be from 0.8:1 to 1.2:1.

As will be appreciated by a person skilled in the art, the ratio of constitutional units may be controlled by varying the ratio of starting materials used when preparing the copolymeric material. For example, the ratio of constitutional units may be controlled by varying a ratio of ε-caprolactone, polyethylene glycol and oxalic acid as starting materials. In this way, the hydrophobic/hydrophilic balance of the resulting copolymeric chains may also be controlled.

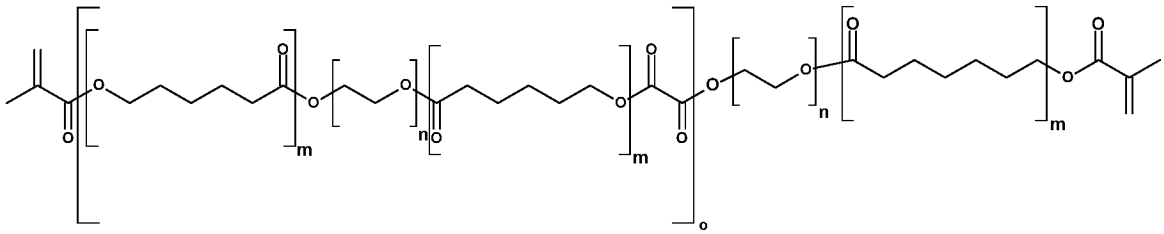
When a polymerisation reaction is conducted between ε-caprolactone, polyethylene glycol and oxalic acid, the following structures (IIa) to (IId) are believed to be the dominant products, with formula (IIa) being believed to be the major product, and formula (IIb) to (IId) believed to be minor products.



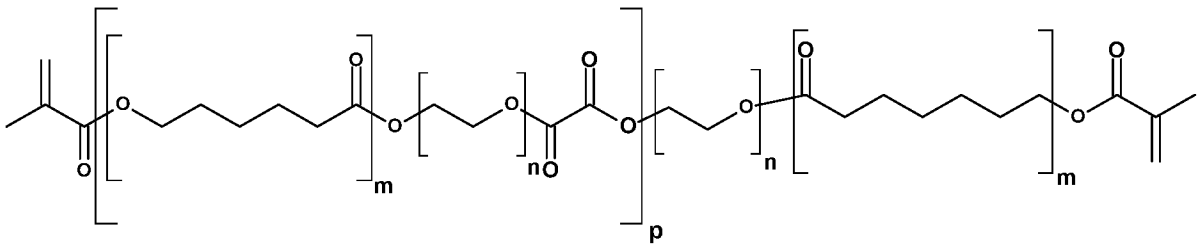
(IIa);



(IIb);



(IIc); and



(IId).

In formula (IIa) to (IId), m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 15:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 15:1; and

o and p are integers selected from 1 to 5.

In some embodiments of the invention that may be mentioned herein, m, n, o and p may be selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 6:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 6:1.

In some embodiments of the invention that may be mentioned herein, m, n, o and p may be selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 5.5:1;

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 5.5:1; and

the molar ratio of constitutional units of formula (Ib) to (Ic) is from 0.8:1 to 1.2:1.

In some embodiments of the invention that may be mentioned herein, the one or more copolymers may include the copolymer according to formula (IIa).

The invention provides a gel nail polish formulation comprising a copolymeric material according to the invention. Such a gel nail polish formulation may be prepared by mixing a copolymeric material according to the invention with a gel nail polish formulation, such as a commercially available gel nail polish formulation. Alternatively, the gel nail polish formulation may be formed around the use of the copolymeric material disclosed herein. A gel nail polish formulation according to the invention may be suitable for forming a base coat, a colour coat, or a top coat of a gel nail polish.

Thus, in some embodiments of the invention that may be mentioned herein, the gel nail polish formulation may be a base coat gel nail polish formulation. In some embodiments of the invention that may be mentioned herein, the gel nail polish formulation may be a colour coat gel nail polish formulation. In some embodiments of the invention that may be mentioned herein, the gel nail polish formulation may be a top coat gel nail polish formulation.

As will be appreciated by a person skilled in the art, many different gel nail polish formulations exist and such formulations may comprise a wide range of ingredients. Examples of suitable components and weight percent amounts of these components are provided in Tables A-C below. Nevertheless, a person skilled in the art will appreciate that other formulations are possible. In some embodiments of the invention, a gel nail polish formulation may be prepared by adding the copolymeric material of the invention to a commercially available gel nail polish formulation.

Table A: Exemplary base coat formulation

| **Typical formulation of a base coat nail gel** | **Chemical name** | **Weight Percentage** |
|---|---|---|
| **Commercial photocrosslinkers** | Di-HEMA TrimethylhexylDicarbamate | 2-20% |
| | Hexamethylene diacrylate | 20-50% |
| **Monomers** | 2-hydroxylethyl methacrylate | 5-20% |
| | Hydroxypropyl methacrylate | 5-20% |
| **Photoinitiators** | Trimethylbenzoyl diphenylphosphine oxide | 0.5-4% |

| | | |
|---|---|---|
| | Hydroxycyclohexyl phenyl ketone | 0.5-4% |
| **Solvent** | Butyl acetate | 5-20% |
| | Ethyl acetate | 5-20% |
| **Copolymeric material of the invention** | | 5-20% |

Table B: Exemplary colour coat formulation

| **Typical formulation of a colour coat gel** | **Chemical name** | **Weight Percentage** |
|---|---|---|
| **Photocrosslinkers** | Di-HEMA TrimethylhexylDicarbamate | 2-20% |
| | Triethyleneglycol Dimethacrylate | 2-10% |
| | Trimethylolpropane Trimethacrylate | 2-10% |
| **Polymerizable monomers** | 2-hydroxylethyl methacrylate | 5-20% |
| | Hydroxypropyl methacrylate | 5-20% |
| | 2-norbonyl acrylate | 5-20% |
| **Photoinitiators** | Trimethylbenzoyl diphenylphosphine oxide | 0.5-4% |
| | Hydroxycyclohexyl phenyl ketone | 0.5-4% |
| **Colorants and other ingredients** | Sucrose Acetate Isobutyrate, Sucrose Benzoate, Stearalkonium Hectorite, Ethyl Acetate, Silica, Benzophenone, Hydroxycyclohexyl phenyl ketone, Mica, Titanium Dioxide, Red 201, Red 6, Yellow 10, , Red 7 (Lake), Blue 1 | 5-20% |

Table C: Exemplary top coat formulation

| **Typical formulation of a base coat gel** | **Chemical name** | **Weight Percentage** |
|---|---|---|
| **Photocrosslinkers** | Di-HEMA TrimethylhexylDicarbamate | 2-20% |
| | Acrylates/Carbamate Copolymer (Urethane Acrylate) | 5-20% |
| | Pentaerythritol tetraacrylate | 5-20% |
| | Pentaerythritol triacrylate | 5-20% |
| | Tripropylene glycol triacrylate | 5-20% |
| | Trimethylolpropane Trimethacrylate | 5-20% |
| **Polymerizable monomers** | 2-hydroxylethyl methacrylate | 5-20% |

| | | |
|---|---|---|
| | Hydroxypropyl methacrylate | 5-20% |
| | 2-norbonyl acrylate | 5-20% |
| **Photoinitiators** | Trimethylbenzoyl diphenylphosphine oxide | 0.5-4% |
| | Hydroxycyclohexyl phenyl ketone | 0.5-4% |
| **Other solvent or ingredients** | butyl acetate, sucrose benzoate, benzyl dimethyl ketal | 5-20% |
| **Copolymeric material of the invention** | | 5-20% |

A gel nail polish formulation according to the invention may be applied and cured by standard means known in the art, to form a gel nail polish. For example, a gel nail polish formulation may be coated onto a nail (e.g. using a brush), and multiple coats/layers may be applied. As will be understood by a person skilled in the art, a base coat gel nail polish formulation may be applied first, followed by one or more layers of colour coat gel nail polish formulation (also known as gel polish), and finally a top coat gel nail polish formulation. Each coat/layer will be cured (e.g. under UV light) before the subsequent coat/layer is applied. The copolymeric material of the invention may be included in any or all of the coats/layers.

The invention also provides a method of removing from a nail a gel nail polish formed by curing a gel nail polish formulation according to the invention, said method comprising the steps of:

(i) providing a nail coated with a gel nail polish formed by curing a gel nail polish formulation according to the invention; and

(ii) subjecting the nail to pulsed ultrasonic irradiation at a frequency of from 750 kHz to 1.5 MHz over a period of time until full or partial delamination of the gel nail polish from the nail is achieved.

Subjecting the nail to pulsed ultrasonic irradiation may comprise subjecting the nail to regular or intermittent bursts of ultrasonic irradiation over the period of time. For example, the nail may be subjected to regular bursts of ultrasonic irradiation.

Since ultrasonic irradiation in water may be uncomfortable for a subject, it is important that the gel nail polish may be removed without requiring excessively intense or long irradiation. From a perspective of convenience, it is desirable that the removal process is relatively quick. Thus, in some embodiments of the invention that may be mentioned herein, the cumulative

ultrasound pulse time may be from about 6 to about 30 seconds, and the total irradiation period may be from about 1 to about 10 minutes.

Therefore, a gel nail polish comprising the copolymeric material of the invention may be removed by, for example, immersing a subject's hands into an ultrasonication water bath, and then subjecting the subject's hands to bursts of pulsed ultrasound operating at a frequency of about 750 kHz to 1.5 MHz with a spatial peak intensity of from 1 to 5 W $cm^{-2}$ in water. Any appropriate duration of ultrasound irradiation may be utilised. For example, in some embodiments of the invention that may be mentioned herein, the cumulative ultrasound pulse time may be from about 6 to about 30 seconds, and the total irradiation period may be from about 1 to about 10 minutes.

Ultrasound irradiation in water may produce inertial cavitation events, which in turn may generate reactive oxygen species (ROS) such as hydroxyl radicals, singlet oxygen, superoxide and hydrogen peroxide. The ROS may react with oxalate ester groups, resulting in decarboxylation and cleavage of crosslinks in the copolymeric material. Thus, in some embodiments of the invention that may be mentioned herein, the ultrasound may be applied at a peak negative pressure sufficient to generate inertial cavitation events at an interface of the gel nail polish. A skilled person will appreciate that the peak negative pressure sufficient to generate inertial cavitation events at an interface of the gel nail polish will vary depending on other properties of the ultrasound irradiation, such as the frequency of the ultrasound irradiation. In some embodiments of the invention, the peak negative pressure may be about 2.0 MPa to about 5.0 MPa. However, a skilled person will appreciate that other pressures may be used.

While many possible parameters for the ultrasound irradiation are discussed herein, a person skilled in the art will be able to select appropriate ultrasound conditions that are suitable for generating cavitation without causing significant adverse effects for a subject. All such appropriate ultrasound conditions may be used as part of the invention described herein.

The invention also provides the use of a copolymeric material according to the invention as a crosslinking agent (i.e. the invention also provides the use of a copolymeric material according to the invention in which the copolymers comprise capping units of formula (Id) as a crosslinking agent).

The copolymeric material according to the invention in which the one or more copolymers are not capped with capping units of formula (Id) may be made by a one-step or two-step method, both of which are provided by the invention.

The one-step method comprises the steps of:

(a) providing a mixture comprising caprolactone, oxalic acid and polyethylene glycol in the presence of a catalyst; and

(b) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the polymeric material.

The polyethylene glycol may have any appropriate molecular weight, given the required molecular weight for the resulting copolymer. In some embodiments of the invention that may be mentioned herein, the polyethylene glycol may have a molecular weight of about 400.

In some embodiments of the invention that may be mentioned herein, the catalyst may be $Ti(BuO)_4$ or *para*-toluenesulfonic acid, provided that when the catalyst is *para*-toluenesulfonic acid a solvent is part of the mixture and water is removed from the reaction as it progresses. In such cases, the solvent may be toluene.

The two step method comprises the steps of:

(1) providing a mixture comprising oxalic acid, polyethylene glycol and a catalyst;

(2) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the intermediate mixture; and

(3) reacting the intermediate mixture with caprolactone to form the copolymeric material.

As will be appreciated by a person skilled in the art, the two step method provides increased control of the composition of the final copolymeric material, because the length/molecular weight of the oxalate and polyethelyne glycol blocks may be controlled before caprolactone is introduced to the copolymeric backbone. This provides greater control of the respective lengths of the hydrophilic PEG/oxalate blocks and the hydrophobic caprolactone blocks.

In accordance with the two-step method, the invention provides a method of preparing a copolymeric material according to the invention, where the one or more copolymers are not capped with capping units of formula (Id), said method comprising the steps of:

(a) providing an intermediate mixture comprising a catalyst and the reaction product of the reaction of oxalic acid with a polymeric or oligomeric ethylene glycol; and

(b) reacting the mixture with caprolactone to form the copolymeric material.

In some embodiments of the invention, the mixture in step (a) of the above method is obtained by the steps of:

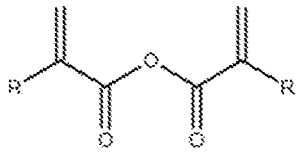
(i) providing a mixture comprising oxalic acid, polyethylene glycol and a catalyst; and

(ii) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the intermediate mixture.

The invention also provides a method of preparing a copolymeric material according to the invention in which the copolymers are capped with capping units of formula (Id), the method comprising the steps:

(A) providing a copolymeric material according to the invention, where the one or more copolymers are not capped with capping units of formula (Id); and

(B) reacting the copolymeric material of step (A) with a compound of formula (III) to provide a copolymeric material according to the invention in which the copolymers are capped with capping units of formula (Id),



(III),

where R is as defined above.

The copolymeric material of the invention may be used in any other application which involves crosslinking, where it may be desirable to reverse a crosslinking reaction with ultrasound irradiation. Thus, the capping groups may be selected to act as a crosslinking agent in any suitable polymeric material, and then a cured material including crosslinks formed by a copolymeric material according to the invention may be "uncured" by ultrasound irradiation. Examples of such applications in which the copolymeric material of the invention may be used include hair cosmetics (e.g. hair styling products), and dental cosmetics (e.g. dental bracket adhesives).

The invention is illustrated by the below Examples, which are not to be construed as limitative.

**Examples**

Materials

Polyethylene glycols (PEG), methyl methacrylate, ε-caprolactone, titanium *tert* butoxidem *p*-toluene sulfonic acid were purchased from Sigma Aldrich. Solvents used in the study as dry tetrahydrofuran (THF), methylene chloride ($CH_2Cl_2$), diethyl ether ($Et_2O$), and toluene were obtained by passing commercially available pre-dried, oxygen-free formulations through activated alumina columns. Methanol (MeOH), and *N*,*N*'-dimethylformamide (DMF) were purchased in anhydrous form and used without further purification. Ethyl acetate (EtOAc), diethyl ether ($Et_2O$), water, methylene chloride ($CH_2Cl_2$), acetone and hexanes were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated.

Analytical techniques

*Nuclear magnetic resonance (NMR) spectroscopy*

NMR spectra were recorded on Bruker DRX-400 or Bruker AV-600 instruments and calibrated using residual undeuterated solvent as an internal reference. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, pent = pentet, hex = hexet, br = broad.

*Gel permeation chromatography (GPC)*

GPC was conducted on a Waters 717 plus autosampler equipped with a Waters 515 pump and a Waters 2414 refractive index (RI) detector. 2 columns: 2 x PLgel 10um Mixed-B (500 to 10,000,000) were applied in sequence for separation. Dimethylformamide was used as the eluent at 0.8 mL/min with column and detector temperature at 50 °C. Poly(methyl methacrylate) standards were used for conventional calibration ranging from 500 to 1 000 000 Daltons.

*TGA*

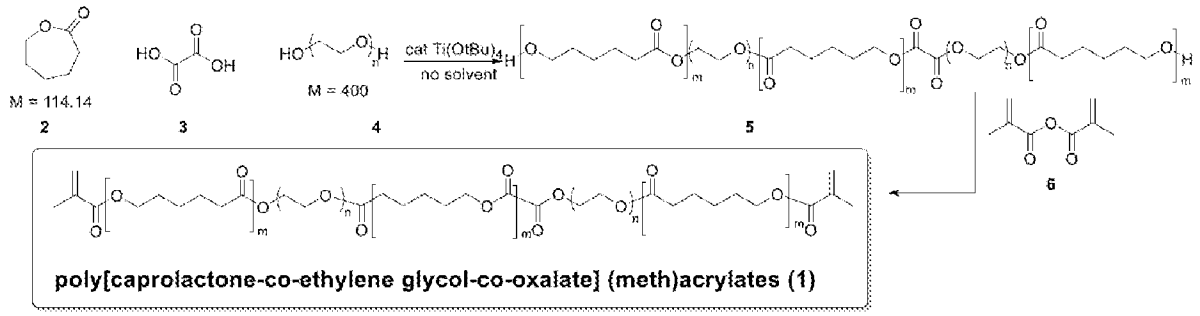
*TGA* was studied using SDT Q600 V20.9 Build 20 instrument with a 10 °C-per-minute increase from 25 °C to 800 °C.

**Example 1. Preparation of poly[caprolactone-co-ethylene glycol-cooxalate] copolymers**

Oxalate ester groups were incorporated into the structure of photo-crosslinkers **1** containing oligocaprolactones and oligoethylene glycols in the backbone as shown in FIG. 1.

A range of poly[caprolactone-co-ethylene glycol-cooxalate] copolymers **1** were obtained by the procedure outlined below. The hydrophobicity of the photocrosslinkers can be modified by

increasing or decreasing the amount of Ɛ-caprolactone **2** and oxalic acid **3**. Similarly, the hydrophilicity of the photocrosslinkers can be easily modified by changing the stoichiometric ratios of polyethylene glycols (PEGs) **4** or by changing PEG's molecular weights.




*Representative procedure to prepare poly[caprolactone-co-ethylene glycol-co-oxalate] copolymers (**5**)*

PEG (2000 mg, 5 mmol, 1 equiv.), oxalic acid (360.28 mg, 4 mmol, 0.8 equiv.) and Ɛ-caprolactone (2853.5 mg, 25 mmol. 5 equiv.) were added to a 10 mL microwave vial. The vial was then sealed and heated at 100 °C under a pressure reduced to 80 mbar for 20 hours (h). After cooling the reaction mixture to room temperature, $Ti(BuO)_4$ (20 mg) was added via a syringe and the reaction mixture was heated at 140 °C for 20 h. After cooling the reaction mixture to room temperature, 100 mL of dichloromethane was added to dissolve the product. Some insoluble materials were removed by filtration, followed by evaporation of dichloromethane. The crude product was then washed with diethyl ether (3 × 10 mL) to afford the desired product **5b** (5 g, 96%).

**5b**: $^1$H NMR (400 MHz, Chloroform-d) δ 4.44 – 4.40 (m, 4H), 4.27 (td, *J* = 6.7, 1.1 Hz, 12H), 4.24 – 4.19 (m, 15H), 4.05 (td, *J* = 6.7, 1.2 Hz, 28H), 3.81 – 3.77 (m, 4H), 3.73 (t, *J* = 4.5 Hz, 4H), 3.71 – 3.57 (m, 182H), 2.40 – 2.23 (m, 48H), 1.80 – 1.73 (m, 15H), 1.72 – 1.49 (m, 80H), 1.40 (ddtd, *J* = 15.3, 9.9, 7.9, 7.4, 5.9 Hz, 44H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.5, 157.9, 129.0, 126.4, 77.4, 77.2, 77.0, 76.7, 72.5, 70.8, 70.7, 70.6, 70.56, 70.49, 70.45, 70.37, 70.2, 69.2, 68.4, 66.85, 66.80, 65.88, 64.19, 64.15, 63.47, 63.44, 61.7, 34.13, 34.0, 33.99, 28.35, 28.31, 28.00, 25.54, 25.50, 25.29, 25.25, 24.58, 24.50, 24.45, 24.38 ppm.

This procedure was to other reactions using different stoichiometric amounts of PEGs, oxalic acid and Ɛ-caprolactone to make other products. Specifically, **5c** (1.5 g) was obtained in 41% yield and **5a** (1.66 g) was obtained in 25% yield. The synthesis of **5a-c** was later optimized with the use of catalytic amounts of para-toluene sulfonic acid in toluene in a Dean-stark system (see Example 6).

Subsequent esterification of **5** with methacrylic anhydride in dichloromethane afforded desired photocrosslinkers **1**.

*Representative procedure to prepare poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates (**1**)*

Poly[caprolactone-co-ethylene glycol-co-oxalate] **5b** (4.5 g, 2 mmol, 1 equiv.), methacrylic anhydride (3468.60, 20 mmol, 10 equiv.), triethyl amine (2276.78, 20 mmol, 1 equiv.) and dichloromethane (20 mL) were added to a 100 mL round-bottom flask (RBF). The reaction mixture was maintained under stirring in dark condition for 20 h. A 2 N aqueous solution of HCl was added to acidify the mixture to pH~2 to remove triethyl amine by extraction. The excess of methacrylic anhydride was quenched with a saturated aqueous sodium bicarbonate solution. The dichloromethane was then separated, dried and evaporated to dryness. The crude product was then washed with diethyl ether (3 × 10 mL) to afford the desired product **1b** (4 g, 88%).

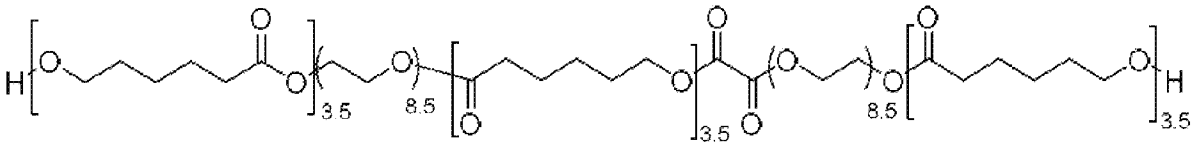
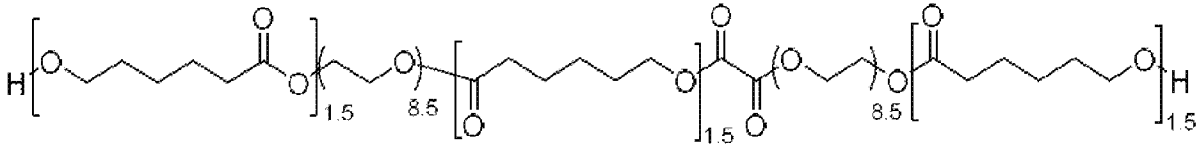
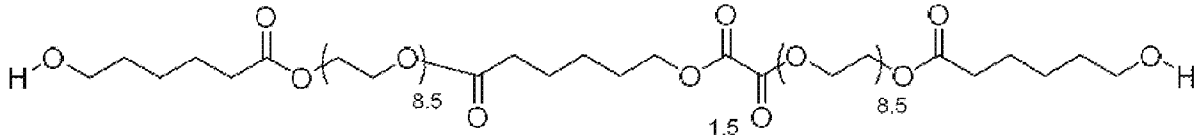
**1b**. $^{1}$H NMR (400 MHz, Chloroform-d) δ 6.21 (t, *J* = 1.0 Hz, 4H), 5.82 – 5.77 (m, 4H), 4.43 – 4.37 (m, 4H), 4.26 (td, *J* = 6.8, 1.0 Hz, 14H), 4.23 – 4.18 (m, 14H), 4.04 (t, *J* = 6.7 Hz, 28H), 3.77 (dd, *J* = 5.6, 4.2 Hz, 3H), 3.73 – 3.57 (m, 164H), 2.31 (dtd, *J* = 15.2, 7.5, 3.2 Hz, 41H), 1.99 (t, *J* = 1.3 Hz, 12H), 1.79 – 1.50 (m, 94H), 1.48 – 1.31 (m, 43H) ppm. $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.7, 173.6, 173.5, 163.2, 158.0, 135.9, 129.1, 76.84, 70.78, 70.70, 70.66, 69.3, 66.9, 64.3, 64.2, 63.5, 34.2, 34.12, 34.08, 28.4, 28.1, 25.63, 25.60, 25.38, 24.67, 24.59, 24.55 ppm.

This same procedure can be applied to other poly[caprolactone-co-ethylene glycol-co-oxalates] to prepare corresponding dimethacrylates. From **5a** (1.86g), **1a** was obtained (1.5 g) in 78% yield. From **5c** (1.6 g), **1c** was obtained (1.1 g) in 65% yield.

Results and discussion

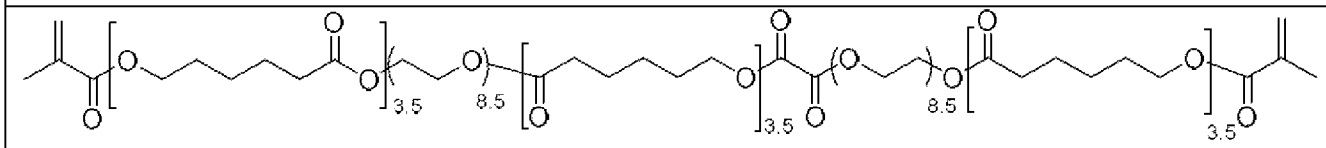
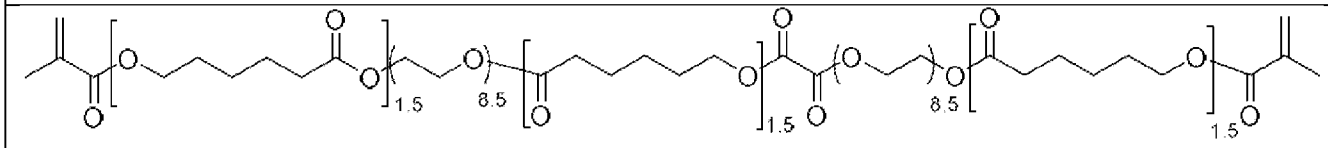
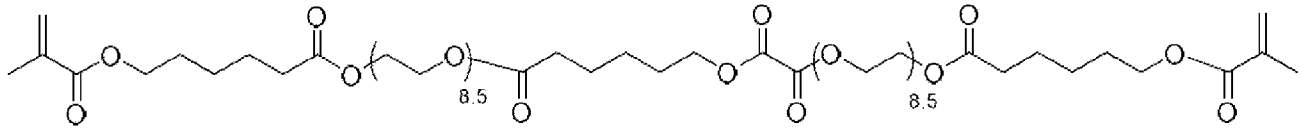
Using this approach, a range of poly[caprolactone-co-ethylene glycol-co-oxalate] copolymers **1** was obtained easily in high yields by a solvent-less ring opening polymerization and esterification process at temperatures between 100 °C and 120 °C in multigram scales (Table 1 and Table 2). It is important to note that prior to heating at 140 °C with the addition of $Ti(BuO)_4$ at a reduced pressure (~ 80 mbar), it is necessary to heat the mixture at 100 °C without the catalyst to prevent formation of insoluble materials. Tin(II) 2-ethylhexanoate was shown to work as effectively as $Ti(BuO)_4$ but it is not preferred due to its toxicity.

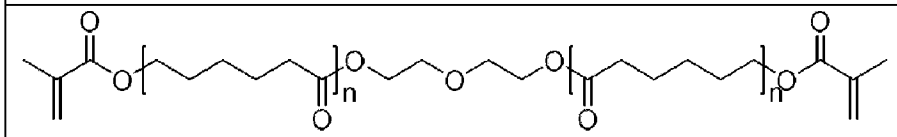
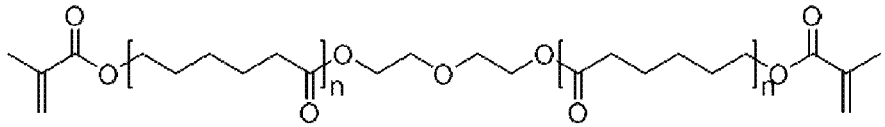
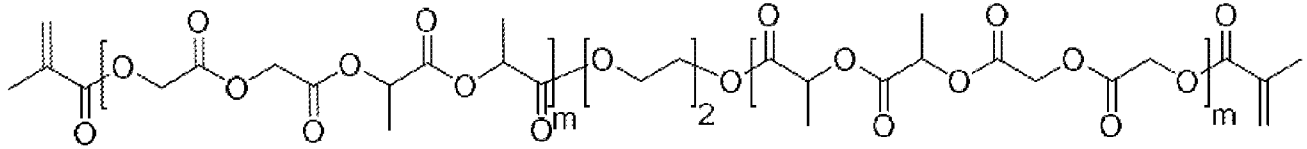
**Table 1.** Intermediate **5**.

| Intermediate 5 | Initial stoichiometric ratio (PEG 400/Oxalic acid/ Ɛ-caprolactone) | Product structure[a] | Number average molecular weight (Mn) (PDI)[b] |
|---|---|---|---|
| **5a** | **1 : 0.8 : 15** |  | 2254 (1.38) |
| **5b** | **1 : 0.8 : 5** |  | 1906 (1.28) |
| **5c** | **1 : 0.8 : 2.5** |  | 1917 (1.27) |

[a] Structure deduced by $^{1}H$-, $^{13}C$-, $^{1}H$-$^{13}C$ Heteronuclear Multiple Bond Correlation (HMBC) and GPC analysis; and [b] GPC determined using dimethylformamide as solvent and poly(methyl methacrylate) standards.

**Table 2**. Poly[caprolactone-co-ethylene glycol-co-oxalate] (meth)acrylates (**1**).

| Poly[caprolactone-co-ethylene glycol-co-oxalate] (meth)acrylates (**1**) | **Temp °C (10% weight loss) [a]** | **Temp °C (5% weight loss) [a]** | **Mn (PDI)** |
|---|---|---|---|
|  **1a** | 269.9998 | 202.368 | 2230 (1.40) |
|  **1b** | 174.4385 | 144.5301 | 2665 (1.37) |
|  **1c** | not yet determined | not yet determined | 2084 (1.32) |

| Comparison with non-oxalate crosslinkers | | | |
|---|---|---|---|
|  **Mn ~ 500 (HK-7)** | 274.0852 | 139.4918 | 530 |
|  **Mn ~ 2000 (YQ-1) or HK-1** | 339.5291 | 303.7742 | 2000 |
|  Polylactide/glycolide 1k Da; LA/GA 1:1 ratios (biodegradable photocrosslinker)- **poly(lactic-*co*-glycolic) acid (PLGA)-diMA** | 114.0962 | 95.60874 | 1000 |

[a] Determined by TGA.

Therefore, with a simple polyesterification and ring-opening, a range of photocrosslinkers **1** was obtained in a two-step sequence.

**Example 2. UV-curing profile assessment of individual photocrosslinkers**

In order to evaluate the photo-curing ability of the individual photocrosslinkers **1** prepared in Example 1, a concentrated butyl acetate solution (100 mg in 50 µL solvent) of the linker was subjected it to *in situ*-curing rheology in the presence of phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide (BAPO, 3 mg) as the photoinitiator.

*UV rheology*

All rheological measurements were done on MCR702 MultiDrive rheometer (Anton-Paar Instruments, Austria, Europe). UV-rheology study was conducted using a quartz glass base and disposable 25 mm parallel plate geometry. OmniCure S1500 Spot UV Curing System was used as a UV light source with a filter to provide 365 nm wavelength and the intensity used was fixed at 25% intensity which equates to 40 mW/cm$^2$ as measured using UV radiometer GENUV MG-07S.

***1** as additives to commercial UV gels*

Several mixtures were prepared containing 10% or 20% weight percent of the additives (**1a**, **1b** or **1c**) with a commercial UV gel selected from Gellyfit topcoat gel, Gellyfit basecoat gel, Lolly topcoat gel, and Lolly basecoat gel.

Results and discussion

The photocrosslinkers **1** were able to form films with relatively strong storage moduli in the range of between $10^5$ and $10^7$ Pascal (FIG. 2).

The three compounds (**1a**, **1b** and **1c**) were then investigated as additives to commercial UV gels in the Singapore market (FIG. 3). After consideration of a range of nail gel products (FIG. 3), the premium Lolly and Gellyfit gels were used to demonstrate the applicability of the polymer additives. Both **1b** and **1c** did not reduce the rigidity of the Gellyfit topcoat gel after the UV-curing step (Table 3).

A benchmarking methodology was developed for the formulations containing additives with commercial formulation gels. The comparison parameters which were derived from the UV-curing rheology (Table 3) enabled an estimate as to which photocrosslinkers would be suitable as additives for a specific commercial gel.

- Max G' [Pa]: the maximum rigidity of the UV-cured thermoset
- Max G' t [s]: the time for the cured thermoset to reach the maximal rigidity
- SG G' [Pa]: rigidity at the sol-gel transition point
- SG t [s]: the time to reach sol-gel transition point
- hardening ratio = (Max G')/(SG G')
- hardening time [s] = Max G't [s] - SG t [s]
- hardening index = hardening ratio / hardening time

**Table 3.** UV-curing data overview.

| Formulation [a] | Max G' [Pa] | SG G' [Pa] | Max G' t [s] | SG t [s] | Hardening Ratio | Hardening Time [s] |
|---|---|---|---|---|---|---|
| **1a**-GT 20-80 | 8.58E+07 | 9.61E+05 | 191 | 73.5 | 89 | 117 |
| **1a**-GB 20-80 | 9.95E+05 | 1.69E+03 | 186 | 117.3 | 590 | 69 |
| **1a**-GT 10-90 | 1.44E+06 | 7.92E+05 | 186 | 72.0 | 2 | 114 |
| **1a**-GB 10-90 | 9.50E+06 | 3.19E+03 | 188 | 100.9 | 2976 | 87 |
| **1b**-GT 20-80 | 4.36E+07 | 3.52E+04 | 188 | 77.5 | 1239 | 111 |
| **1b**-GB 20-80 | 1.39E+06 | 1.73E+03 | 186 | 113.5 | 804 | 72 |
| **1b**-GT 10-90 | 1.15E+08 | 1.27E+04 | 186 | 69.9 | 9058 | 116 |
| **1b**-GB 10-90 | 5.98E+05 | 4.30E+02 | 185 | 123.9 | 1390 | 61 |
| **1b**-LT 10-90 | 6.06E+07 | 6.60E+03 | 188 | 75.9 | 9184 | 112 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **1b**-LB 10-90 | 2.34E+07 | 1.81E+03 | 186 | 77.8 | 12941 | 108 |
| **1c**-GT 20-80 | 1.09E+08 | 5.25E+02 | 208 | 93.7 | 208230 | 114 |
| **1c**-GB 20-80 | 1.25E+06 | 1.91E+02 | 187 | 109.4 | 6566 | 78 |
| **1c**-GT 10-90 | 1.04E+08 | 5.13E+01 | 211 | 94.4 | 2027746 | 117 |
| **1c**-GB 10-90 | 5.91E+05 | 3.61E+02 | 187 | 112.5 | 1636 | 75 |
| **1c** | 1.47E+05 | 2.15E+02 | 187 | 127.2 | 683 | 60 |
| **1c**-LT 10-90 | 9.82E+07 | 3.45E+02 | 189 | 76.7 | 284871 | 112 |
| **1c**-LB 10-90 | 4.22E+06 | 7.04E+03 | 188 | 92.2 | 600 | 95 |

[a] abbreviation: GT = Gellyfit topcoat, GB = Gellyfit basecoat; LT = Lolly topcoat, LB = Lolly basecoat.

The UV-rheology study shows that **1c** did not appear to significantly impact the rigidity of Gellyfit topcoat, suggesting that **1c** has excellent chemical compatibility with Gellyfit topcoat gels.

**Example 3. Ultrasound-induced delamination of UV-cured coatings from acrylic nail surfaces**

Multiple formulations of nail polish were prepared for different layers with examples provided in Table 4 for UV-curing on artificial acrylic nails for high-intensity focused ultrasound (HIFU) experiments.

*UV-curing of coatings on artificial acrylic nail plates*

Different formulations of the different nail polishes were prepared by mixing poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates (prepared in Example 1) or other photocrosslinkers in 10 to 30 weight percent with commercial base-, color- and top-coat gels

(Lolly and Gellyfit brands) and n-butyl acetate as the solvent (50 µL for 100 mg of the total weight of the gel) (see Table 4). The gels' stability was observed over at least 24 h. The nails were applied on acrylic nails (Ivtor, fake nails artificial nature, and short oval manicure) with each layer cured for 3 − 5 min under UV (UV nail lamp, Melody Susie, 365 nm) with UV light intensity of 4-5 mW/cm$^2$.

**Table 4.** Formulations of the different nail polishes.

| Sample Code | Composition, solvent and procedure |
|---|---|
| MN11-031Film-Set 1 | **Base coat**: Lolly basecoat (80 mg), **1a** (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (80 mg), **1a** (20 mg), n-BuOAc (50 µL) |
| MN11-031Film-Set 2 | **Base coat**: Lolly basecoat 100 mg (no addition of the linker)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (80 mg); **1a** (20 mg), n-BuOAc (50 µL) |
| MN11-031Film-Set 3 | **Base coat**: Lolly basecoat (90 mg), **1a** (10 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (90 mg), **1a** (10 mg), n-BuOAc (50 µL) |
| MN11-031Film-Set 4 | **Base coat**: Lolly basecoat 100 mg (no addition of the linker)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (80 mg), **1b** (20 mg), n-BuOAc (50 µL) |
| MN11-031Film-Set 5 | **Base coat**: Lolly basecoat 100 mg (no addition of the linker)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (80 mg), **1b** (20 mg), n-BuOAc (50 µL) |
| MN11-031Film-Set 6 | **Base coat**: Lolly basecoat (90 mg), **1b** (10 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (90 mg), **1b** (10 mg), n-BuOAc (50 µL) |
| MN11- | **Base coat**: Lolly basecoat (80 mg), HK-7 (20 mg), n-BuOAc (50 µL) |

| | |
|---|---|
| 031Film-Set 7 | **Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (80 mg); HK-7 (20 mg), n-BuOAc (50 µL) |
| MN11-<br>031Film-Set 8 | **Base coat**: Gellyfit basecoat (80 mg), **1a** (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Gellyfit topcoat (80 mg), **1a** (20 mg), n-BuOAc (50 µL) |
| MN11-<br>031Film-Set 9 | **Base coat**: Gellyfit basecoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Gellyfit topcoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL) |
| MN11-<br>031Film-Set<br>10 | **Base coat**: Lolly basecoat (80 mg), 1c (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Lolly topcoat (no addition of linker) |
| MN11-<br>025RNX6-Set<br>1 | **Base coat**: Gellyfit basecoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Gellyfit topcoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL) |
| MN11-<br>025RNX6-Set<br>2 | **Base coat**: Gellyfit basecoat (100 mg)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Gellyfit topcoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL) |
| MN11-<br>025RNX6-Set<br>3 | **Base coat**: Gellyfit basecoat (80 mg), **1c** (20 mg), n-BuOAc (50 µL)<br>**Color coat**: Gellyfit color (no addition of linker)<br>**Top coat**: Gellyfit topcoat (100 mg) |

To confirm the importance of the oxalate ester bonds, new formulations in the YE02-025R5 series were prepared (Table 5).

**Table 5.** New formulations in the YE02-025R5 series.

| **Sample Code** | **Composition, solvent and procedure** |
|---|---|
| Gellyfit_ctrl | **Base coat**: Gellyfit basecoat |

| | |
|---|---|
| | **Color coat**: Gellyfit color<br>**Top coat**: Gellyfit topcoat |
| YE02-25R5_1 | **Base coat**: Gellyfit basecoat (80 mg) + **1a** (20 mg) + BuOAc (50 µL)<br>**Color coat**: Gellyfit color (90 mg) + **1a** (10 mg)<br>**Top coat**: Gellyfit topcoat (80 mg) + **1a** (20 mg) + BuOAc (50 µL) |
| YE02-25R5_2 | **Base coat**: Lolly basecoat (80 mg) + **1a** (20 mg) + BuOAc (50 µL)<br>**Color coat**: Gellyfit color (90 mg) + **1a** (10 mg)<br>**Top coat**: Lolly topcoat (80 mg) + **1a** (20 mg) + BuOAc (50 µL) |
| YE02-25R5_3 | **Base coat:** Gellyfit basecoat (80 mg) + YQ-1 (20 mg) + BuOAc (50 µL)<br>**Color coat**: Gellyfit color (90 mg) + YQ-1 (10 mg)<br>**Top coat**: Gellyfit topcoat (80 mg) + YQ-1 (20 mg) + BuOAc (50 µL) |

*Pulsed ultrasound induced delamination of UV-cured coatings from acrylic artificial nail surfaces − general HIFU experimental setup for material interaction studies*

A conventional HIFU setup was used in all HIFU experiments.

A HIFU multielement transducer with a centre frequency of 1.1 MHz (H-102, Sonic Concepts, Washington, USA) was connected to the function generator (TPO-32, Sonic Concepts, Washington, USA) via an electrical impedance matching network. The function generator was set to incoherent setting NO16 to apply a frequency blur and increase the beam profile to 5 mm x 10 mm, after which a sine wave burst was transmitted through the function generator towards the transducer. An immersion transducer (V319, Olympus) functioned as a passive cavitation detector (PCD) and was coaxially aligned to the HIFU transducer's focal point, wherein the acoustic reflections were passed through a high pass filter to cut out the driving frequency and visualised on an oscilloscope. The acoustic noise data was simultaneously saved to a computer for later signal processing. FIG. 5 presents the HIFU system with a representative image of clip-based nail holders for fixing coated acrylic nails into the reaction chamber for ultrasonic irradiation. As depicted in FIG. 5A, there is an ultrasound setup 500. The ultrasound setup 500 includes a reaction chamber 502, a passive cavitation detector (PCD) 504, a water tank 506, a manual XYZ stage controller 508, a matching network 510, a radio-frequency (RF) power amplifier 512, a function generator 514, a personal computer (PC)

516, an oscilloscope 518, and a high pass filter 520 (high pass filter cutoff frequency, $f_c$ = 2.50 MHz).

*Pulsed ultrasound induced delamination of UV-cured coatings from acrylic artificial nail surfaces − ultrasonic irradiation of dual-responsive nail coatings*

For irradiation of additive films and coatings applied onto acrylic nails, the materials were soaked for 5 min in distilled water before fixing into a custom-build reaction chamber. For the coatings on acrylic nails, a nail-plate was designed to clip the nail into place (FIG. 5B). The backing of the holder was machined from acoustic dampening foam (Precision Acoustics, UK) as it can more effectively absorb the incident acoustic wave without warping as compared to acrylic (FIG. 5B). The acoustic focus was set to the acrylic nail and irradiation occurred over 1 or 3 intervals of 10 min for a maximum irradiation time of 30 min at a 10% duty cycle, pulse length of 10 msec, and 4.4 MPa peak negative pressure. Later experiments were focused on lowering the acoustic parameters to utilize either a 2% or 5% duty cycle over 5- or 10-min irradiation and 2.2 or 4.4 MPa peak negative pressure.

*Mechanical scoring of coatings*

Following treatment (i.e. soaking or ultrasonic irradiation), the artificial nails were abraded by blunt-tip steel tweezers using light to moderate force along the vertical axis. To prevent movement of the nails during coating removal, the nails were fixed onto the nail holder and scoring was typically recorded for post-hoc qualitative analysis and comparisons to control groups.

Results and discussion

The films made from Lolly gels were removed much more easily than GellyFit. With the aim to find a biosafe ultrasound conditions for future device development, all further experiments were performed with a maximum irradiation time of 10 min and duty cycle of 5% or lower.

**Table 6.** HIFU-outcome of the different formulations in Table 4.

| **Sample Code** | **HIFU-outcome [a]** |
|---|---|
| MN11-031Film-Set 1 | 10% DC tested (Removal possible) |
| MN11-031Film-Set 2 | 10% and 5% DC tested (Removal possible in all cases) |
| MN11-031Film-Set 3 | not tested |
| MN11-031Film-Set 4 | not tested |

| | |
|---|---|
| MN11-031Film-Set 5 | 10% and 5% DC tested (Removal possible in all cases) |
| MN11-031Film-Set 6 | 5% DC tested (Removal possible) |
| MN11-031Film-Set 7 | not tested |
| MN11-031Film-Set 8 | 5% DC tested |
| MN11-031Film-Set 9 | 10% and 5% DC tested (Removal at 10% possible) |
| MN11-031Film-Set 10 | -- |
| MN11-025RNX6-Set 1 | 5% DC tested (Complete removal observed) |
| MN11-025RNX6-Set 2 | 5% DC tested (Complete removal observed) |
| MN11-025RNX6-Set 3 | 5% DC tested (Complete removal observed) |

[a] abbreviation: DC = duty cycle.

To confirm the importance of the oxalate ester bonds, new formulations were assessed in the YE02-025R5 series (Table 5). In this series, YQ-1 (with structure presented in Table 2) was a polycaprolactone (PCL)-based additive without oxalate to compare against **1a** containing additives specifically YE02-025R5_1. Furthermore, as this series comprises the **1a** additive in all three commercial coatings complete removal of the additive containing coatings was observed when subjected to ultrasound at a 5% duty cycle and 4.4 MPa peak negative pressure. Comparatively, the control films did not exhibit any removal of the coatings (FIG. 6).

As complete removal was observed for all coatings, the ultrasound parameters were varied to investigate if film breakdown was possible with less irradiation time, lower pressures and duty cycles. It was observed that a 2% duty cycle, 5 min of irradiation and 2.2 MPa peak negative pressure were sufficient to only induce partial removal of the YQ-1 containing coatings, whereas full removal of the oxalate containing coatings was still observed (Table 7). Broad band cavitation was observed in all parameters tested for GellyFit-ctrl, YE02-025 set 1 and set 3 coatings. The findings suggest that the oxalate containing additives likely interact better with cavitation for more efficient breakdown of the films by mechanical scoring with tweezers than the YQ-1 or control coatings not containing any additives. Some variability was also observed for the cavitation dynamics, however, given the proximity of the acoustic focus to the acrylic nail and the chamber backing, reflections at these rigid boundaries will be picked up by the PCD, attributing to a higher noise floor and masking the cavitation dynamics within the system.

**Table 7.** Removal of the oxalate containing coatings.

| | 2%, 2.2 MPa | | 2%, 4.4 MPa | | 5%, 4.4 MPa | |
|---|---|---|---|---|---|---|
| **Irradiation Time (min)** | 5 | 10 | 5 | 10 | 5 | 10 |
| YE02-025R5 set 1 | Full | -- | Full | Full | Full | Full |
| YE02-025R5 set 2 | -- | -- | -- | -- | -- | -- |
| YE02-025R5 set 3 | Partial | -- | Full | Full | Full | Full |
| GellyFit-ctrl | -- | -- | -- | No | No | No |

For the YE02-025R5 series of coatings, the findings indicate that the addition of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates **1a-c** into the additive promotes robust removal of the coatings with less intense ultrasonic irradiation. Given that the experimental design assessed ultrasonic irradiation of different coatings on acrylic nails, it cannot be concluded if the present parameters are satisfactorily low enough to minimize tissue trauma if used on biological samples. It has been reported that the *in vitro* response of cell suspensions to ultrasound can vary from the tissue response in an organotypic and *in-* or *ex-vivo* system. Given the complex architecture of subcutaneous tissue, particularly in the fingertip, further work into the biosafety and cavitation dynamics of the present approach using different ultrasonic parameters can be quantified by *ex vivo* cadaver or animal model. The degree of tissue trauma can then be quantified by gross visual assessment for superficial thermal damage and histologically for any damage to subcutaneous tissue.

**Example 4. Stability of the UV-cured coatings on acrylic nail surfaces at various pH**

As many of the additives utilized herein incorporate at least one type of biodegradable polymer (e.g. PCL, PLGA, etc), the general stability of the coatings was assessed.

*Stability experiments*

The coatings (prepared in Example 3) were continuously soaked in either 0.1 M citrate buffer (pH 3), deionized water (pH ~6-7), or 1 M tris buffer (pH 9) (Table 8). Coating removal was assessed by scoring the nails with blunt-tipped metal tweezers by following the protocol in Example 3.

Results and discussion

Table 8 shows whether the coatings were intact by the end of the soaking session or expressed partial/complete removal of the coatings.

**Table 8.** Stability analysis of select MN11-025R6 and YE03-025R5 series coated nails by soaking in pH buffers up to 7 days.

| Sample | Outcome |
|---|---|
| MN11-025R6_1 | Film removal after 6 days in water and tris buffer, mostly intact in citrate buffer after 7 days of soaking |
| MN11-025R6_2 | Film removal observed in water after 6 days. Abrasions observed after soaking for 7 days in citrate buffer and tris buffer. |
| MN11-025R6_3 | Topcoat removal after 6 days of soaking in water, else intact after 7 days of soaking in citrate buffer and tris buffer. |
| MN11-025R6_4 | Film removal after 6 days of soaking in all pH conditions |
| MN11-025R6_5 | Topcoat removal observed after 6 days in all pH conditions, complete removal of films observed after 7 days |
| YE03-025R5_1 | Film removal after 4 days in citrate buffer, film removal around substrate edges observed in water and tris buffer |
| YE03-025R5_2 | Fill removal observed in tris buffer after 24 h. Film removal after 48 h in water, while partial to full removal observed in citrate buffer. |
| YE03-025R5_3 | Abrasions observed on films, but otherwise intact after 6 days of soaking in all pH conditions |
| GellyFit_ctrl | Intact after 6 days of soaking in all pH conditions |

As such, the use of these photo-crosslinkers as a single additive to commercial gel nails achieves the desired efficient ultrasound-induced delamination from the nail surfaces (within 5 to 10 min with 5% duty cycle of ultrasound), while retaining long-lasting stability, scratch resistance and shiny appearance criteria.

Therefore, described herein are a class of photo-crosslinkers, poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates **1**, which are UV-curable and have application as a single

additive to commercial gel nails to provide a therapeutic ultrasound-triggered delamination from coating nail surfaces. In addition, the present technology demonstrates the design, synthesis, UV-curing properties and performances of the products **1** as polymer additives to provide new stimuli-responsiveness to commercial gels.

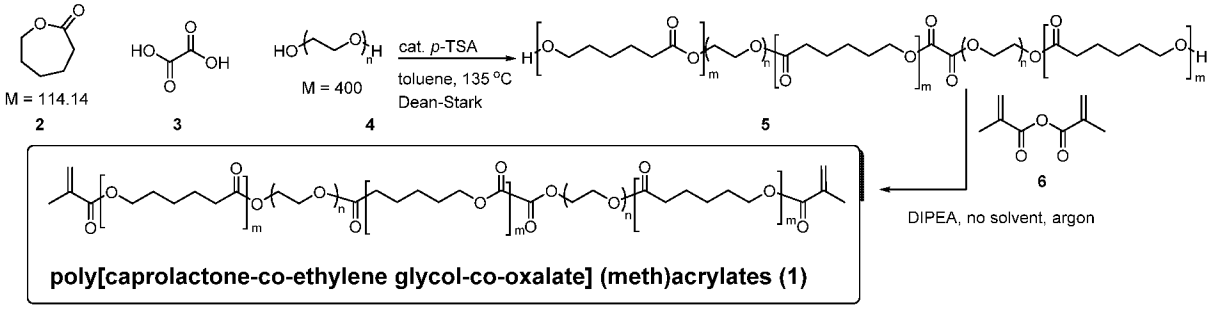
**Example 5. Delamination of cured nail polish coatings**

Conventional ultrasonic devices based on continuous wave low frequency ultrasound function in decoupling of acrylic nails and polish from natural tissue in the presence of acetone. However, low frequency ultrasound at 20 and 30 kHz did not result in successful delamination of the UV-cured coatings of the invention from artificial acrylic nail surfaces (YE02-25R5_1 prepared in Example 3).

However, a high intensity pulsed ultrasound system at 1.1 MHz frequency was found to successfully delaminate the UV-cured coatings. Various parameters were also assessed, as low as a peak negative pressure of 2.2 MPa and 2% duty cycle over 5 min, to delaminate the coatings (FIG. 7). In comparison with the current commercial sonic nail removal technology that relies on using continuous wave low frequency ultrasound and acetone to remove the artificial nails, nail coatings prepared with the polymer additives described herein could be delaminated with pulsed ultrasound operating above 1 MHz with a mechanical index of at least 2.0 in water within 5 to 10 min of ultrasound exposure. Importantly, the ultrasonic conditions are shown to be important for the delamination to work as 20 and 30 kHz ultrasonic bath and probe are unable to provide a similar outcome. As higher frequency ultrasound (> 100 kHz) is known to generate more chemical effects on cavitation, the UV-cured coatings likely interact with radicals generated by sonolysis for chemical breakdown.

While the above results demonstrate that the coatings may be readily delaminated under the conditions tested, it is believed that other conditions may also be used. For example, as the frequency of the ultrasound is lowered, the pressure required for cavitation also decreases. Accordingly, it is believed that the coatings may be readily delaminated using a lower mechanical index of, for example, from 1.7 to 1.9, which may still be sufficient for cavitation. In such cases, it may be desirable to use ultrasound having a minimum driving frequency of 750 kHz or greater, to avoid undesirable effects on body tissue (e.g. heating) that can occur at lower frequencies.

**Example 6. Optimized 2-step synthesis of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates 1**




*Representative procedure to prepare poly[caprolactone-co-ethylene glycol-co-oxalate] diol **5** in one-pot step*

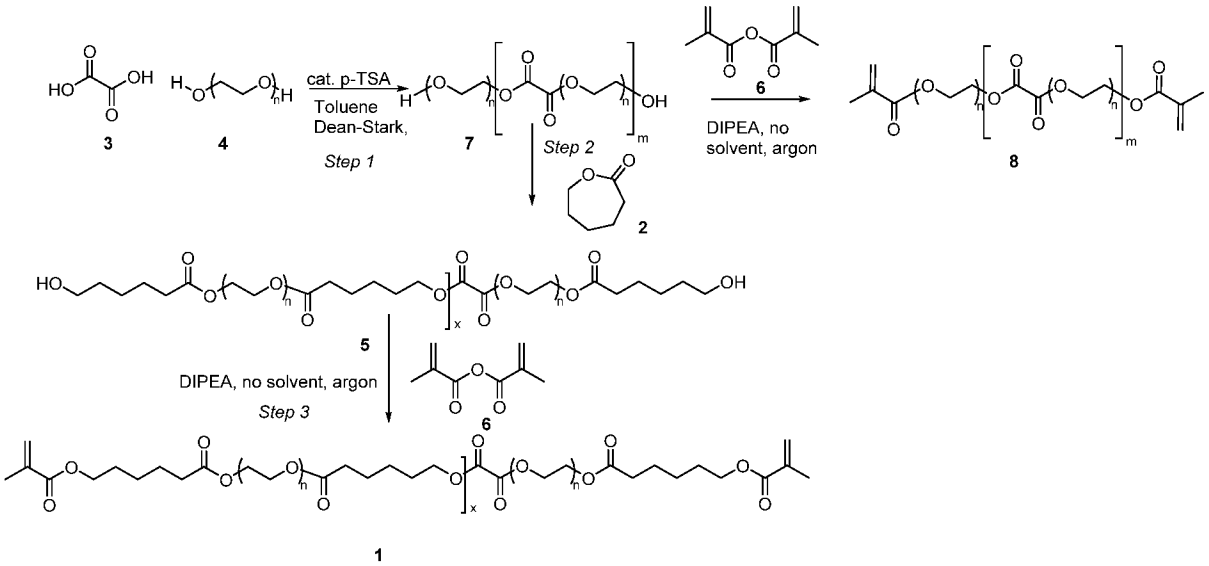
Oxalic acid **2** (2161.7 mg, 24 mmol, 1 equiv.), Ɛ-caprolactone **3** (13696.8 mg, 120 mmol. 5 equiv.), polyethylene glycol MW400 **4** (PEG, 9600 mg, 24 mmol, 1 equiv.), *para*-toluene sulfonic acid (228 mg, 0.05 equiv) and toluene (30 mL) were added to a 100 mL RBF. The mixture was heated at 135 °C in a Dean-stark system for 20 h during which water was formed and eliminated. After cooling to room temperature, another small portion of PEG **4** was added to ensure that any carboxylic end group would be converted into ester and therefore afford a diol product. The mixture was then heated again for another 6 h. Toluene was evaporated after reaction and a diethyl ether/petroleum ether mixture (1:4 v/v ratio) was used to wash the products (8 × 50 mL) to afford the desired product **5**, which was further dried under vacuum at 100 °C for another 1 h. The desired diol product **5** was obtained in a quantitative yield (number average molecular weight (Mn) = 2205, PDI = 2.663).

The $^{1}H$, $^{13}C$, $^{1}H$-$^{13}C$ HMQC, $^{1}H$-$^{13}C$ HMBC and $^{1}H$-$^{1}H$ COSY confirmed that product **5** formed by the one-pot procedure contains a mixture of isomers (FIG. 8). All of them can be methacrylated and subsequently undergo photo-curing reaction to form stable coatings.

*Representative procedure to prepare poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylate **1***

Diol **5** (2100 mg, 0.95 mmol, 1 equiv) and *N,N*-diisopropylethylamine DIPEA (1.71 mL, 10 equiv) were added to a 10 mL RBF. Methacrylic anhydride (1.42 mL, 10 equiv) was added dropwise under a flow of nitrogen. After 20 h overnight reaction at room temperature, ethyl acetate (50 mL) was added. The organic phase was washed with 2 N HCl (10 mL), followed by addition of saturated brine. The product was extracted using ethyl acetate. The combined organic layers were dried with $MgSO_4$ and concentrated under reduced pressure at a temperature not higher than 37 °C. The crude product was washed three times with a mixture of solvent consisting of diethyl ether and petroleum ether in a 1:4 v/v ratio to afford 1100 mg of product **1** (Mn = 2,479; PDI = 2.158).

**Example 7. Synthesis of block poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates 1 in three steps**




*Representative procedure to prepare poly[caprolactone-co-ethylene glycol] diol **7***

Oxalic acid **3** (1080.8 mg, 1 equiv), polyethylene glycol MW 400 **4** (4800 mg, 1 equiv), *p*-toluenesulfonic acid (*p*-TSA, 114 mg, 0.05 equiv) and toluene (20 mL) were added to a 100 mL RBF. The mixture was heated at 135 °C in a Dean-stark system for 24 h during which water was formed and eliminated. After cooling to room temperature, the 2nd portion of **4** (1440 mg) was then added and the mixture was re-heated for another 16 h. Toluene was evaporated to provide the crude product, which was subsequently washed with diethyl ether/petroleum ether mixture (1:4 v/v ratio). The desired product **7** was obtained as a colorless oil in a 90% yield (Mn 1,698, PDI 1.684).

*Representative procedure to prepare block poly[caprolactone-co-ethylene glycol-co-oxalate] diol **5***

Diol **7** (1698 mg, 1 mmol, 1 equiv) and Ɛ-caprolactone **3** (570 mg, 5 mmol. 5 equiv.) were added to a 25 mL RBF. The mixture was stirred and maintained at 120 °C. After 20 h of heating, a 80 mbar vacuum was applied while the heating was maintained for 1 h to dry the product. After cooling to room temperature, the crude product was washed with diethyl ether/petroleum ether mixture (1:4 v/v ratio) to afford the desired product **5**.

*Poly[caprolactone-co-ethylene glycol] dimethacrylate **8***

Poly[caprolactone-co-ethylene glycol] dimethacrylate **8** was prepared by following the protocol for **1** in Example 6.

**Example 8. Assessment of mechanical strength after curing**

The mechanical strengths of the films after UV-curing reactions were analysed to benchmark the products (prepared in Examples 6 and 7) with commercial photocrosslinkers that are used in UV gel nails such as triethylene glycol dimethacrylate (**TEG diMA**), and diurethane dimethacrylate, mixture of isomers (**diHEMA**) (FIG. 9).

*Typical procedure to assess mechanical strengths of the cured film by UV-rheology*

4 mg of hydroxycyclohexyl phenyl ketone was added to a shell vial containing 100 mg of viscous liquid of a photocrosslinker (*i.e.* diMA **1**, diMA **8**, TEG diMA or diHEMA). The mixture was stirred for 1 min with a spatula followed by UV rheology measurements as described in Example 2.

Results and discussion

Specifically, the UV-curing experiments determined that the time for the curing reaction to take place and complete was about 120 seconds for all cases. The rigidity of the film made of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates **1** (diMA **1**) was slightly decreased compared to those of TEG diMA, diHEMA and poly[caprolactone-co-ethylene glycol] dimethacrylate **8** (diMA **8**) (FIG. 4). However, these values can be considered as similar to the rigidity of the film made of commercial Gellyfit topcoat gel. Interestingly, when diMA **1** and diMA **8** were formulated with Gellyfit topcoat gel, the rigidity of the films were slightly higher than the original films. These results suggest that the photocrosslinkers of the invention would have a good chance of being used as additives to commercial gels, and do not weaken the rigidity of the UV-cured coatings.

**Example 9. Degradation experiments with 0.5 M hydrogen peroxide solution**

In order to explain the breakdown of the UV-cured films in water under HIFU irradiation, additional degradation experiments were performed on the films using 0.5 M aqueous $H_2O_2$ solutions (FIG. 10).

*Degradation experiments with 0.5 M hydrogen peroxide solution*

Photocrosslinkers **1b**, **8**, polycaprolactone dimethacrylate (PCL diMA) and TEG diMA were first used to form solid films under UV curing reactions by following the UV-curing protocol in Example 2. Subsequently, these films were submerged in 0.5 M aqueous $H_2O_2$ solutions for 8 days.

Results and discussion

The experiments showed that oxalate groups present in the UV-cured matrix helped it to respond better to hydrogen peroxide, resulting in a higher percentage of the degradation of the corresponding films (FIG. 11). This work can contribute to the justification of the importance of incorporating oxalate groups in the photocrosslinkers' structure for a better responsiveness toward ultrasound and reactive hydroxyl radicals.

**Example 10. Structure-property relationship of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates 1**

The structure-property relationship of poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates **1** (prepared in Example 6) is summarized in FIG. 12. The mechanical strengths of the UV-cured films were slightly decreased when the percentage of PCL was increased. FIG. 12 depicts that:

(a) with increased PCL percentage, the thermal stability and molecular weights were decreased;

(b) tetraethylene glycol (TetraEG) vs PEG400: with shortened ethylene glycol (EG) chain, thermal stability was decreased. When PEG percentage was increased over PCL and oxalate, the thermal stability was decreased; and

(c) increase in the percentage of oxalate led to a decreased thermal stability compared to PEGs.

As the EG chain of TetraEG is shorter than that of PEG400, logically, there will be more oxalate groups in the polymer backbone of TetraEG than that of PEG400 after the condensation reaction. Consequently, a clear strong coloration of the reaction mixture to brown instead of yellowish was observed for TetraEG. In addition, $^{1}H$ NMR analysis of the crude product of TetraEG showed that its reaction mixture contained many impurities, which suggest thermal degradation. These results suggest that the product from TetraEG is not as thermally stable as the one from PEG400.

TGA (Table 9) shows that the new photocrosslinkers **1** are generally stable above 140 °C (above the reaction temperature for polymer synthesis). However, an increase in the percentage of oxalate bonds decreased the thermal stability. The photocrosslinkers are shown to be more thermally stable than the PLGA linker.

**Table 9.** TGA analysis of **5b**, **5a**, PEG400, **7**, **1a** and **1b**.

| Compound | 5% wt loss | 50% wt loss |
|---|---|---|

| | (°C) | (°C) |
|---|---|---|
| **5b** | 116.6 | 267.7 |
| **5a** | 185.9 | 280.6 |
| PEG400 | 183.5 | 254.9 |
| **7** | 163.6 | 222 |
| **1a** | 202.51 | 378.9 |
| **1b** | 145 | 362 |

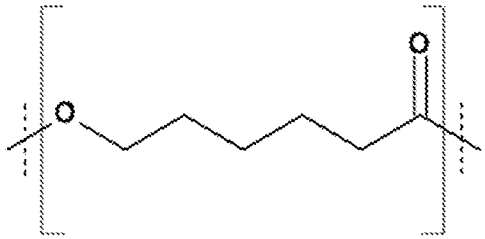
As demonstrated by the above Examples, the invention provides the following benefits.

- The poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates are UV-curable and may easily be cured to form films and gels for use as surface coatings on a nail.
    - The copolymers are thermally stable above 140°C, which is above the required reaction temperature for polymer synthesis.
    - The copolymers may be prepared having have molecular weight ranges within 1,000 to 10,000 Daltons, which ensures excellent solubility in gel nail polish formulation solvents such as butyl acetate or ethyl acetate.
- The poly[caprolactone-co-ethylene glycol-co-oxalate] dimethacrylates may be easily prepared by simple methods.
- The hydrophobic-hydrophilic balance of the copolymers may be easily tuned by varying the initial ratios of polyethylene glycols, Ɛ-caprolactone and oxalic acid during the polymer synthesis.
- The copolymers may be cured with 365 nm UV light to form films with rigidity in the range between $10^5$ and $10^7$ Pascal.
- The copolymeric material of the invention is compatible with commercial gel nails for long term storage.
- When formulated with commercial gel nails such as Lolly and Gellyfit gels, the rigidity of the UV-cured coatings is in a similar range of the coatings made by the pure commercial gels.
- The inventors demonstrated the use of copolymers as a single additive to commercial gel nails to achieve efficient ultrasound-induced delamination from the nail surfaces (within 5 to 10 minutes with 5% duty cycle of ultrasound), while retaining long-lasting stability, scratch resistance and shiny appearance.
- In comparison with the current commercial sonic nail removal technology that relies on using low frequency ultrasound and acetone to remove the artificial nails, nail coatings

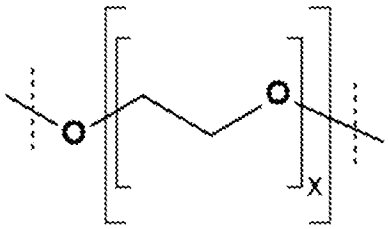
prepared with the polymer additives could be delaminated with pulsed ultrasound within 5 to 10 minutes' ultrasound exposure without requiring acetone.

**Claims**

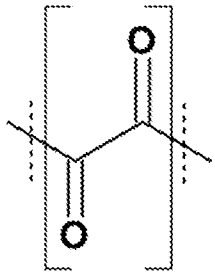
1. A copolymeric material comprising one or more random copolymers, where each of the one or more copolymers comprises each of the constitutional units of formulae (Ia), (Ib) and (Ic):



(Ia)



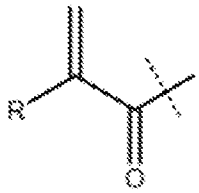
(Ib)



(Ic),

where each of the dotted lines represents a point of attachment of each constitutional unit to a further constitutional unit *via* an ester linkage; and
x is an integer for from 2 to 15, wherein
each of the copolymers in the copolymeric material have a number average molecular weight of from 800 to 10,000 Daltons.

2. The copolymeric material according to Claim 1, wherein each of the one or more copolymers further comprises two capping units of formula (Id):



(Id)

wherein R represents H or a $C_{1-6}$ alkyl group; and
the dashed line represents the point of attachment to the rest of the copolymer *via* an ester linkage.

3. The copolymeric material according to Claim 2, wherein R represents H or methyl, optionally wherein R represents methyl.

4. The copolymeric material according to any one of the preceding claims, wherein each of the one or more copolymers is a random copolymer or a random block copolymer.

5. The polymer according to any one of the preceding claims, wherein each of the one or more copolymers comprises from 1 to 5 constitutional units of formula (Ic), such as from 1 to 4 constitutional units of formula (Ic), such as from 2 to 3 constitutional units of formula (Ic).

6. The copolymeric material according to any one of the preceding claims, wherein in formula (Ib), x is an integer of from 4 to 12, such as from 5 to 8.

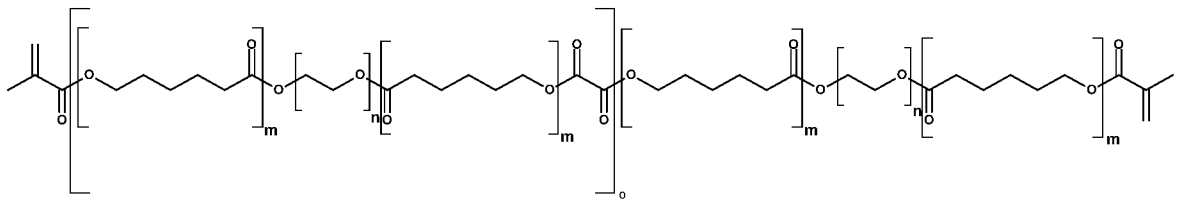
7. The copolymeric material according to any one of the preceding claims, wherein each of the one or more copolymers have a number average molecular weight of from 1,000 to 2,500 Daltons.

8. The copolymeric material according to any one of the preceding claims, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 15:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 15:1,
optionally wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 10:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 10:1.

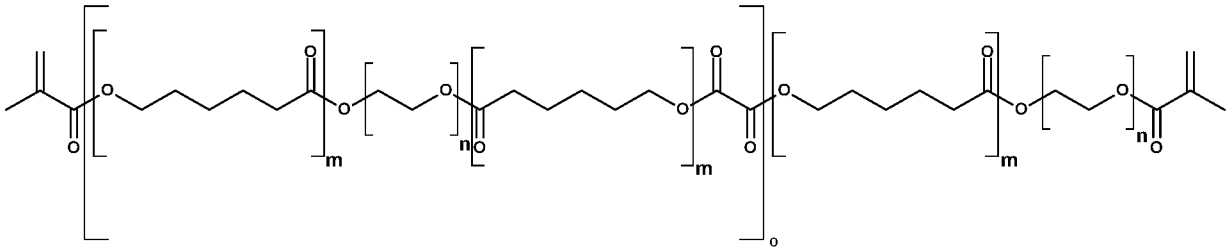
9. The copolymeric material according to any one of the preceding claims, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 6:1; and
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 6:1.

10. The copolymeric material according to any one of the preceding claims, wherein:
the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 5.5:1;
the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 5.5:1; and
the molar ratio of constitutional units of formula (Ib) to (Ic) is from 0.8:1 to 1.2:1.

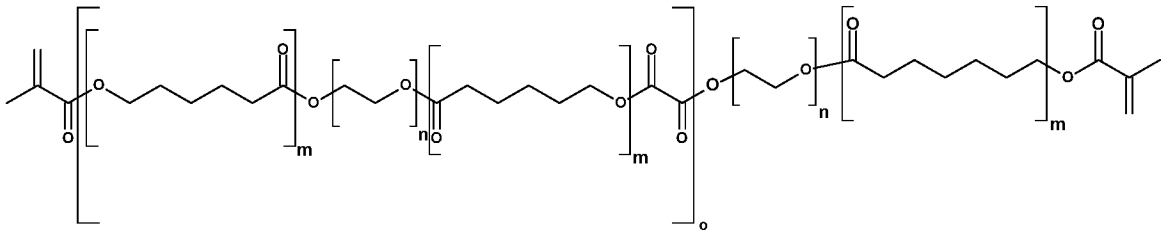
11. The copolymeric material according to any one of the preceding claims, wherein the one or more copolymers is selected from one or more of the formula (IIa), (IIb), (IIc) and (IId):



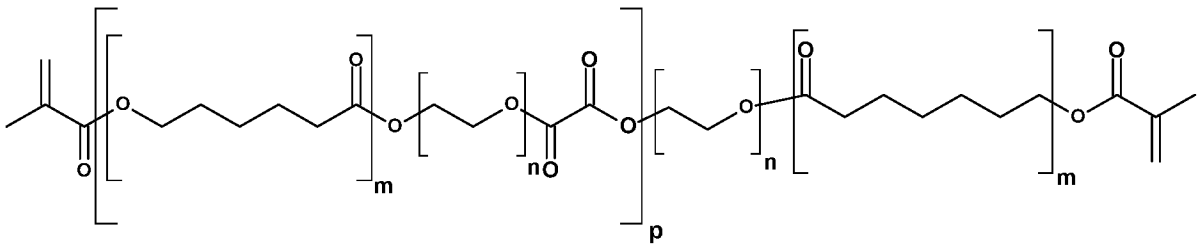
(IIa);



(IIb);



(IIc); and



(IId),

where m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 3:1 to 15:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 3:1 to 15:1; and

o and p are integers selected from 1 to 5.

12. The copolymeric material according to Claim 11, wherein m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 6:1; and

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 6:1.

13. The copolymeric material according to Claim 11, wherein m, n, o and p are selected such that:

the molar ratio of constitutional units of formula (Ia) to (Ib) is from 4.5:1 to 5.5:1;

the molar ratio of constitutional units of formula (Ia) to (Ic) is from 4.5:1 to 5.5:1; and

the molar ratio of constitutional units of formula (Ib) to (Ic) is from 0.8:1 to 1.2:1.

14. The copolymeric material according to any one of Claims 11 to 13, wherein the one or more copolymers includes the copolymer according to formula (IIa).

15. A gel nail polish formulation comprising a copolymeric material according to any one of Claims 1 to 14.

16. A method of removing from a nail a gel nail polish formed by curing a gel nail polish formulation according to Claim 15, said method comprising the steps of:

(i) providing a nail coated with a gel nail polish formed by curing a gel nail polish formulation according to Claim 15; and

(ii) subjecting the nail to pulsed ultrasonic irradiation at a frequency of from 750 kHz to 1.5 MHz over a period of time until full or partial delamination of the gel nail polish from the nail is achieved.

17. The method according to Claim 16, wherein step (ii) comprises subjecting the nail to regular or intermittent bursts of ultrasonic irradiation over the period of time.

18. The method according to Claim 16 or 17, wherein the cumulative ultrasound pulse time is from about 6 to about 30 seconds, and the total irradiation period is from about 1 to about 10 minutes.

19. The method according to any one of Claims 16 to 18, wherein the ultrasound is applied at a peak negative pressure sufficient to generate inertial cavitation events at an interface of the gel nail polish,

optionally wherein the peak negative pressure is from about 0.25 MPa to 5.0 MPa,

more optionally wherein the peak negative pressure is from about 2.0 MPa to about 5.0 MPa.

20. The method according to any one of Claims 16 to 18, wherein the ultrasound has a spatial peak intensity of from 1 to 5 W $cm^{-2}$.

21. Use of a polymer according to Claim 2, or according to any one of Claims 3 to 14 as dependent on Claim 2, as a crosslinking agent.

22. A method of preparing a copolymeric material according to any one of Claims 1 and Claims 4 to 14, as dependent upon Claim 1, where the one or more copolymers are not capped with capping units of formula (Id), said method comprising the steps of:

(a) providing a mixture comprising caprolactone, oxalic acid and polyethylene glycol in the presence of a catalyst; and

(b) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the polymeric material.

23. A method of preparing a copolymeric material according to any one of Claims 1 and Claims 4 to 14, as dependent upon Claim 1, where the one or more copolymers are not capped with capping units of formula (Id), said method comprising the steps of:

(a) providing an intermediate mixture comprising a catalyst and the reaction product of the reaction of oxalic acid with polyethylene glycol; and

(b) reacting the mixture with caprolactone to form the copolymeric material.

24. The method according to Claim 23, wherein the mixture in step (a) of Claim 22 is obtained by the steps of:

(i) providing a mixture comprising oxalic acid, polyethylene glycol and a catalyst; and

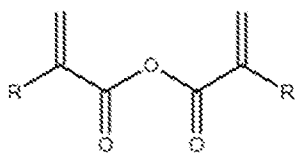
(ii) heating the mixture at a temperature of from 100°C to 150°C for a period of time to form the intermediate mixture.

25. The method according to any one of Claims 23 to 24, wherein the catalyst is $Ti(BuO)_4$ or *para*-toluenesulfonic acid, provided that when the catalyst is *para*-toluenesulfonic acid a solvent is part of the mixture and water is removed from the reaction as it progresses, optionally wherein the solvent is toluene.

26. A method of preparing a copolymeric material according to any one of Claims 2 and Claims 3 to 14, as dependent upon Claim 2, said method comprising the steps of:

(A) providing a copolymeric material according to any one of Claims 1 and Claims 4 to 14, as dependent upon Claim 1, where the one or more copolymers are not capped with capping units of formula (Id); and

(B) reacting the copolymeric material according to any one of Claims 1 and Claims 4 to 14, as dependent upon Claim 1, where the one or more copolymers are not capped with capping units of formula (Id) with a compound of formula (III) to provide a copolymeric material according to Claim 2 or any one of Claims 3 to 13 as dependent on Claim 2,



(III),

where R is as defined in Claim 2 or 3.

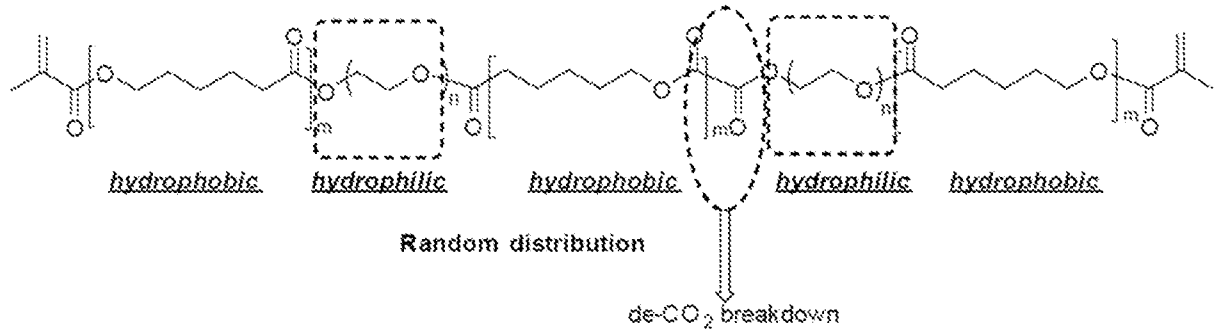

hydrophobic
hydrophilic
hydrophobic
hydrophilic
hydrophobic
Random distribution
de-$CO_2$ breakdown

FIG. 1

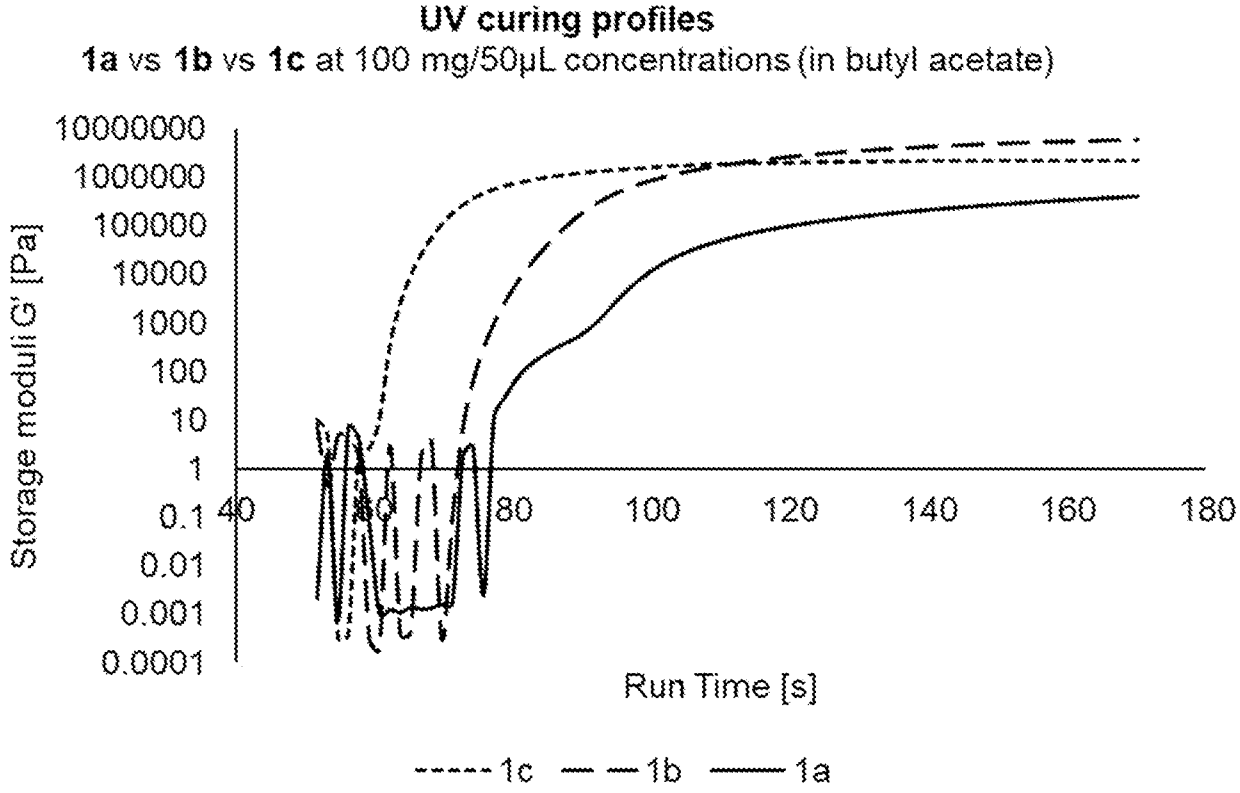

UV curing profiles
1a vs 1b vs 1c at 100 mg/50µL concentrations (in butyl acetate)
Storage moduli G' [Pa]
10000000
1000000
100000
10000
1000
100
10
1
0.1
0.01
0.001
0.0001
40
60
80
100
120
140
160
180
Run Time [s]
1c
1b
1a

FIG. 2A

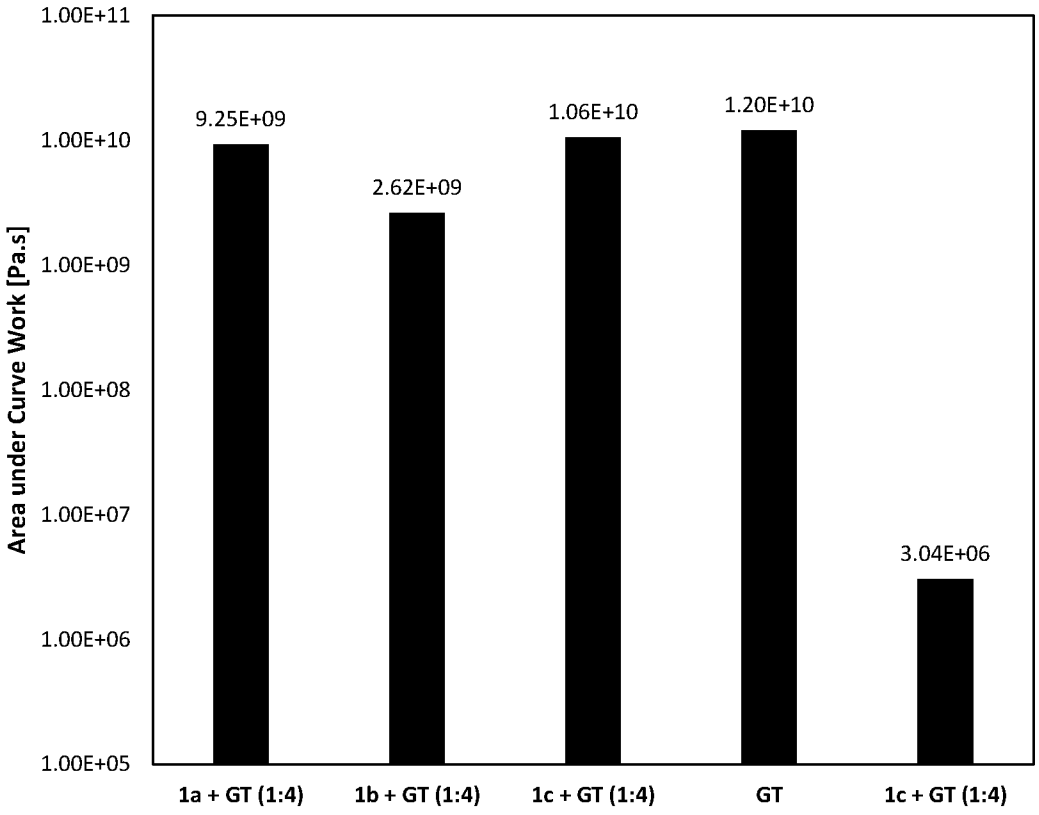

1.00E+11
1.00E+10
1.00E+09
1.00E+08
1.00E+07
1.00E+06
1.00E+05
Area under Curve Work [Pa.s]
9.25E+09
2.62E+09
1.06E+10
1.20E+10
3.04E+06
1a + GT (1:4)
1b + GT (1:4)
1c + GT (1:4)
GT
1c + GT (1:4)

FIG. 2B

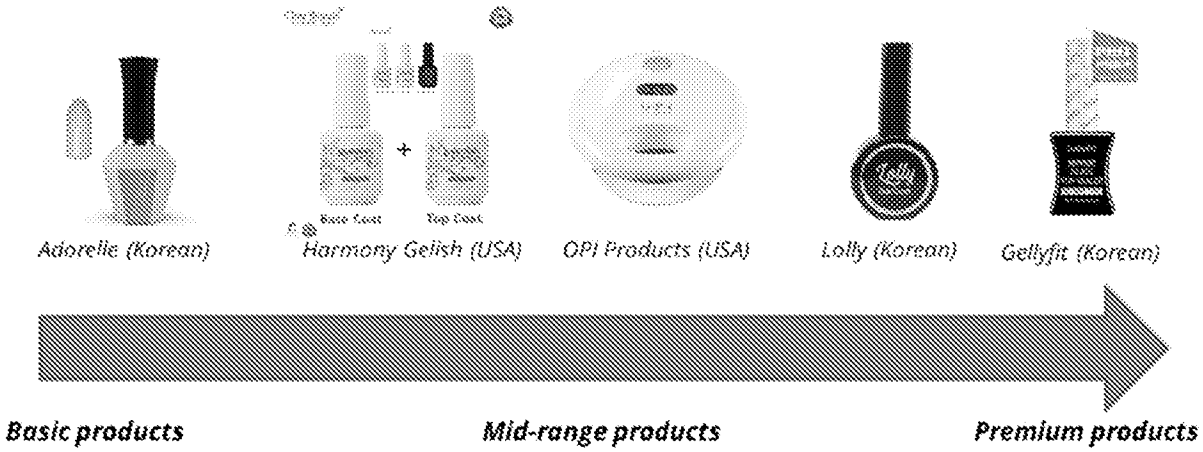

Adorelle (Korean)
Harmony Gelish (USA)
OPI Products (USA)
Lolly (Korean)
Gellyfit (Korean)
Basic products
Mid-range products
Premium products

FIG. 3

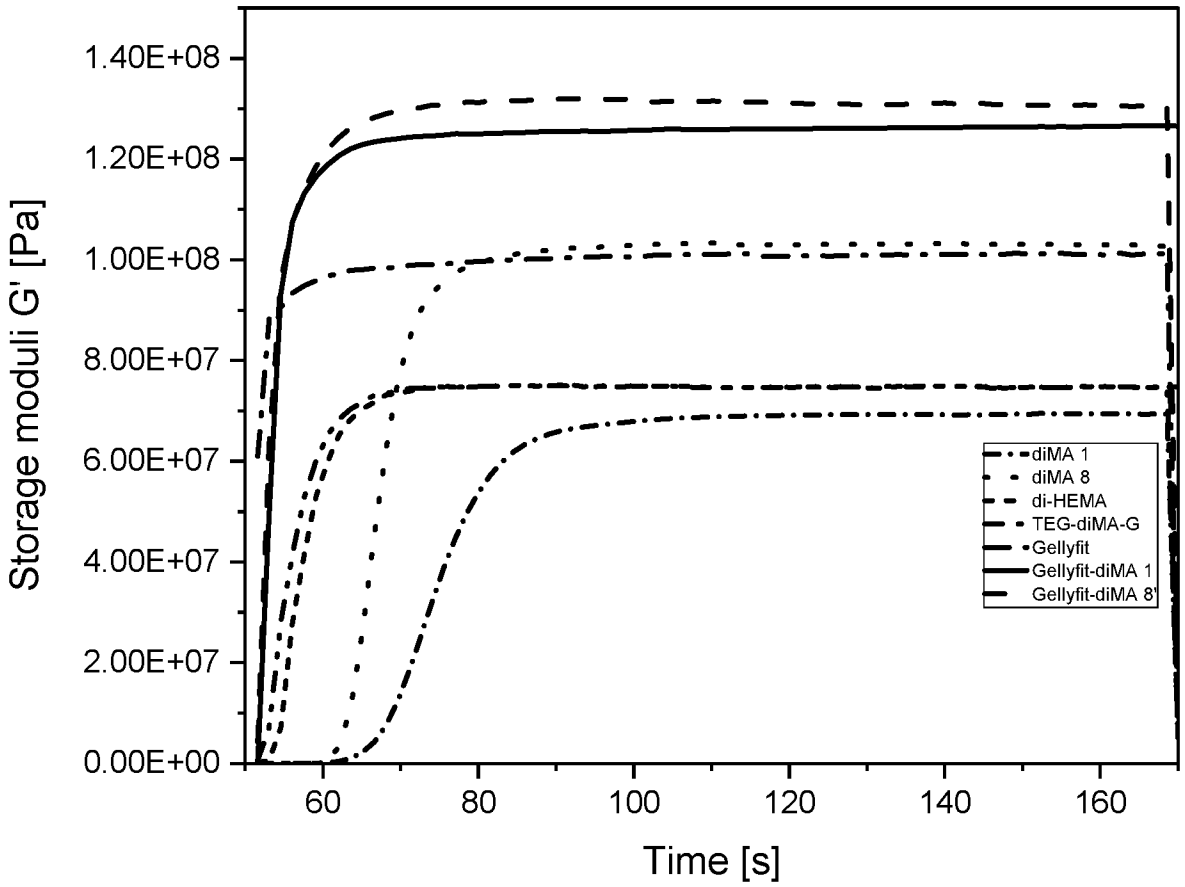

Storage moduli G' [Pa]
1.40E+08
1.20E+08
1.00E+08
8.00E+07
6.00E+07
4.00E+07
2.00E+07
0.00E+00
60
80
100
120
140
160
Time [s]
diMA 1
diMA 8
di-HEMA
TEG-diMA-G
Gellyfit
Gellyfit-diMA 1
Gellyfit-diMA 8'

FIG. 4

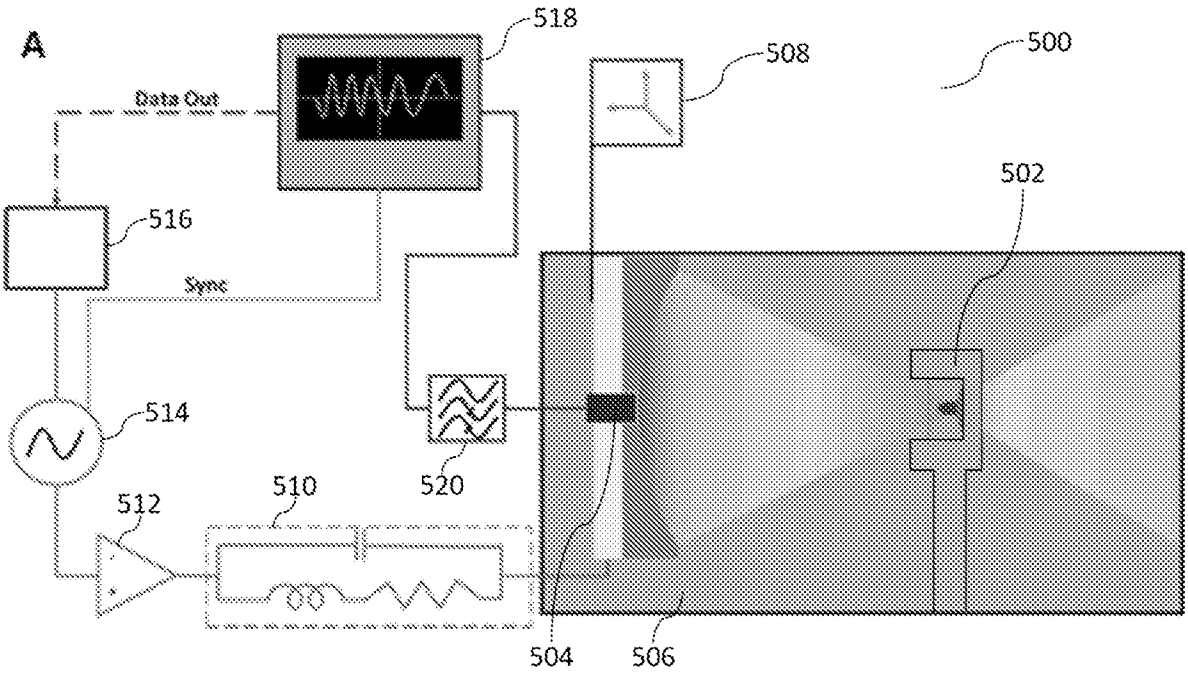

A
518
508
500
Data Out
502
516
Sync
514
520
510
512
504
506

FIG. 5A

B

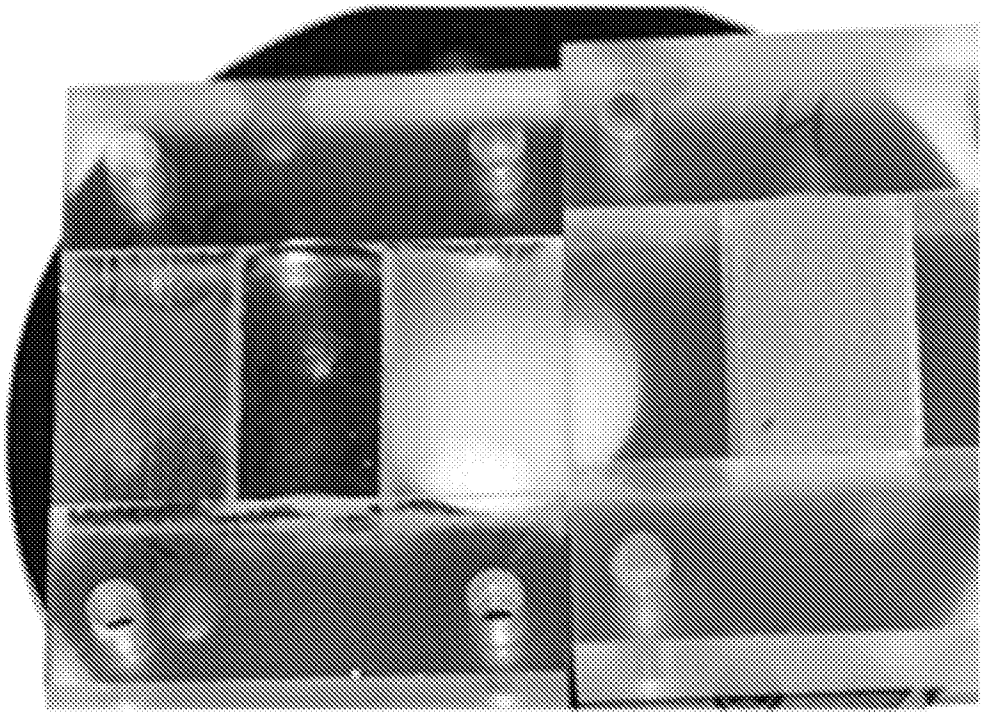


FIG. 5B

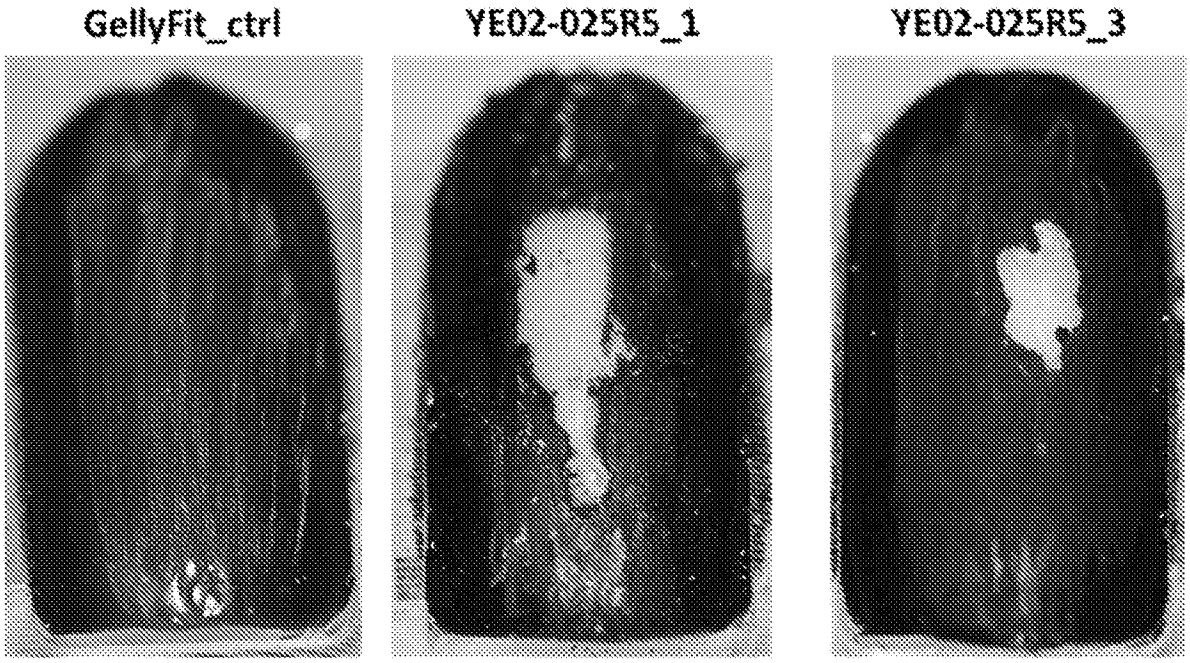
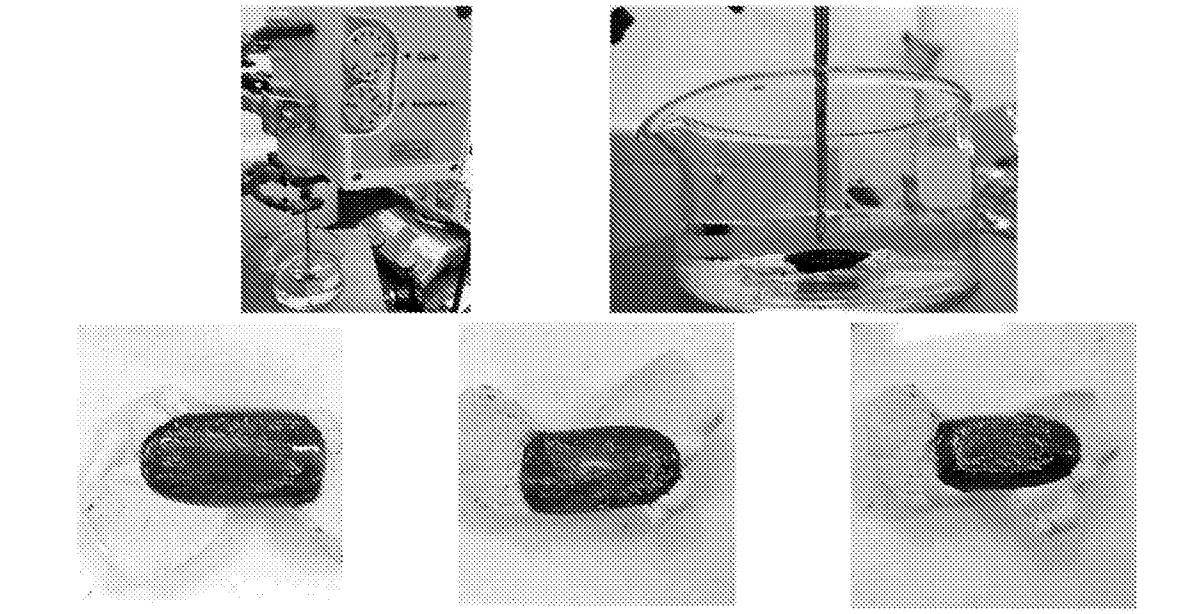
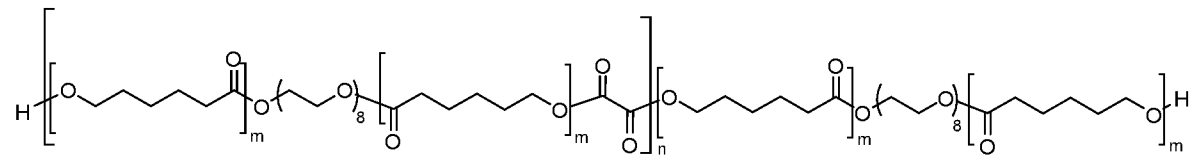



FIG. 6

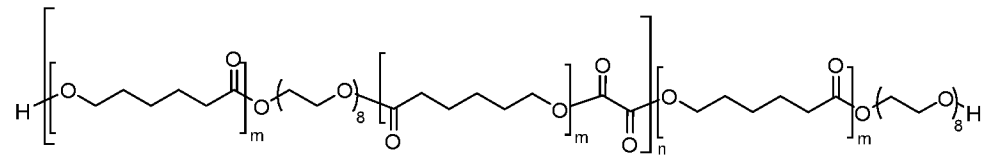


10 min, 50% duty cycle, 50% amplitude, 30 kHz | 10 min, 60% duty cycle, 100% amplitude, 30 kHz | 10 min, 100% duty cycle, 100% amplitude, 30 kHz

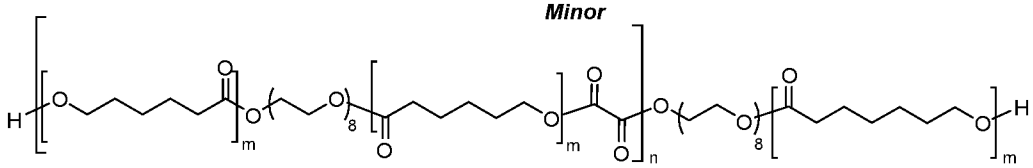
FIG. 7



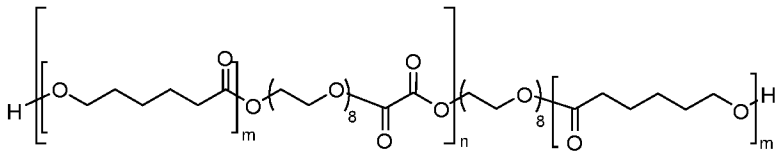
***Major***



***Minor***

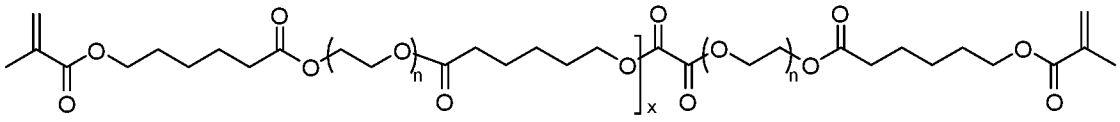


***Minor***

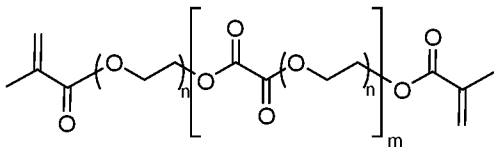


***Minor***

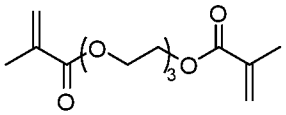
FIG. 8



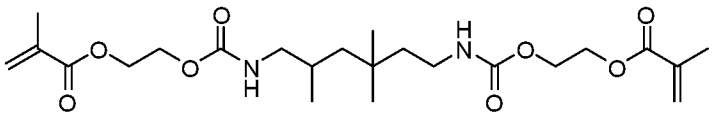
1



8



triethylene glycol dimethacrylate (**TEG diMA**)



R = H or $CH_3$ (~1:1)

**Diurethane dimethacrylate, mixture of isomers**
**(Di-HEMA Trimethylhexyl dicarbamate)**

FIG. 9

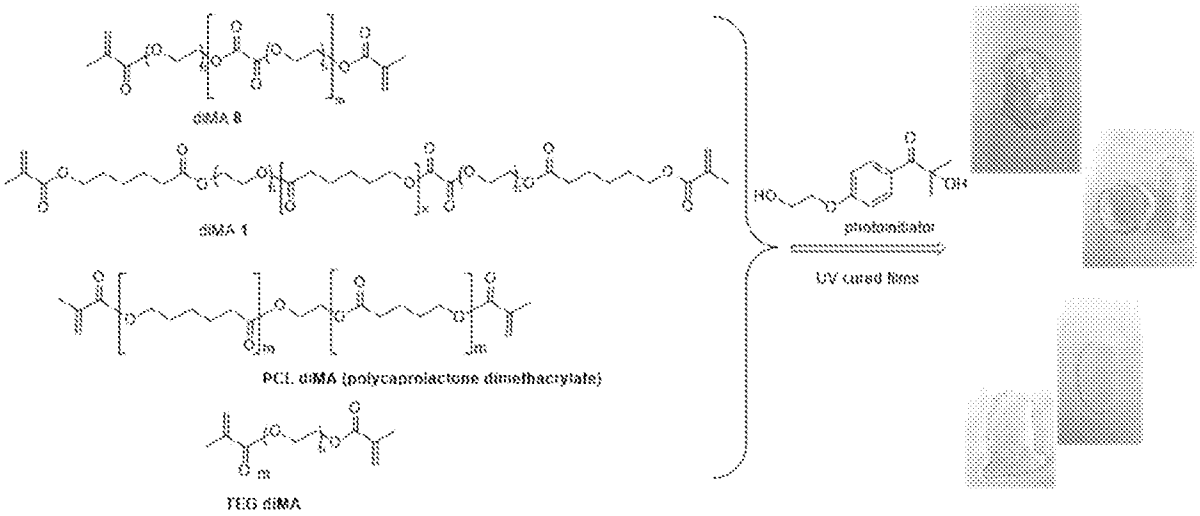



FIG. 10

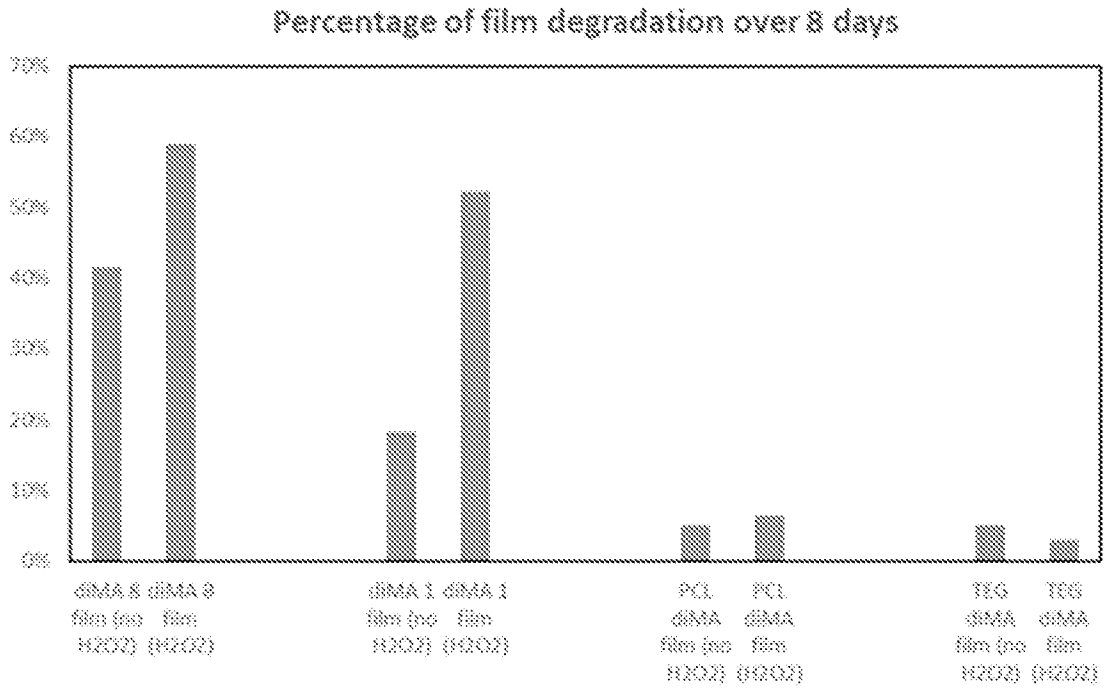

Percentage of film degradation over 8 days
70%
60%
50%
40%
30%
20%
10%
0%
dBMA 8 film (no H2O2)
dBMA 8 film (H2O2)
dBMA 1 film (no H2O2)
dBMA 1 film (H2O2)
PCL dBMA film (no H2O2)
PCL dBMA film (H2O2)
TEG dBMA film (no H2O2)
TEG dBMA film (H2O2)

FIG. 11

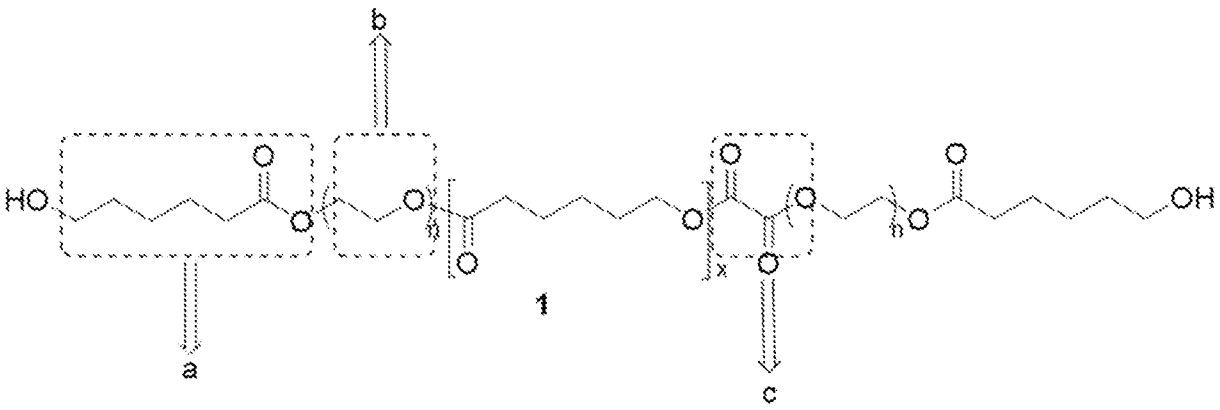

HO
OH
O
n
x
a
b
c
1

FIG. 12