

Description

Title of Invention: Polymer With Low Moisture Vapour Transmission Rate

Technical Field

- 5 The present invention relates to a polymer comprising repeating units of a bulk monomer, an adhesion promoting monomer, a diluent monomer and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon. The present invention also relates to a polymer composition comprising the polymer and a photoinitiator, a method for synthesizing the polymer or the polymer composition, and a gasket comprising the polymer.

10 Background Art

- In the Hard Disk Drive (HDD) industry, the impetus towards low Moisture Vapour Transmission Rate (MVTR) is high as the form factor has increasingly become smaller, resulting in the need for low MVTR to produce more reliable drives. For example, in helium filled drives, it is extremely important to keep the helium in place for several days before the
15 final welding process.

In conventional thermally cured epoxy based formulations for low MVTR gaskets, most, if not all, of the formulations utilize silica based thixotropes which may contain 'harmful' compounds such as silane which can be detrimental to the HDD. HDD failure due to stiction is commonly attributed to the presence of silane or silane related compounds.

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

Summary

- In an aspect, there is provided a polymer comprising repeating units of: a bulk monomer; an adhesion promoting monomer; a diluent monomer; and a thixotrope monomer, wherein the
25 thixotrope monomer is substantially free of silicon.

- Advantageously, the polymer may have low Moisture Vapour Transmission Rate (MVTR) properties. Advantageously, the bulk monomer may have low moisture intake properties which may be critical for achieving the low MVTR properties of the polymer. Advantageously, the bulk monomer may form a low moisture absorbing flexible polymer which may confer a first
30 level of moisture repellency to the polymer. Further advantageously, the loading of the remaining volumetric space with a hydrophobic thixotrope may provide an arduous path for water molecules and therefore may provide a second level of moisture repellency.

The remaining monofunctional monomers such as the adhesion promoting monomer and diluent monomer may advantageously additionally have low moisture absorption properties and may act as diluents for the polymer due to their low viscosity properties. The adhesion promoting monomer may be a hydroxylalkyl acrylate. Advantageously, hydroxylalkyl acrylates may replace and therefore circumvent the use of silane-type adhesion promoters.

Advantageously, the monomers of the polymer as defined above is substantially free of silane or silicon compounds, therefore facilitating the use of the polymer in applications where the use of silane or silicone compounds are not desired. In addition, since the thixotropes of the polymer as defined above is substantially free of any silicon, it may advantageously result in the polymer having a higher flow rate. Advantageously, this may translate to more efficient dispensability of the polymer, and therefore higher production output. Further advantageously, the polymer as defined above may have low outgas properties, which may meet the specifications of HDDs.

In another aspect, there is provided a polymer composition comprising the polymer as defined above and a photoinitiator.

Advantageously, the photoinitiator may be a combination of a surface cure initiator and a depth cure photoinitiator to provide a non-tacky surface and through cure of the polymer after UV irradiation, respectively.

In another aspect, there is provided a method for synthesizing the polymer as defined above or a polymer composition as defined above, comprising the step of contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon, to form a mixture.

Further advantageously, the polymer may be UV-curable. By using a UV-curable polymer, the product, such as the formed-in-place gasket (FIPG) may be cured in-situ and thus may eliminate the need for extensive use of thixotropes.

In another aspect, there is provided a polymer composition obtainable by contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon.

In another aspect, there is provided a gasket comprising the polymer as defined above.

Definitions

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

"Alkyl" as a group or part of a group refers to a straight or branched aliphatic hydrocarbon group, preferably a C₁-C₃₀ alkyl, preferably a C₁-C₁₂ alkyl, more preferably a C₁-C₁₀ alkyl, most preferably C₁-C₆ unless otherwise noted. Examples of suitable straight and branched C₁-C₆ alkyl substituents include methyl, ethyl, n-propyl, 2-propyl, n-butyl, sec-butyl, t-butyl, hexyl, and the like. The group may be a terminal group or a bridging group.

"Alkenyl" as a group or part of a group denotes an aliphatic hydrocarbon group containing at least one carbon-carbon double bond and which may be straight or branched preferably having 2-12 carbon atoms, more preferably 2-10 carbon atoms, most preferably 2-6 carbon atoms, in the normal chain. The group may contain a plurality of double bonds in the normal chain and the orientation about each is independently E or Z. Exemplary alkenyl groups include, but are not limited to, ethenyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl and nonenyl. The group may be a terminal group or a bridging group.

"Cycloalkyl" refers to a saturated monocyclic or fused or spiro polycyclic, carbocycle preferably containing from 3 to 9 carbons per ring, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and the like, unless otherwise specified. It includes monocyclic systems such as cyclopropyl and cyclohexyl, bicyclic systems such as decalin, and polycyclic systems such as adamantane. A cycloalkyl group typically is a C₃-C₁₂ alkyl group. The group may be a terminal group or a bridging group.

"Aryl" as a group or part of a group denotes (i) an optionally substituted monocyclic, or fused polycyclic, aromatic carbocycle (ring structure having ring atoms that are all carbon) preferably having from 5 to 12 atoms per ring. Examples of aryl groups include phenyl, naphthyl, and the like; (ii) an optionally substituted partially saturated bicyclic aromatic carbocyclic moiety in which a phenyl and a C₅₋₇ cycloalkyl or C₅₋₇ cycloalkenyl group are fused together to form a cyclic structure, such as tetrahydronaphthyl, indenyl or indanyl. The group may be a terminal group or a bridging group. Typically an aryl group is a C₆-C₁₈ aryl group.

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

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

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

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4,

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

There is provided a polymer comprising repeating units of:

- 10 a bulk monomer;
- an adhesion promoting monomer;
- a diluent monomer; and
- a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon.

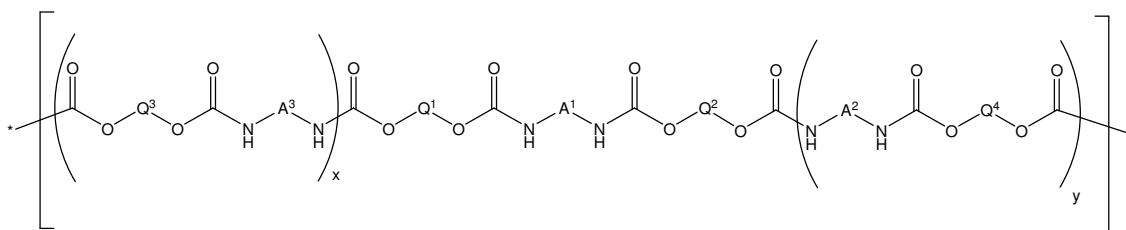
There is also provided a polymer essentially consisting of repeating units of:

- 15 a bulk monomer;
- an adhesion promoting monomer;
- a diluent monomer; and
- a thixotrope monomer, , wherein the thixotrope monomer is substantially free of silicon.

The polymer may be substantially free of any solvents.

- 20 The polymer may be substantially free of silicon. For the purposes of this disclosure, silicon may be elemental silicon or any derivative thereof, including silanes, siloxanes, silica and any mixture thereof. The polymer may not comprise silicon, silica, or silane.

The repeating unit of the bulk monomer may have the following structure:

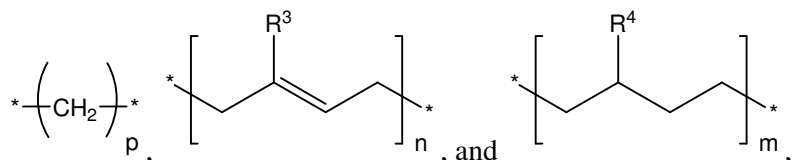


wherein Q^1 , Q^2 , Q^3 and Q^4 may be independently optionally substituted, linear or branched, alkyl or alkenyl;

A^1 , A^2 and A^3 may be independently optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl;

5 and x and y may be independently 0 or 1.

Q^1 , Q^2 , Q^3 and Q^4 may be independently selected from the group consisting of the following:

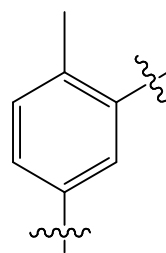
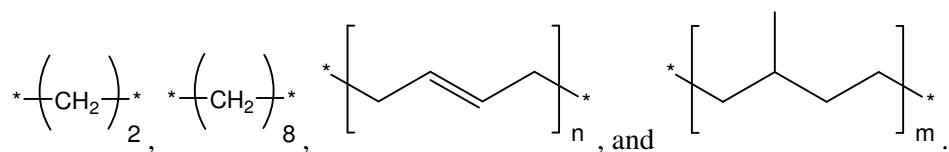


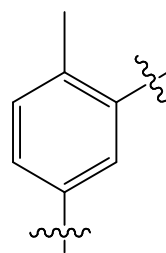
wherein n, m and p may be independently an integer selected from 1 to 20,

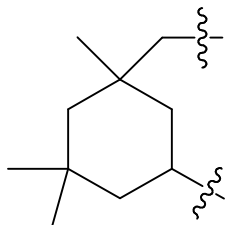
R^3 may be hydrogen or alkyl and

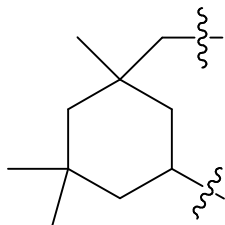
10 R^4 may be alkyl.

Q^1 , Q^2 , Q^3 and Q^4 may be independently selected from the group consisting of the following:



A^1 , A^2 and A^3 may be independently selected from the group consisting of alkyl, ,

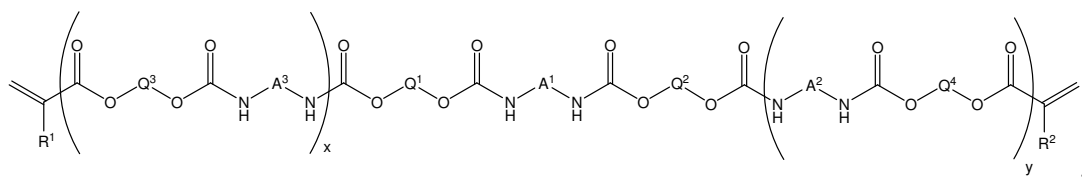


or , wherein the bond broken by  represents where the molecule is attached to the rest of the polymer.

15

A^1 , A^2 and A^3 may be independently selected from the group consisting of C_1 - C_{20} alkyl, C_1 - C_5 alkyl, C_1 - C_{10} alkyl, C_1 - C_{15} alkyl, C_5 - C_{10} alkyl, C_5 - C_{15} alkyl, C_5 - C_{20} alkyl, C_{10} - C_{15} alkyl, C_{10} - C_{20} alkyl, and C_{15} - C_{20} alkyl.

The bulk monomer may have the following structure:

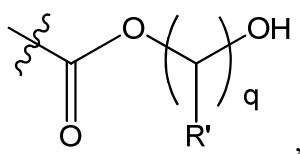


R^1 and R^2 may be independently hydrogen or methyl.

Adhesion promoting monomer

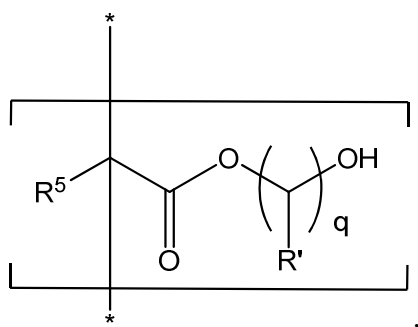
The adhesion promoting monomer may comprise a hydroxylalkyl acrylate.

- 5 The adhesion promoting monomer may comprise the following structure:



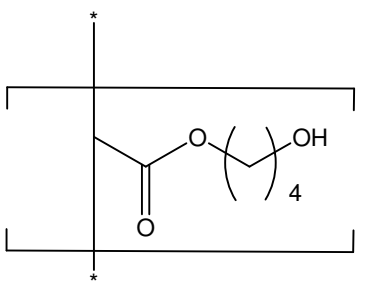
wherein R' may be hydrogen or alkyl and q may be an integer selected from 1 to 10.

The repeating unit of the adhesion promoting monomer may have the following structure:

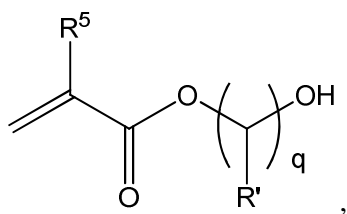


- 10 wherein R^5 is hydrogen or alkyl.

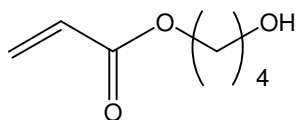
The repeating unit of the adhesion promoting monomer may have the following structure:



The adhesion promoting monomer may have the following structure:

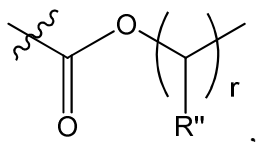


The adhesion promoting monomer may have the following structure:



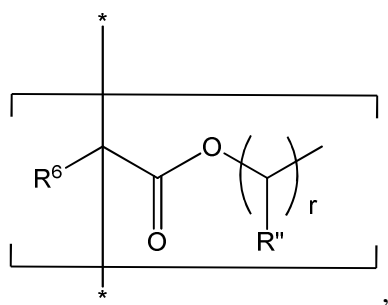
Diluent monomer

- 5 Therein the diluent monomer may comprise the following structure:



wherein R'' may be independently hydrogen or alkyl and r may be an integer selected from 1 to 20.

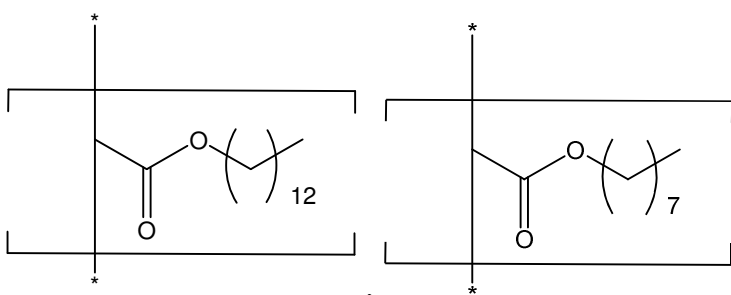
The repeating unit of the diluent monomer may have the following structure:



10

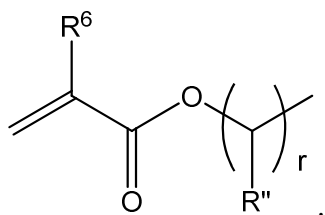
wherein R⁶ is hydrogen or alkyl.

The repeating unit of the diluent monomer may be selected from the group having the following structure:

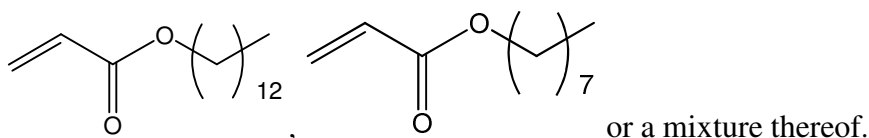


or a mixture thereof.

The diluent monomer may have the following structure:



The diluent monomer may be selected from the group having the following structure:

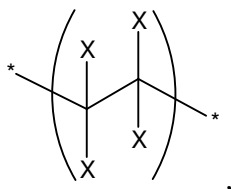


- 5 The diluent monomer may be selected from the group consisting of n-octyl acrylate, lauryl acrylate (dodecyl acrylate), stearly acrylate (octadecyl acrylate) and any mixture thereof.

The diluent monomer n-octyl acrylate may be added to the bulk monomer at a weight percentage in the range of about 20% to about 80% prior to polymerization.

Thixotrope monomer

- 10 The repeating unit of the thixotrope monomer may have the following structure:



wherein X may be halogen.

X may be fluorine.

- 15 The thixotrope monomer may be substantially free of silicon. For the purposes of this disclosure, silicon may be elemental silicon or any derivative thereof, including silanes, siloxanes, silica and any mixture thereof. The thixotrope monomer may not comprise silicon, silica, or silane.

The polymer may comprise:

- 20 about 30 wt% to about 60 wt%, about 30 wt% to about 40 wt%, about 30 wt% to about 50 wt%, about 40 wt% to about 50 wt%, 40 wt% to about 60 wt% or about 50 wt% to about 60 wt% of the bulk monomer,

about 0.2 wt% to about 2 wt%, about 0.2 wt% to about 0.5 wt%, about 0.2 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.5 wt% to about 2 wt%, or about 1 wt% to about 2 wt% of the adhesion promoting monomer,

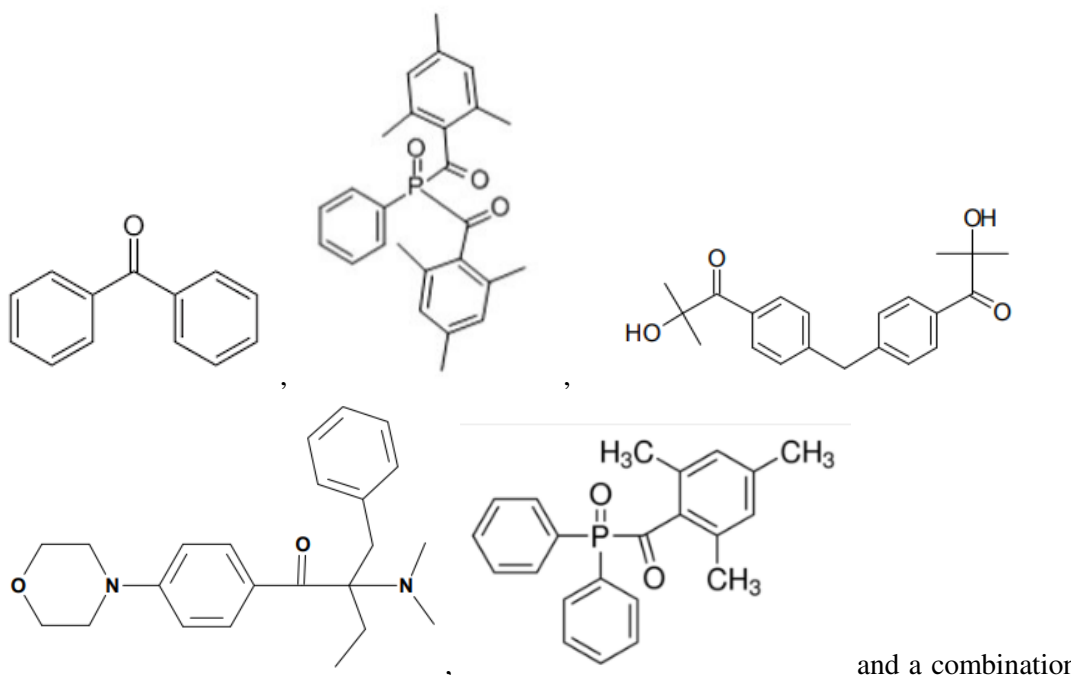
about 5 wt% to about 30 wt%, about 5 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 5 wt% to about 30 wt%, about 5 wt% to about 25 wt%, about 5 wt% to about 20 wt%, about 10 wt% to about 15 wt%, about 10 wt% to about 20 wt%, about 10 wt% to about 25 wt%, about 10 wt% to about 30 wt%, about 15 wt% to about 20 wt%, about 15 wt% to about 25 wt%, about 15 wt% to about 30 wt%, about 20 wt% to about 25 wt%, or about 25 wt% to about 30 wt% of the diluent monomer, and

about 30 wt% to about 50 wt%, about 30 wt% to about 40 wt%, or about 40 wt% to about 50 wt% of the thixotrope monomer,

wherein the total wt% is 100%.

There is also provided a polymer composition comprising the polymer as defined above and a photoinitiator.

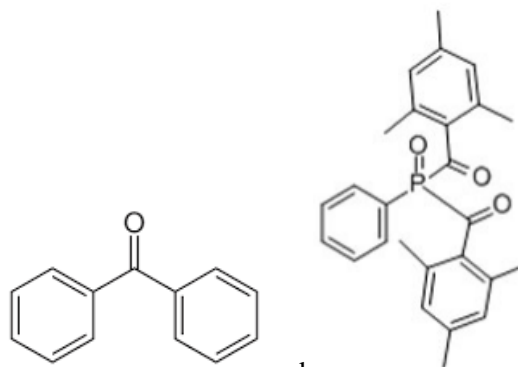
The photoinitiator may be selected from the group consisting of the following structures:



thereof.

and a combination

The photoinitiator may be a combination of a surface curing photoinitiator and a deep curing photoinitiator. The surface curing photoinitiator may facilitate fast curing, while the deep curing photoinitiator may facilitate complete curing to ensure the polymer retains the desirable properties.



The photoinitiator may be a combination of

and

The polymer composition may comprise:

about 30 wt% to about 60 wt%, about 30 wt% to about 40 wt%, about 30 wt% to about 50 wt%, about 40 wt% to about 50 wt%, 40 wt% to about 60 wt% or about 50 wt% to about 60 wt% of the bulk monomer,

about 0.2 wt% to about 2 wt%, about 0.2 wt% to about 0.5 wt%, about 0.2 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.5 wt% to about 2 wt%, or about 1 wt% to about 2 wt% of the adhesion promoting monomer,

about 5 wt% to about 30 wt%, about 5 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 5 wt% to about 30 wt%, about 5 wt% to about 25 wt%, about 5 wt% to about 20 wt%, about 10 wt% to about 15 wt%, about 10 wt% to about 20 wt%, about 10 wt% to about 25 wt%, about 10 wt% to about 30 wt%, about 15 wt% to about 20 wt%, about 15 wt% to about 25 wt%, about 15 wt% to about 30 wt%, about 20 wt% to about 25 wt%, or about 25 wt% to about 30 wt% of the diluent monomer,

about 0.3 wt% to about 1.5 wt%, about 0.3 wt% to about 0.5 wt%, about 0.3 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.5 wt% to about 1.5 wt%, or about 1 wt% to about 1.5 wt% of the photoinitiator, and

about 30 wt% to about 50 wt%, about 30 wt% to about 40 wt%, or about 40 wt% to about 50 wt% of the thixotrope monomer,

wherein the total wt% is 100%.

There is also provided a method for synthesizing the polymer as defined above or a polymer composition as defined above, comprising the step of contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon, to form a mixture.

The bulk monomer, the adhesion promoting monomer, the diluent monomer, the photoinitiator and the thixotrope monomer may be contacted at the following weight percentage:

about 30 wt% to about 60 wt%, about 30 wt% to about 40 wt%, about 30 wt% to about 50 wt%, about 40 wt% to about 50 wt%, about 40 wt% to about 60 wt% or about 50 wt% to about 60 wt% of the bulk monomer,

5 about 0.2 wt% to about 2 wt%, about 0.2 wt% to about 0.5 wt%, about 0.2 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.5 wt% to about 2 wt%, or about 1 wt% to about 2 wt% of the adhesion promoting monomer,

10 about 5 wt% to about 30 wt%, about 5 wt% to about 10 wt%, about 5 wt% to about 15 wt%, about 5 wt% to about 30 wt%, about 5 wt% to about 25 wt%, about 5 wt% to about 20 wt%, about 10 wt% to about 15 wt%, about 10 wt% to about 20 wt%, about 10 wt% to about 25 wt%, about 10 wt% to about 30 wt%, about 15 wt% to about 20 wt%, about 15 wt% to about 25 wt%, about 15 wt% to about 30 wt%, about 20 wt% to about 25 wt%, or about 25 wt% to about 30 wt% of the diluent monomer,

15 about 0.3 wt% to about 1.5 wt%, about 0.3 wt% to about 0.5 wt%, about 0.3 wt% to about 1 wt%, about 0.5 wt% to about 1 wt%, about 0.5 wt% to about 1.5 wt%, or about 1 wt% to about 1.5 wt% of the photoinitiator, and

about 30 wt% to about 50 wt%, about 30 wt% to about 40 wt%, or about 40 wt% to about 50 wt% of the thixotrope monomer,

wherein the total wt% is 100%.

20 The bulk monomer, adhesion promoting monomer, the diluent monomer, the photoinitiator and the thixotrope monomer may be mixed sequentially in that order to form the mixture.

The bulk monomer, adhesion promoting monomer, and the diluent monomer may be mixed in any order, then the photoinitiator and the thixotrope monomer may be mixed sequentially in that order to form the mixture.

The mixture may be irradiated with UV-radiation.

25 The UV irradiation may be UV-A and may be performed at an intensity in the range of about 2 J/cm² to about 14 J/cm², about 2 J/cm² to about 5 J/cm², about 2 J/cm² to about 10 J/cm², about 5 J/cm² to about 10 J/cm², about 5 J/cm² to about 14 J/cm², or about 10 J/cm² to about 14 J/cm².

30 The UV irradiation may be performed at a temperature in the range of about 120 °C to about 180 °C, about 120 °C to about 140 °C, about 120 °C to about 160 °C, about 140 °C to about 160 °C, about 140 °C to about 180 °C, or about 160 °C to about 180 °C, for a duration in the range of about 2 hours to about 4 hours, about 2 hours to about 3 hours or about 3 hours to about 4 hours.

The mixture may be irradiated in situ using spot curing.

There is also provided a polymer composition obtainable by contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon.

There is also provided a gasket comprising the polymer as defined above.

5 **Brief Description of Drawings**

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

10 **Fig. 1**

[Fig. 1] is a schematic representation of the experimental set-up for measuring Moisture Vapor Transmission Rate (MVTR).

Fig. 2

15 [Fig. 2] is a photographic image of the experimental set-up for measuring Moisture Vapor Transmission Rate (MVTR), where (A) is the view from the top and (B) is the view from the side.

Fig. 3

[Fig. 3] is a graph showing the viscosity of inventive formulation U1 against shear rate.

Fig. 4

20 [Fig. 4] is a schematic representation of the setup for spot-curing as the formulation of the present application is being dispensed.

Fig. 5

[Fig. 5] is a graph showing the cure depth of the inventive formulation against dosage of UV-A radiation.

25 **Fig. 6**

[Fig. 6] is a graph showing the outgas as measured by thermogravimetric analysis at different irradiation energies and temperature.

Examples

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

5 Example 1: Materials and Methods

Table 1. Raw materials used

Raw Material	CAS	Chemical Name	Supplier
KRM 8984	Trade Secret/ 2499-59-4	Aliphatic urethane diacrylate/ n-octylacrylate	DAICEL-ALLNEX LTD, Tokyo, Japan
4-HBA	2478-10-6	4-Hydroxybutyl Acrylate	BASF, Ludwigshafen, Germany
SR489D	3076-04-8	Tridecyl Acrylate Esters	Sartomer, Cedex, France
Additol BP	119-61-9	Benzophenone	Allnex, Frankfurt am Main, Germany
Irgacure 819	162881-26-7	Phosphine oxide, phenylbis(2,4,6-trimethyl benzoyl)	BASF, Ludwigshafen, Germany
J14	9002-84-0	Polytetrafluoroethylene	3M Dyneon, St Paul, Minnesota USA

The base resin used is KRM 8984 which is an olefin-based urethane acrylate which has very low moisture intake.

10 4-HBA is used as an adhesion promoter to facilitate adhesion of the polymer to metal substrates.

SR489D is used as a diluent monomer as it has low moisture intake.

Additol BP is a photoinitiator for surface curing, for fast curing purposes.

Irgacure 819 is a photoinitiator for depth cure.

J14 is used both as a thixotrope and a gap-filler.

15 Example 2: Formulations

The monomers of Table 2 were mixed together to form the inventive formulation. The bulk monomer KRM 8984 was mixed with 4-hydroxybutyl acrylate and SR489D, then Additol BP and Irgacure 819 was added, and finally J14 was added, in that order.

Table 2. Experimental formulation

Raw Material	U1 (wt%)
KRM 8984	44.7
4-Hydroxybutyl Acrylate	0.4
SR489D	14.0
Additol BP	0.4
Irgacure 819	0.5
J14	40.0

Comparative Example 1: Comparative Formulations

The monomers of Table 3 were mixed together to form the comparative formulations.

5 **Table 3. Comparative formulations**

Raw Material	Chemical name	C1 (wt%)	C2(wt%)	Supplier
L207	1,3-Butadiene, 2-methyl-, polymer with 1,3-butadiene, hydroxy-terminated, hydrogenated, oxidized	27.2	-	Kuraray, Tokyo, Japan
Epon 872	Fatty acids, C18-unsatd., dimers, polymers with bisphenol A and epichlorohydrin	-	32.4	Hexion, Columbus, Ohio, USA
Pripol 2033	Dimerdiol Fatty diol, C36 branched	16.3	18.6	Croda, Snaith, UK
YX8000	hydrogenated bisphenol A and epichlorohydrin	4.9	-	Japan Epoxy Resins, Tokyo, Japan
Vikolox 14	1,2-Epoxytetradecane	3.1	5.1	Arkema, Colombes, France
NK 200	Silicon dioxide(Surface treated Silicon dioxide)	7.8	-	Evonik Industries, Essen, Germany
A200	Silicon dioxide(Surface treated Silicon dioxide)	-	3.1	Evonik Industries, Essen, Germany
Purified Heloxy 107	Diglycidyl ether of cyclohexane dimethanol	1.0	1.8	Hexion, Columbus, Ohio, USA
NaCure Super XC-7231	Ammonium Hexafluoroantimonate	0.1	0.1	King Industries Specialty Chemical, Norwalk, Connecticut, USA

Example 3: Properties

The following properties were tested:

1. **Colour:** Assessed purely by visual analysis.
2. **Flow rate:** A measurement of how fast the material flows out of a 18 X 0.25" gage needle at 85 Psi within 60 seconds.
3. **Viscosity:** Measured on the TA Instrument AR2000 rheometer with a 20 mm, 2°C cone and plate geometry.
4. **Slump:** A means of measurement to understand how much a material can hold its shape overtime. If the material can hold its shape, the slump will be low as compared to one that does not. A measurement of the width of a bead at 0 min and after 1 hour. The difference between the two is a quantitative measurement.
5. **MVTR:** Measured based on JIS Z0208/ASTM F1249 moisture pervious cup method (Fig. 1):
 - a. Moisture absorbing agent 104 was placed at the bottom of a metal cup 102 with about a 3 mm gap between the cast film 103 and the absorbing agent 104.
 - b. The cast film 103 of 1 mm thickness, was placed above the absorbing agent 104, and the surrounding area was sealed with sealing agent such as paraffin.
 - c. The cup 102 was placed in a humidity test chamber 101 maintained at 40 °C and 90% relative humidity (RH).
 - d. After 22 days, the cup 102 was taken out from the chamber 101 and its mass was measured using a weighing balance.
 - e. Moisture permeability was calculated as follows:

$$\text{Moisture permeability } g/m^2 \cdot 24h = (240 \times m) / (t \times s)$$

where s : permeable area (cm²);

t : total time interval between the two weightings, i.e. 24 hours, 48 hours, 96 hours, etc; and

m : total increase in mass over the two weighing intervals.

Fig. 2 is a photographic image of the metal cup 102 with the cast film 103.

A comparison of the test results are shown in Table 4 below:

Table 4. Properties of the inventive and comparative formulations

Sample no.	Test Description	Unit of Measurement	U1	C1	C2
1	Color before cure	Visual	White	White	White
2	Flow rate	g/min	1.34	0.23	0.20
3	Slump	mil	< 1.0	< 1.0	< 1.0
4	Viscosity at 0.33 s^{-1}	Pa.s	745	2195	5111
5	MVTR	$\text{g/m}^2.\text{day}$	4.46	3.63	6.56

Table 4 shows that inventive formulation U1 has the highest flow rate without having the silica based thixotropy in the formulation which C1 and C2 do. This means that it will be more efficiently dispensed during production of the formed-in-place gasket (FIPG) on the base plate of the hard disk drive (HDD).

The above is confirmed by the viscosity measurement, where inventive formulation U1 has the lowest viscosity followed by the comparative formulations C1 and finally C2. Thus, in terms of efficiency in dispensing, it will also be in that order, with U1 being the most efficient and C2 being the least efficient.

All the formulations showed good slump property. Even though inventive formulation U1 does not contain a silica based thixotrope, it showed good slump properties, and its shear thinning property was attributed to incorporation of J14. Furthermore, since U1 is a UV cured polymer, slump property may not be an issue, as spot curing would mitigate the issue of slumping, as further discussed in Example 4.

The UV cured U1 formulation performed just as well as the thermally cured formulations C1 and C2 in terms of MVTR. U1 has better performance as compared to C2 and slightly lower MVTR performance as compared to C1. However, it is important to note that since U1 does not contain any silica based thixotrope, there are no issues in terms of silane contamination in the inventive formulation.

Example 4: Non-Silica Thixotropy Approach

J-14 which is a non-silica-based polymer was coincidentally used as a gap filler which also acted as a thixotrope. As can be seen in Fig. 3, as the shear rate increases, the viscosity decreases, exhibiting a shear thinning property in inventive formulation U1.

Example 5: Depth of Cure

In addition, in-situ UV-curing may enable the use of a very small amount of thixotropes. The dispensing equipment can be equipped with a spot cure system (Fig. 4) to cure the material as it is being dispensed. In Fig. 4, formulation 407 is inside a dispense syringe 403. As pressure 401 is applied, the formulation 407 is squeezed out of the dispense needle 405 onto substrate 406 and is cured in situ using a spot cure system 408. Horizontal speed 402, and vertical gap 404

together with the pressure 401 determines the thickness of the formulation 407 to be dispensed on the substrate 406. In this way, slump is not a critical parameter to consider for UV cured FIPG.

- 5 Cure depth is important in UV cured materials, as insufficient irradiation may result in uncured material which in turn may result in undesirable physical properties such as hardness, compression and MVTR. In addition, cleanliness properties such as outgas may be affected. Three irradiation conditions were explored on the H/H+ bulb for the inventive formulation U1 (Fig. 5). All the conditions met the requirement for FIPG as the typical bead size is about 0.7 mm or less than 1 mm, allowing for complete curing of the beads.

10 Example 6: Outgas Optimization

Outgas optimization was performed at four different UV energies and three different temperatures. In all the experiments, the polymers were baked for 3 hours, and mass loss was measured by thermal gravimetric analysis (TGA). The results of the mass loss by % is shown in Table 5 below and Fig. 6.

15 **Table 5. Outgas Optimization**

Irradiation (UVA) Temperature				
	3 J/cm ²	6 J/cm ²	8 J/cm ²	12 J/cm ²
140 °C	0.03007	0.02625	0.02617	0.02827
150 °C	0.05316	0.04588	0.05049	0.04816
160 °C	0.07564	0.06728	0.06026	0.0607

Based on the above results, it was found that performance at 6J/cm² and 8 J/cm² irradiation after baking at 140 °C gave the best results.

Industrial Applicability

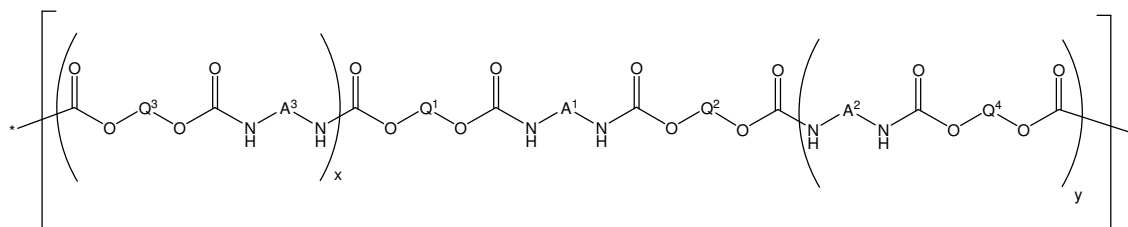
5 The polymer composition may be useful for forming formed-in-place gasket (FIPG) in the hard disk drive (HDD) industry. The polymer composition may be useful in any application that requires low moisture vapour transmission rate (MVTR) through the polymer. The polymer may be further useful in any application where the use of silicon and any derivatives thereof is undesirable.

The polymer composition may be further useful for forming a gasket for a display bezel or in general applications which require low MVTR, such as in surfaces of containers for sensitive electronic components.

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

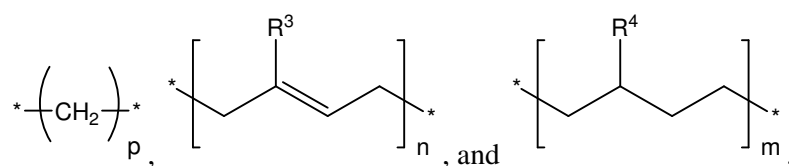
Claims

1. A polymer comprising repeating units of:
 - a bulk monomer;
 - an adhesion promoting monomer;
 - 5 a diluent monomer; and
 - a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon.
2. The polymer composition of claim 1, wherein the repeating unit of the bulk monomer has the following structure:



- 10 wherein Q^1 , Q^2 , Q^3 and Q^4 are independently optionally substituted, linear or branched, alkyl or alkenyl;

A^1 , A^2 and A^3 are independently selected from the group consisting of optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted aryl, and any mixture thereof; and x and y are independently 0 or 1.
- 15 3. The polymer according to claim 2, wherein Q^1 , Q^2 , Q^3 and Q^4 are independently selected from the group consisting of the following:

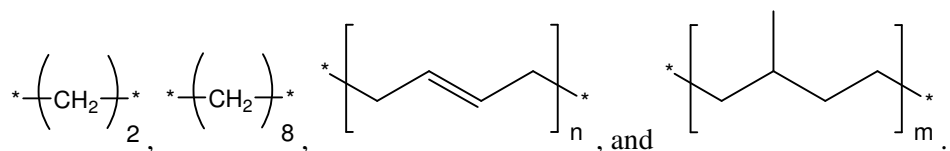


wherein n , m and p are independently an integer selected from 1 to 20,

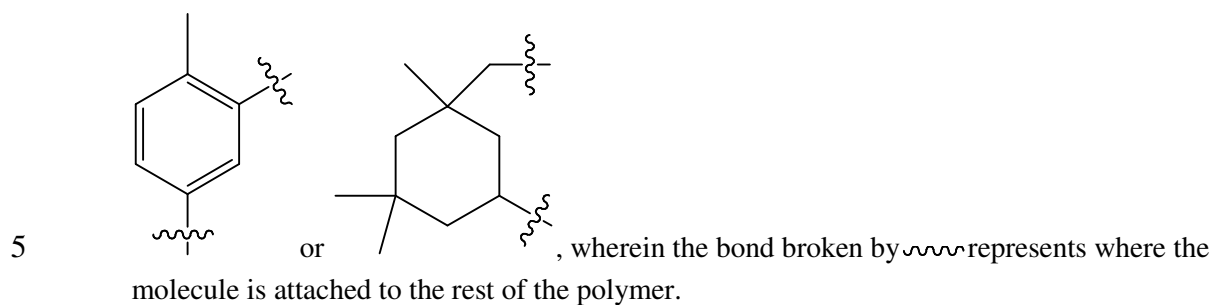
R^3 is hydrogen or alkyl and

R^4 is alkyl.

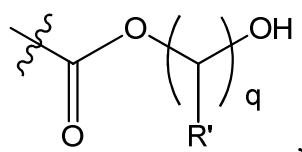
4. The polymer according to claim 2 or 3, wherein Q^1 , Q^2 , Q^3 and Q^4 are independently selected from the group consisting of the following:



5. The polymer according to any one of claims 2 to 4, wherein A^1 , A^2 and A^3 is independently selected from the group consisting of alkyl,

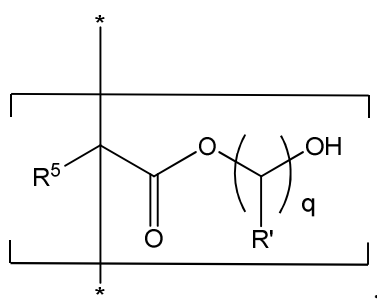


6. The polymer according to any one of the preceding claims, wherein the adhesion promoting monomer comprises the following structure:



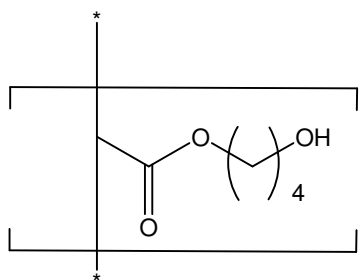
10 wherein R' is hydrogen or alkyl and q is an integer selected from 1 to 10.

7. The polymer according to claim 6, wherein the repeating unit of the adhesion promoting monomer has the following structure:

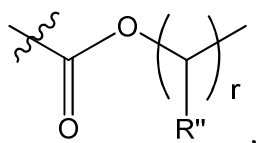


wherein R^5 is hydrogen or alkyl.

- 15 8. The polymer according to claim 6 or 7, wherein the repeating unit of the adhesion promoting monomer has the following structure:

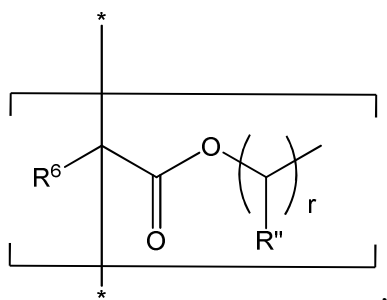


9. The polymer according to any one of the preceding claims, wherein the diluent monomer comprises the following structure:



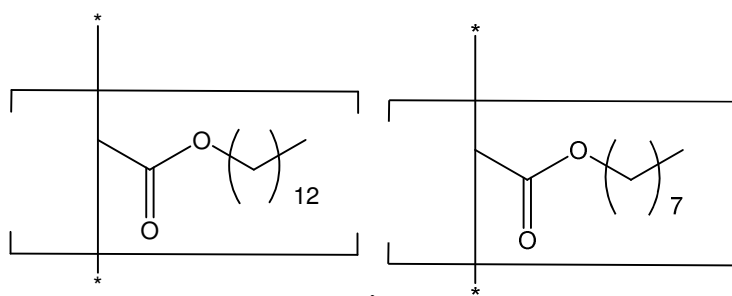
- 5 wherein R'' is hydrogen or alkyl and r is an integer selected from 1 to 20.

10. The polymer according to claim 9, wherein the repeating unit of the diluent monomer has the following structure:



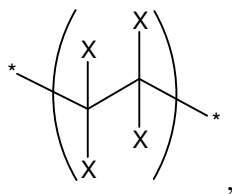
wherein R⁶ is hydrogen or alkyl.

- 10 11. The polymer according to claim 9 or 10, wherein the repeating unit of the diluent monomer is selected from the group having the following structure:



or a mixture thereof.

12. The polymer according to any one of the preceding claims, wherein the repeating unit of the thixotrope monomer has the following structure:



wherein X is halogen.

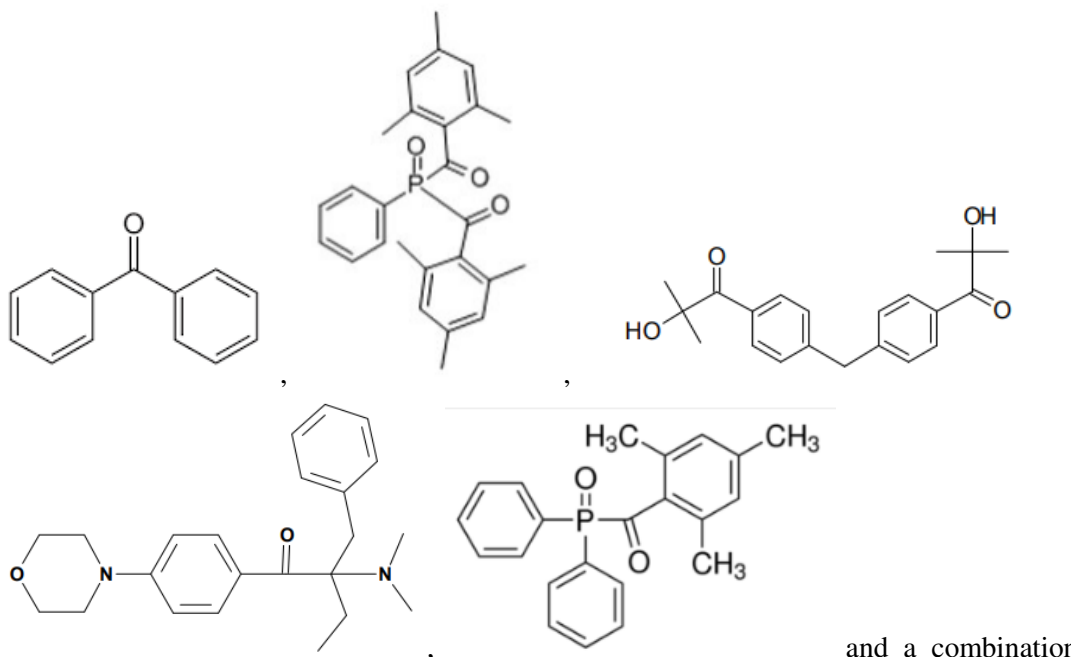
13. The polymer according to claim 12, wherein X is fluorine.

14. The polymer according to any one of the preceding claims, wherein the polymer comprises:

- 5 about 30 wt% to about 60 wt% of the bulk monomer,
 about 0.2 wt% to about 2 wt% of the adhesion promoting monomer
 about 5 wt% to about 30 wt% of the diluent monomer, and
 about 30 wt% to about 50 wt% of the thixotrope monomer,
 wherein the total wt% is 100%.

10 15. A polymer composition comprising the polymer of claims 1 to 14 and a photoinitiator.

16. The polymer composition according to claim 15, wherein the photoinitiator is selected from the group consisting of the following structures:



and a combination

15 thereof.

17. The polymer composition according to claim 15 or 16, wherein the polymer composition comprises:

about 30 wt% to about 60 wt% of the bulk monomer,

about 0.2 wt% to about 2 wt% of the adhesion promoting monomer

about 5 wt% to about 30 wt% of the diluent monomer,

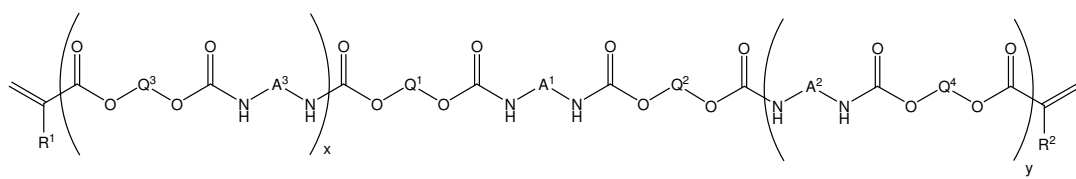
about 0.3 wt% to about 1.5 wt% of the photoinitiator, and

5 about 30 wt% to about 50 wt% of the thixotrope monomer,

wherein the total wt% is 100%.

18. A method for synthesizing the polymer according to any one of claims 1 to 14 or a polymer composition according to any one of claims 15 to 17, comprising the step of contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon, to form a mixture.

19. The method according to claim 18, wherein the bulk monomer has the following structure:

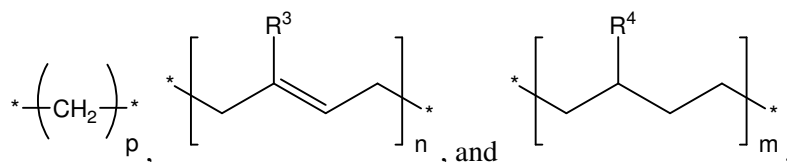


15 wherein Q^1 , Q^2 , Q^3 and Q^4 are independently optionally substituted, linear or branched, alkyl or alkenyl;

A^1 , A^2 and A^3 are independently selected from the group consisting of optionally substituted alkyl, optionally substituted cycloalkyl or optionally substituted aryl, and

R^1 and R^2 are independently H or alkyl.

20. The method according to claim 19, wherein Q^1 , Q^2 , Q^3 and Q^4 are independently selected from the group consisting of the following:

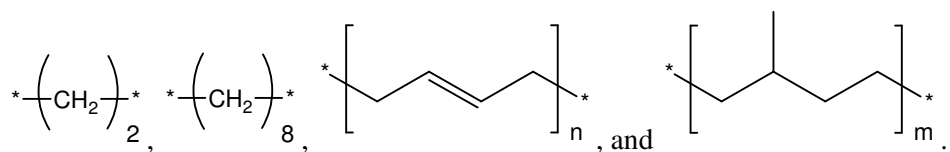


wherein n, m and p are independently an integer selected from 1 to 20,

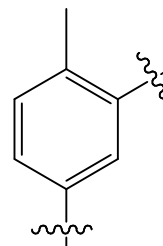
R^3 is hydrogen or alkyl and

R^4 is alkyl.

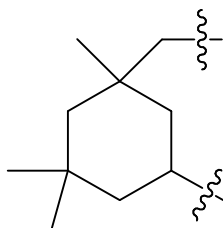
21. The method according to claim 19 or 20, wherein Q^1 , Q^2 , Q^3 and Q^4 are independently selected from the group consisting of the following:



22. The method according to any one of claims 19 to 21 wherein A^1 , A^2 and A^3 is



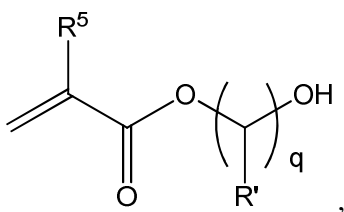
- 5 independently selected from the group consisting of alkyl, or



, wherein the bond broken by $\sim$ represents where the molecule is attached to the rest of the polymer.

23. The method according to any one of claims 19 to 22, wherein R^1 and R^2 are independently hydrogen or methyl.

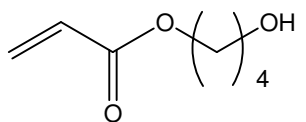
- 10 24. The method according to any one of claims 18 to 23, wherein the adhesion promoting monomer has the following structure:



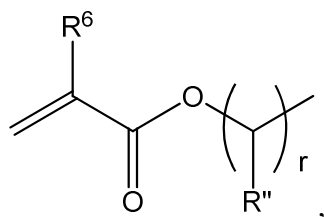
wherein R' and R^5 are independently hydrogen or alkyl and

q is an integer selected from 1 to 10.

- 15 25. The method according to any one of claims 24, wherein the adhesion promoting monomer has the following structure:



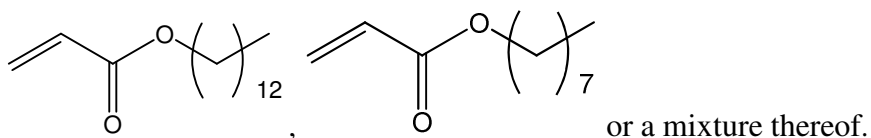
26. The method according to any one of claims 18 to 25, wherein the diluent monomer has the following structure:



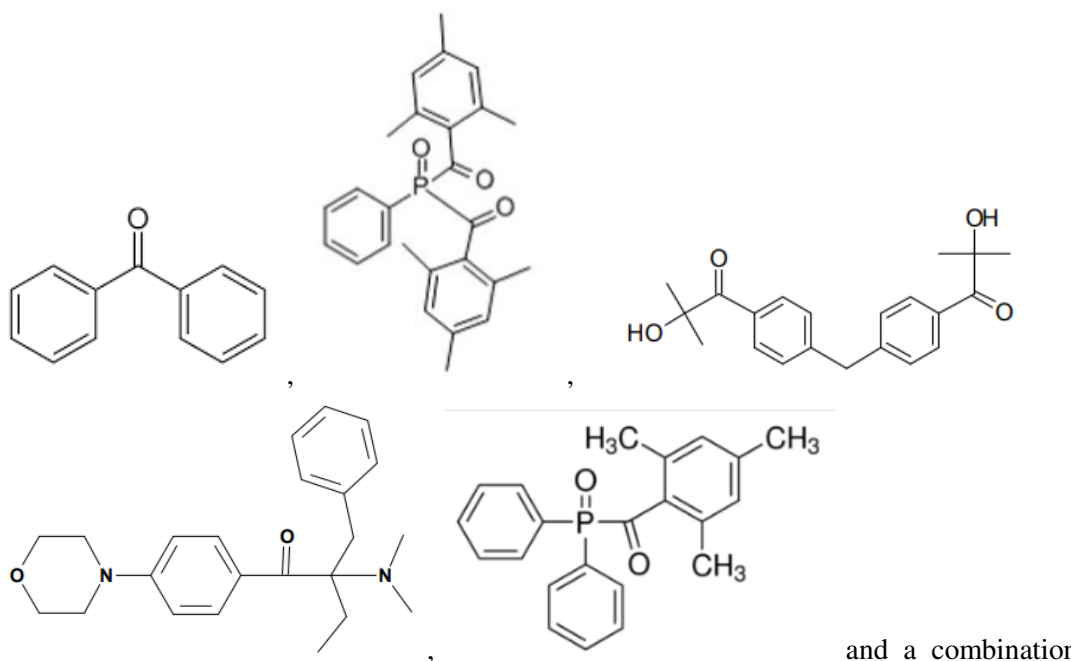
wherein R'' and R⁶ are independently hydrogen or alkyl, and

5 r is an integer selected from 1 to 20.

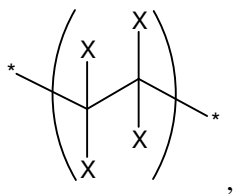
27. The method according to claim 26, wherein the diluent monomer is selected from the group consisting of the following structure:



28. The method according to any one of claims 18 to 27, wherein the photoinitiator is selected from the group consisting of the following structures:



29. The method according to any one of claims 18 to 28, wherein the repeating unit of the thixotrope monomer comprises the following structure:



wherein X is halogen.

30. The method according to any one of claims 18 to 29, wherein the bulk monomer, the adhesion promoting monomer, the diluent monomer, the photoinitiator and the thixotrope monomer are contacted at the following weight percentage:

about 30 wt% to about 60 wt% of the bulk monomer,

about 0.2 wt% to about 2 wt% of the adhesion promoting monomer

about 5 wt% to about 30 wt% of the diluent monomer,

about 0.3 wt% to about 1.5 wt% of the photoinitiator, and

about 30 wt% to about 50 wt% of the thixotrope monomer,

wherein the total wt% is 100%.

31. The method according to any one of claims 18 to 30, wherein the bulk monomer, adhesion promoting monomer, the diluent monomer, the photoinitiator and the thixotrope monomer are mixed sequentially in that order to form the mixture.

32. The method according to any one of claims 18 to 31, wherein the mixture is irradiated with UV-radiation.

33. The method according claim 32, wherein the UV irradiation is UV-A and is performed at an intensity in the range of about 2 J/cm² to about 14 J/cm².

34. The method according to claim 33, wherein the UV irradiation is performed at a temperature in the range of about 120 °C to about 180 °C for a duration in the range of about 2 hours to about 4 hours.

35. The method according to any one of claims 18 to 34, wherein the mixture is irradiated in situ using spot curing.

36. A polymer composition obtainable by contacting a bulk monomer, an adhesion promoting monomer, a diluent monomer, a photoinitiator and a thixotrope monomer, wherein the thixotrope monomer is substantially free of silicon.

37. A gasket comprising the polymer according to any one of claims 1 to 14 or 36.