(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 May 2007 (03.05.2007)

PCT

(10) International Publication Number
WO 2007/048586 A2

(51) International Patent Classification:
C08G 18/67 (2006.01) *G03F 7/027* (2006.01)
C09D 175/16 (2006.01)

(21) International Application Number:
PCT/EP2006/010265

(22) International Filing Date: 25 October 2006 (25.10.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05023240.4 25 October 2005 (25.10.2005) EP

(71) Applicant *(for all designated States except US)*: **CYTEC SURFACE SPECIALTIES, S.A.** [BE/BE]; Square Marie Curie, 11, B-1070 Brussels (BE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **KONISHI, Toru** [JP/JP]; 45 Miyukigaoka, Tsukuba-shi, Ibaraki 305-0841 (JP). **MAEJIMA, Noburu** [JP/JP]; 45 Miyukigaoka, Tsukuba-shi, Ibaraki 305-0841 (JP). **ITO, Makiya** [JP/JP]; 45 Miyukigaoka, Tsukuba-shi, Ibaraki 305-0841 (JP).

(74) Agent: **KIRK, Martin**; Cytec Surface Specialties, S.A., Anderlechtstraat, 33, B-1620 Drogenbos (BE).

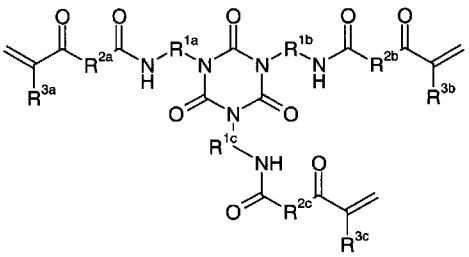
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

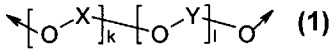
Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

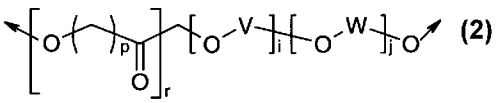
(54) **Title:** POLYMER AND COMPOSITIONS



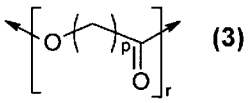
(I)



(1)



(2)



(3)

(57) **Abstract:** There are disclosed urethane acrylates of Formula (1) : where R^{1a}, R^{1b} and R^{1c} each independently represent C_{2-15}hydrocarbylene, preferably linear C_{3-12}alkylene (such as , C_{4-8}alkylene; e.g. hexylene); a isophorone unit and/or a tolyl unit. R^{2a}, R^{2b} and R^{2c} each independently represent: a divalent moiety of Formula (2) where X and Y independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and k is from O to 30; I is from O to 30; and 'k + I' is from 1 to 30; and/or a divalent moiety of Formula (3) where V and W independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and i is from 0 to 30; j is from 0 to 30; and 'i + j' is from 1 to 30; p is from 1 to 10; and r is from 1 to 10; and R^{3a} R^{3b} and R^{3c} each independently represent H or methyl (i.e. R^3 forms respectively part of an acrylate or a methacrylate group); with the provisos that at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula (2); at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula (3); and when R^2 represents a divalent moiety of Formula (3), the sub moiety within Formula (3), is attached directly to the amide group in Formula (1). The UAs of Formula (1) are of non crystalline and of low viscosity and are suitable for preparing polymeric flexibilizers suitable for tenting applications. A process for preparing these urethane acrylate is also described.

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Polymer and compositions

This invention relates to the field of urethane acrylate resins curable by actinic radiation such as UV radiation and/or e-beam.

Urethane acrylates are conveniently used to prepare radiation curable resin compositions for use as flexibilisers, plasticizers and/or softeners. Often such urethane acrylates comprise isocyanurate groups.

However most of the conventional urethane acrylates have various disadvantages for use in the aforementioned applications, especially when used in tenting applications.

As used herein the term "tenting" refers to the following process for producing circuit boards. In a first step a dry film of photo-curable resin (known as a photo-resist) is applied to a laminate clad in copper foil. In a second step, curing (usually UV) radiation is applied to the coated laminate through a negative image of the circuit to be produced. The photo-resist is thus cured only in those areas that correspond to the desired circuit. In the next, development, step the substrate is dipped into developer or etchant and the copper foil will be removed where it is not protected by cured photo-resist. The photo-resist is removed (stripped) in a final step to reveal the underlying copper circuit.

However if the photo-resist does not have sufficiently good tenting properties then copper foil will not be sufficiently protected from the developer. In a worse case breaks will appear in the circuit will make the board unusable and even holes in desired pattern may have other undesirable effects (such as a undesirable change in the electrical properties of the circuit). It is also desirable in tenting applications for the photo resist to have sufficient flexibility to be easy to apply and use as well as to provide improved resistance to development to protect of the circuit image. This can be achieved by use of flexibilisers, softeners and/or plasticizers and/or improving the inherent properties of the photo-resist.

The disadvantages of known urethane acrylates include some or all of the following. The urethane acrylates develop scum in the polymer composition and/or are too highly crystalline. If di-functional urethane acrylates are used the compositions are too soft but if highly functional urethane acrylates are used the resin is too brittle. Modifying the urethane acrylate to address these issues can result in the polymer composition losing robust tenting strength.

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Various isocyanurate based urethane acrylates are known, for example those described below.

JP 57-55914-A (Hitachi Chem.) discloses urethane acrylate containing dry film photo-resist composition for solder masks and/or plating resists. However, those urethane acrylates have good chemical and/or thermal resistance but poor tenting strength.

JP 59-157112 discloses the comparative examples herein (see below) with poly caprolactone modifications.

JP 62-050315 discloses PTMG based urethane acrylates.

JP 62-215618 discloses urethane acrylates from polyisocyanate / polyetherpolyol / monohydroxyalkylacrylate combination with THEIC tri(meth)acrylates and monofunctional (meth)acrylates.

JP 62-290705 discloses solder resist formulation including THEIC tri(meth)acrylates, PPG or PEG based urethane (meth)acrylates

JP 63-027518 describes PTMG/H12MDI based urethane acrylates.

JP 63-090525 discloses urethane acrylates from polyisocyanate / polyetherpolyol / monohydroxyalkylacrylate / HO-R^1-S-R^2-OH (where R^1 and R^2 denote alkyl chains).

JP 63-090526 describes urethane acrylate from polyisocyanate/ polyesterpolyol (M_w 600-4000) / diol (M_w 60-200) / monohydroxyalkylacrylate. The following structures are those exemplified TDI / polyesterpolyol (M_w 1000) / 1,4-butanediol or 1,6-hexanediol or 3-methyl-1,6-pentanediol / HEA.

JP 63-270719 discloses PTMG based urethane acrylates.

JP 02-034620 discloses (a) urethane (meth)acrylates (b) mono and multi functional unsaturated compounds (c) phosphineoxide derivatives as photo initiators. The following three types of urethane acrylates are the only ones exemplified (i) HEA / TDI / PTMG #1000 / TDI / HEA (ii) HPA / HDI / PTMG #2000 / HDI / HPA and (iii) HEA / TDI / PPG , PTMG copolymer #2000 / TDI / HEA.

JP 04-130119 describes materials similar to the comparative examples described later in this application.

JP 04-306218 describes polyisocyanate mixture having isocyanurate structure and allophanate structure by reacting with HDI or HDI / IPDI and C_{6-9} aliphatic alcohol. There is no radiation curable functional group within the claimed structures.
JP 05-117348 discloses TDI based urethane acrylates for high refractive index.

JP 05-273754-A (Sunopco) discloses isocyanurate based urethane acrylate having chemical and thermal resistances for liquid photo-imageable solder masks.

JP 06-093066 also discloses UV-PUD compounds.

JP 06-145273 discloses UV-PUD compounds.

JP 09-003147 describes polyisocyanate hardener, polyisocyanate modified paint and adhesive formulations by using HDI / IPDI blends partially reacted with primary alcohol. There is no radiation curable functional group within the claimed structures.

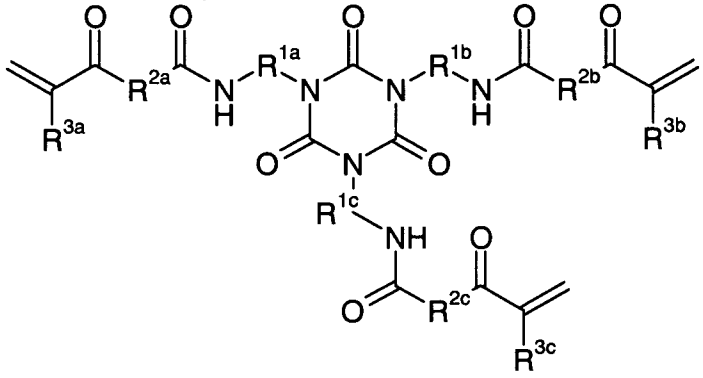
JP 09-087338 discloses poly organosiloxane based urethane acrylates.

JP 2001-117224-A (Hitachi Chem); JP 2001-174988-A (Hitachi Chem); JP 2002-196484-A (Hitachi Chem); and JP 2002-207292-A (Hitachi Chem.) each disclose dry film photo resist compositions for tenting applications. The compositions comprise urethane acrylate(s) with alkylene oxide units added which are stated to improve tenting performance. However, these compositions remain insufficiently improved to satisfy current industrial requirements.

It is an object of the present invention to provide improved urethane acrylates and polymer compositions obtainable therefrom which solve some or all of these problems described herein.

The applicant has found surprisingly that if certain urethane acrylates with isocyanurate groups also comprise polycaprolactone and polyethylene glycol moieties they are especially suitable for preparing polymer compositions with excellent tenting properties as these urethane acrylates are non crystalline and have low viscosity.

Therefore broadly in accordance with the present invention there is provided a urethane acrylate represented by Formula 1:



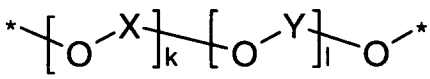
Formula 1

where

R^{1a}, R^{1b} and R^{1c} each independently represent C_{2-15}hydrocarbylene;

R^{2a}, R^{2b} and R^{2c} each independently represent:

a divalent moiety of Formula 2



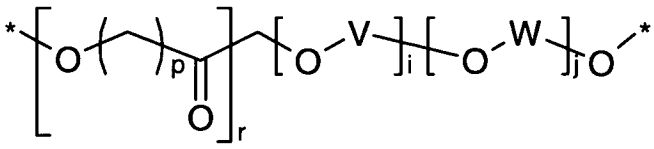
Formula 2

where X and Y independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and

k is from 0 to 30; l is from 0 to 30; and 'k + l' is from 1 to 30;

and/or

a divalent moiety of Formula 3



where V and W independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and

i is from 0 to 30; j is from 0 to 30; and 'i + j' is from 1 to 30;

p is from 1 to 10; and

r is from 1 to 10;

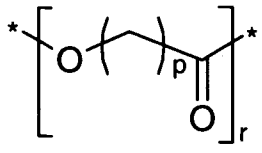
R^{3a} R^{3b} and R^{3c} each independently represent H or methyl (i.e. R^3 forms respectively part of an acrylate or a methacrylate group);

with the provisos that:

at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula 2;

at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula 3; and

when R^2 represents a divalent moiety of Formula 3, the sub-moiety

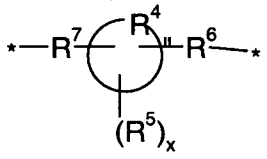


within Formula 3, is attached directly to the amide group in Formula 1.

Preferably R^{1a}, R^{1b} and R^{1c} each independently represent a linear C_{2-15}alkylene, and/or a C_{3-15}hydrocarbylene comprising a cyclic ring.

More preferably the linear alkylene is C_{3-12}alkylene, most preferably C_{4-8}alkylene; for example hexylene.

Most preferably the cyclic hydrocarbylene is a moiety of Formula 4:

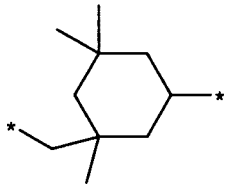


Formula 4

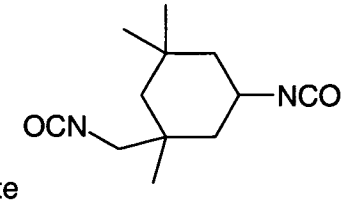
where R^4 denotes a C_{3-8}hydrocarbylene ring (optionally a C_6hydrocarbylene ring, for example phenylene or cyclohexylene);
R^5 is independently C_{1-4}alkyl; and x is 0 to 4 (optionally R^5 is methyl and x is 1 to 3); and R^6 and R^7 independently represent methylene or a direct bond (i.e. where the moiety is attached within Formula 1 via a single bond directly to the ring of Formula 4).

Most preferably the cyclic hydrocarbylene is selected from the group consisting of: isophorone unit(s) and tolyl unit(s).

The term isophorone unit as used herein means any suitable divalent group derived from isophorone. Suitable isophorone units may comprise for example the moiety

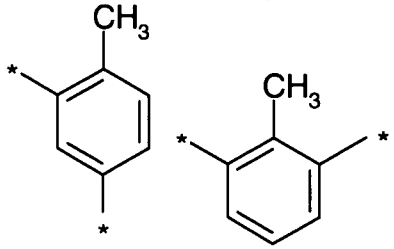


(which may be derived from any suitable precursors such as

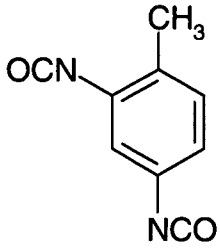


isophorone diisocyanate).

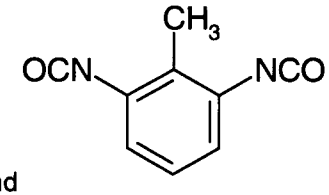
The term tolyl unit as used herein means any suitable divalent group derived from toulene. Suitable tolyl units may comprise for example the moieties



(which may be derived from any suitable precursors

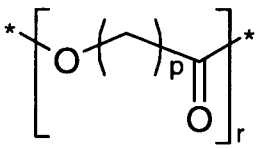
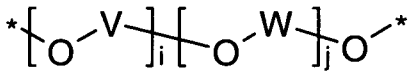


such as suitable isomers of tolylene diisocyanurete (TDI), respectively



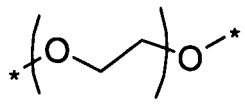
and).

The terms isophorone unit and tolyl unit includes any suitable isomers thereof as the atoms on these moieties which are linked to the rest of the structure of Formula 1 cannot always be readily controlled during the preparation of these urethane acrylates.

R^2 may represent a divalent moiety of Formula 3 that comprises a sub-moiety of formula . As the second proviso makes clear, these sub-moiet(ies) are never attached directly to (meth)acrylate functional group in Formula 1, but the other way round (to the amide). When R^2 is a moiety of Formula 3, it is the  moiety within Formula 3 which would be connected directly to the (meth)acrylate group in Formula 1.

Preferred moieties of Formula 2 are those where: k is from 0 to 20; l is from 0 to 20 and 'k+l' is from 1 to 20; more preferably where k is from 0 to 10; l is from 0 to 10 and 'k+l' is from 6 to 10, most preferably where X and Y are also linear or branched alkylene.

Conveniently Formula 2 is a divalent moiety of Formula 2a



Formula 2a

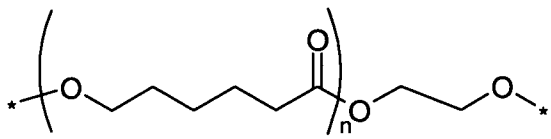
where m is from 2 to 12, more conveniently from 5 to 12, most conveniently from 6 to 10. (i.e. Formula 2a corresponds to Formula 2 above where X and Y are both ethylene and k + l = m)

Preferred moieties of Formula 3 are those where:
i is from 0 to 20; j is from 0 to 20, and 'i+j' is from 1 to 20; and
r is from 1 to 8; and p is from 3 to 6.

More preferred moieties of Formula 3 are those where:
i is from 0 to 10; j is from 0 to 10 and 'i+j' is from 1 to 10; and
r is from 1 to 6; and p is from 3 to 6.

Most preferred moieties of Formula 3 are those where:
i is from 0 to 4; j is from 0 to 4, and 'i+j' is from 1 to 4;
r is from 2 to 4 and p is 4; and
V and W are both non cyclic C_{2-4}alkylene.

Conveniently Formula 3 is a divalent moiety of Formula 3a



Formula 3a

where n is from 1 to 8, more conveniently from 1 to 5; most conveniently from 2 to 4. (i.e. Formula 3a corresponds to Formula 3 above where i is 0, j is 1, W is ethylene, p is 5 and r is n)

The applicant has discovered that urethane acrylates (UA) comprising predominately linking groups of Formula 3 (such as those UA represent by an analogy of Formula 1 where every R^2 represents a moiety of Formula 3a comprising 'n' caprolactone moieties) have too high a crystallinity and/or too high viscosity for the end uses described herein. However urethane acrylates comprising mostly linking groups of Formula 2 (such as those UA represented by an analogy of Formula 1 where every R^2 represents an ethoxy moiety of Formula 2a) have been found to have insufficiently good properties for tenting applications. Therefore to have the desired performance

the urethane acrylates of the present invention contain both type of linking groups (for example both caprolactone units of Formula 3a and ethoxy units of Formula 2a) as indicated in the proviso (R^2 represents both Formulae 2 & 3).

Examples of compounds and / or polymers of the invention are those derived from H(E/P)(M)A-polyethylene glycol, H(E/P)(M)A-polycaprolactone, H(E/P)(M)A-polypropylene glycol, H(E/P)(M)A-poly tetra methylene glycol (PTMG) and/or mixtures thereof. As used herein the term "H(E/P)(M)A" denotes the moieties: HEA (hydroxy ethyl acrylate), HEMA (hydroxy ethyl methacrylate), HPA (hydroxy propyl acrylate) and HPMA (hydroxy propyl methacrylate).

Advantageous materials of the invention are derivatives of H(E/P)(M)A-polyethylene glycol; and HE(M)A-polycaprolactone due to their balance of low cost and good properties. For example HE(M)A-polypropyleneglycol derivatives exhibit less good developing performance and whilst HE(M)A-poly tetra methylene glycol (PTMG) derivatives have excellent tenting properties, they are very expensive.

It is preferred that Formula 1 represents a polymer i.e. a polydisperse mixture of several compounds of Formula 1.

Preferred polymers of Formula 1 have a viscosity range of less than about 30,000 mPa.s, more preferably less than about 20,000 mPa.s, and most preferably less than about 12,000 mPa.s. It is an important optional advantage of the polymers of the invention that they can be treated easily at room temperature.

Preferred polymers of Formula 1 have a weight average molecular weight (Mw) of from about 3000 to about 6000 daltons as the applicant has found that polymers with a Mw of greater than 6000 are less good at developing performance and those with a Mw of lower than 3000 have a worsening tenting performance.

The term 'hydrocarbylene' as used herein denotes a divalent moiety (optionally attached to one or more other moieties) which consists of one or more hydrogen atoms and one or more carbon atoms the free valencies of which are not engaged in a double bond. A hydrocarbylene can be formed by removing two hydrogen atoms from a hydrocarbon (for example from an alkane to form an alkylene). The hydrocarbylene may comprise saturated carbon to carbon single bonds (e.g. in alkyl groups); unsaturated double and/or triple carbon to carbon bonds (e.g. in respectively alkenyl and alkynyl groups); aromatic groups (e.g. in aryl groups) and/or combinations thereof

within the same moiety. Preferred hydrocarbylenes are alkylenes (which are biivalent and saturated).

For certain moieties herein the point(s) of attachment to the larger molecule or free valenc(ies) are indicated in the formulae by a free bond terminating in an asterisk.

The total number of certain atoms is specified for certain substituents for example C_{1-x}alkylene, signifies those alkylenes consisting of "1 to x" carbon atoms. A moiety which comprises a chain of three or more atoms such as $C_{>3}$hydrocarbylene or $C_{>3}$alkylene signifies a moiety in which the chain wholly or in part may be linear, branched and/or form a ring (including spiro and/or fused rings). Preferred hydrocarbylenes are linear or branched; more preferably linear.

Any radical group or moiety mentioned herein (e.g. as a substituent) may be a multivalent or a monovalent radical unless otherwise stated or the context clearly indicates otherwise (e.g. a bivalent hydrocarbylene moiety linking two other moieties). In any of the formulae herein if one or more substituents are not indicated as attached to any particular atom in a moiety (e.g. on a particular position along a chain and/or ring) the substituent may replace any H and/or may be located at any available position on the moiety which is chemically suitable and/or effective.

As used herein chemical terms (other than IUAPC names for specifically identified compounds) which comprise features which are given in parentheses – such as (alkyl)acrylate, (meth)acrylate and/or (co)polymer denote that that part in parentheses is optional as the context dictates, so for example the term (meth)acrylate denotes both methacrylate and acrylate.

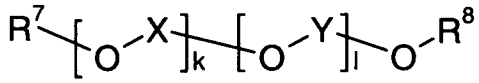
Certain moieties, species, groups, repeat units, compounds, oligomers, polymers, materials, mixtures, compositions and/or formulations which comprise and/or are used in some or all of the invention as described herein may exist as one or more different forms such as any of those in the following non exhaustive list: stereoisomers (such as enantiomers (e.g. E and/or Z forms), diastereoisomers and/or geometric isomers); tautomers (e.g. keto and/or enol forms), conformers, salts, zwitterions, complexes (such as chelates, clathrates, crown compounds, cyptands / cryptades, inclusion compounds, intercalation compounds, interstitial compounds, ligand complexes, organometallic complexes, non stoichiometric complexes, π adducts, solvates and/or hydrates); isotopically substituted forms, polymeric configurations [such as homo or copolymers, random, graft and/or block polymers, linear and/or branched polymers (e.g.

star and/or side branched), cross linked and/or networked polymers, polymers obtainable from di and/or tri valent repeat units, dendrimers, polymers of different tacticity (e.g. isotactic, syndiotactic or atactic polymers)]; polymorphs (such as interstitial forms, crystalline forms and/or amorphous forms), different phases, solid solutions; and/or combinations thereof and/or mixtures thereof where possible. The present invention comprises and/or uses all such forms which are effective as defined herein.

In a yet further aspect of the invention there is provided a process for preparing a urethane acrylate comprising the step of reacting together

(a) Component A comprising at least one C_{2-15}hydrocarbyl diisocyanate isocyanurate;

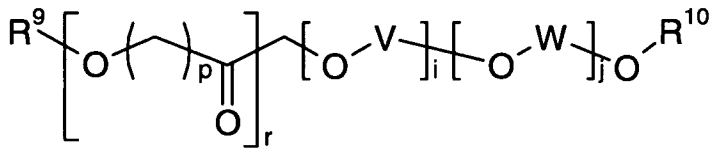
(b) Component B comprising at least one compound of Formula 2b



Formula 2b

where X, Y, k and l are as given herein for Formula 2, and R^7 and R^8 are suitable (meth)acrylate groups which are optionally the same.

(c) Component C comprising at least one compound of Formula 3b



Formula 3b

where V, W, i, j, p and r are as given herein for Formula 3 , and R^9 and R^{10} are suitable (meth)acrylate groups which are optionally the same.

to obtain a urethane acrylate of Formula 1as described herein.

It will be appreciated that the meth(acrylate) groups in Formulae 2b and 3b are selected so they will react (under suitable conditions) with the isocyanate isocyanurate groups of Component A to form the urethane acrylates of Formula 1. Suitable methacrylate groups will be apparent to those skilled in the art and are largely selected from the most available cheap raw materials of Formulae 2b and 3b. Particularly suitable meth(acrylate) groups may be selected from hydroxy ethyl acrylate, hydroxy propyl acrylate; hydroxy ethyl methacrylate and hydroxy propyl methacrylate.

In a preferred process of the present invention Component A may comprises at least one C_{2-10}hydrocarbylene diisocyanate isocyanurate preferably a C_{4-8}alkylene diisocyanate isocyanurate and/or a C_{6-8}alkarylene diisocyanate isocyanurate.

In a preferred process of the present invention Component B may comprise at least one hydroxyC_{1-4}alkoxy(meth)acrylate- (caprolactone)$_n$ where the number of caprolactone units 'n' is given as for Formula 3a above, for example from 1 to 8, more conveniently from 1 to 5; most conveniently from 2 to 4.

In a preferred process of the present invention Component C may comprise at least one (C_{1-4}alkoxy)$_m$(meth)acrylate; where the number of alkoxy units 'm' is given as for Formula 2a above, for example from 2 to 12, more conveniently from 5 to 12; most conveniently from 6 to 10, especially 6, 8 and 10.
Examples of suitable Component A are isophorone diisocyanate (IPDI) isocyanurate; hexamethylene diisocyanate (HDI) isocyanurate; and/or tolylene diisocyanate (TDI) isocyanurate.

Examples of a suitable Component B are H(E/P)(M)A-(di, tri and tetra) caprolactones; for example: hydroxy ethyl acrylate di-caprolactone; hydroxy ethyl methacrylate di-caprolactone; hydroxy ethyl methacrylate tri-caprolactone and/or hydroxy ethyl methacrylate tetra caprolactone.

Examples of a suitable Component C are H(E/P)(M)A-polyethylene glycols, H(E/P)(M)A-polypropylene glycols, H(E/P)(M)A-poly tetra methylene glycols and mixtures thereof. Advantageously Component C may be a H(E/P)(M)A-polyethylene glycol such as hexylene glycol acrylate, hexylene glycol methacrylate, octylene glycol methacrylate and/or decylene glycol acrylate.

Components A, B & C may be reacted together simultaneously or they may be reacted together sequentially, for example Component C may be added to the reaction mixture part way during the reaction of Components A and B.

The process of the invention can be operated using any other suitable methods and equipment and optionally other ingredients may added to Components A, B and C as needed. For example the reaction may occur in presence of a suitable catalyst and/or initiator (such as dibutyl tin dilaurate and/or 3,5-dibutyl-4-hydroxy-toluene). Further features of the process are described in the examples.

The applicant has found that low viscosity urethane acrylates of Formula 1 can be usefully prepared when Component A is hexa(methylene) diisocyanate (HDI)

isocyanurate or tolylene diisocyanate (TDI) isocyanurate which are both commonly available materials.

Unless the context clearly indicates otherwise, as used herein plural forms of the terms herein are to be construed as including the singular form and vice versa.

The term "comprising" as used herein will be understood to mean that the list following is non-exhaustive and may or may not include any other additional suitable items, for example one or more further feature(s), component(s), ingredient(s) and/or substituent(s) as appropriate.

The terms 'effective', 'acceptable' 'active' and/or 'suitable' (for example with reference to any process, use, method, application, preparation, product, material, formulation, compound, monomer, oligomer, polymer precursor, and/or polymers of the present invention and/or described herein as appropriate) will be understood to refer to those features of the invention which if used in the correct manner provide the required properties to that which they are added and/or incorporated to be of utility as described herein. Such utility may be direct for example where a material has the required properties for the aforementioned uses and/or indirect for example where a material has use as a synthetic intermediate and/or diagnostic tool in preparing other materials of direct utility. As used herein these terms also denote that a functional group is compatible with producing effective, acceptable, active and/or suitable end products.

A further aspect of the invention provides use of a urethane acrylate of the invention as described herein, as a flexibilizer, plasticizer and/or softener.

A still further aspect of the invention provides use of a urethane acrylate of the invention as described herein, in a method of tenting.

Many other variations embodiments of the invention will be apparent to those skilled in the art and such variations are contemplated within the broad scope of the present invention.

Further aspects of the invention and preferred features thereof are given in the claims herein.

Examples

The present invention will now be described in detail with reference to the following non limiting examples which are by way of illustration only.

The following abbreviations have been used herein

"HDI" denotes hexamethylene diisocyanate

"HEA" denotes 2-hydroxy ethyl acrylate

"HEMA" denotes 2- hydroxy ethyl methacrylate

"EO" denotes an ethoxy repeat unit

"IPDI" denotes Isophorone di-isocyanate

"THEIC" denotes 1,3,5-tris(hydroxyethyl)isocyanurate

"TDI" denotes tolylene diisocyanate

"DBT" denotes dibutyl tin dilaurate (a catalyst)

"DHT" denotes 3,5-dibutyl-4-hydroxy-toluene (an initiator)

"PMP" denotes para methoxyphenol.

The following ingredients are identified by chemical name and/or trade-name and name of manufacturer.

Trade name	Chemical description	Manufacturer
Desmodur N3300	HDI isocyanurate	Bayer
Sumidur N3300	HDI isocyanurate	Sumika-Bayer
TKA 100P	HDI isocyanurate	Asahi-Kasei Chem.
Placcel FA2D	Polycaprolactone HEA, caprolactone x 2	Daicel
Tone M100	Polycaprolactone HEA, caprolactone x 2	Dow
Placcel FM2D	Polycaprolactone HEMA, caprolactone x 2	Daicel
Placcel FM3	Polycaprolactone HEMA, caprolactone x 3	Daicel
Placcel FM4	Polycaprolactone HEMA, caprolactone x 4	Daicel
Bisomer PEA-6	Polyethylene glycol acrylate, EO x 6	Cognis
Bisomer PEM6-LD	Polyethylene glycol methacrylate, EO x 6	Cognis
Blemmer PE-350	Polyethylene glycol methacrylate, EO x 8	NOF
Blemmer AE-400	Polyethylene glycol acrylate, EO x 10	NOF
Vestant IPDI	IPDI	Degussa
Desmodur T-80	TDI	Bayer
THEIC-PW	THEIC	Shikoku Kasei
CAPA 3091	Polycaprolactone trimethylol propane, Mw 900	Solvay
CAPA 2054	Polycaprolactone diethylene glycol, Mw 550	Solvay

Preparation of examples

Examples 1 to 6 of the present invention and comparative examples Comp I to IV are prepared using the basic method below. Refer to the following Table 1 for the type and amounts of certain ingredients indicated.

Basic Method

Reagent 'A' ('a' gram, NCO% = 'i') is weighed into a 1000ml, separable flask with dibutyl tin dilaurate ('ii' g, 500 ppm) and 3,5-dibutyl-4-hydroxy-toluene ('iii' g, 100ppm). A PTFE coated stirring blade is inserted in the flask's centre neck. To monitor the reaction temperature a thermocouple is inserted through one of the side necks of the flask and into the material. The other side neck is equipped with an Allihn condenser. Reagent 'B' ('b' g) is weighed into a 300ml additional funnel equipped with a Teflon stopcock. The addition funnel containing Reagent 'B' is placed in the neck of flask and a slow drip is started. The flask is gradually heated to 60°C. The reaction temperature is kept under 63°C. As the reaction exotherm begins to die down, Reagent 'C' ('c' g) is weighed into a 500ml addition funnel, which is placed in the neck of flask and a slow drip was started. The reaction temperature is kept under 63°C during the slow drip. After the reaction exotherm died down, the flask is heated to 90°C and the reaction is held at this temperature for 1 hour after which the NCO% is checked every hour until it reduced to < 0.1%. Then p-methoxyphenol ('iv' g, 100ppm) is added to reaction mixture, and the reaction temperature is cooled to 60°C. The material is then poured into dark polyethylene bottles.

Table 1 has the following notes to indicate where the basic method above is modified.

Note 'x' (Examples 5 & 6) After the addition of Reagent C is completed, the reaction is held at 60°C for 2 hours, the NCO% is checked every hour until it reduces to < 0.1% and then the p-methoxyphenol is added .

Note 'y' (Comp I) After the reaction exotherm begins to die down from the addition of Reagent B, the reaction is held at 60°C for 2 hours, the NCO% is checked every hour until it reduces to < 0.1% and then the p-methoxyphenol is added. The reaction mixture is agitated for 1 hour before it is stored and characterised.

Example	Reagent A	'a' /g	'i' / NCO %	Reagent B'	'b' / g	Reagent C	'c' /g	'ii' /g DBT	'iii' / g DHT	'iv' /g PMP
Ex 1	Desmodur N3300	328.18	22.07	Placcel FM4	343.43	Bisomer PEM6-LD	427.13	0.55	0.11	0.11
Ex 2	Sumidur N3300	132.58	21.71	Placcel FM4	132.99	Blemmer PE-350	194.43	0.23	0.046	0.046
Ex 3	Sumidur N3300	181.15	21.71	Placcel FM3	147.49	Blemmer PE-350	271.06	0.30	0.06	0.06
Ex 4	Sumidur N3300	192.72	21.71	Placcel FM2D	120.39	Blemmer PE-350	286.89	0.30	0.06	0.06
Ex 5[x]	Desmodur N3300	198.45	21.8	Tone M100	236.21	Bisomer PEA-6	115.34	0.03	0.06	0.06
Ex 6[x]	TKA 100P	162.11	22.2	Placcel FM3	271.19	Blemmer AE-400	166.71	0.03 (50 ppm)	0.06	0.06
Comp I[y]	Sumidur N3300	137.07	21.71	Placcel FA1DT	162.93	none	NA	0.15	0.03	0.03
Comp II	IPDI	193.93	37.83	Placcel FA2D	300.11	HEIC	75.97	0.285	0.143 (250ppm)	0.029 (50 ppm)
Comp III	TDI	176.63	48.27	HEA	117.37	CAPA 3091	306.6	0.03 (50 ppm)	0.15 (250ppm)	0.03 (50 ppm)
Comp IV	HDI	129.73	50	CAPA 2054	205.72	Placcel FA2D	264.91	0.03 (50 ppm)	0.15 (250ppm)	0.03 (50 ppm)

Table 1 Process parameters

Characterisation of examples

The material obtained from each example is characterised using conventional techniques and equipment. Viscosity is measured with a Brookfield Viscometer® model RVDV-E fitted with a small sample adapter. The viscosity (in mPa.s) is measured at 25°C unless indicated otherwise. Gel permeation chromatography (GPC) is used to measure the weight average molecular weight (M_w) of the material in Daltons. The GPC is performed with a high performance liquid chromatograph from Tosoh Corp. in Japan, model HLC-8220GPC fitted with a TSK gel super HZM-N column, number F0010 and a polystyrene reference is used to calibrate this machine.

The viscosity and M_w data are given in the following Table 2: Note that Comps II, III & IV are crystalline at room temperature.

Table 2

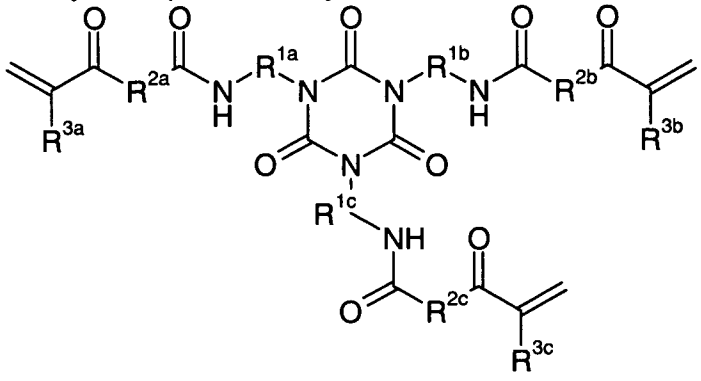
Properties of the Urethane (meth)acrylate examples

Example	M_w / Daltons (on GPC, PST)	Viscosity / mPa.s at 25°C	Appearance
Ex 1	4907	10600	Liquid
Ex 2	7530	26600	Liquid
Ex 3	6700	20600	Liquid
Ex 4	6331	21600	Liquid
Ex 5	5477	23000	Liquid
Ex 6	6020	11980	Liquid
Comp I	3641	69300	Viscous liquid
Comp II	5002	118000 (at 60°C)	White wax
Comp III	6184	99000 (at 60°C)	White wax
Comp IV	4873	1380 (at 60°C)	White wax

Each of the examples Ex 1 to Ex 6 can be advantageously used to prepare a flexibilizer of particular use in tenting applications.

Claims

1 A urethane acrylate represented by Formula 1:



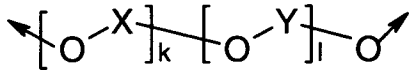
Formula 1

where

R^{1a}, R^{1b} and R^{1c} each independently represent C_{2-15}hydrocarbylene;

R^{2a}, R^{2b} and R^{2c} each independently represent:

a divalent moiety of Formula 2



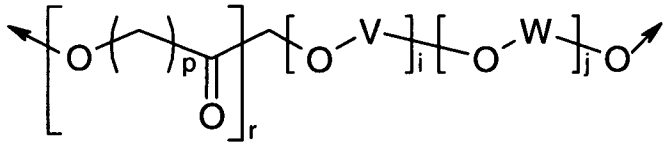
Formula 2

where X and Y independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and

k is from 0 to 30; l is from 0 to 30; and 'k + l' is from 1 to 30;

and/or

a divalent moiety of Formula 3



where V and W independently represent C_{2-10}hydrocarbylene, preferably C_{2-8}alkylene; and

i is from 0 to 30; j is from 0 to 30; and 'i + j' is from 1 to 30;

p is from 1 to 10; and

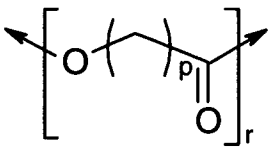
r is from 1 to 10;

R^{3a} R^{3b} and R^{3c} each independently represent H or methyl (i.e. R^3 forms respectively part of an acrylate or a methacrylate group);

with the provisos that:

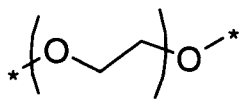
at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula 2;

at least one of R^{2a}, R^{2b} and R^{2c} is a moiety of Formula 3; and

when R^2 represents a divalent moiety of Formula 3, the sub-moiety  within Formula 3, is attached directly to the amide group in Formula 1.

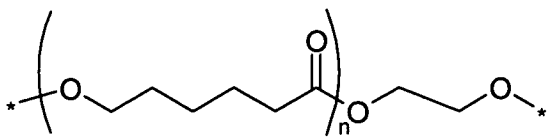
2. A urethane acrylate as claimed in claim 1, in which
R^{1a}, R^{1b} and R^{1c} each independently represent
a linear $C_{2\text{-}15}$alkylene, and/or a $C_{3\text{-}15}$hydrocarbylene comprising a cyclic ring;
R^{2a}, R^{2b} and R^{2c} each independently represent:
a moiety of Formula 2 where:
k is from 0 to 20; l is from 0 to 20 and 'k+l' is from 1 to 20; and/or
a moiety of Formula 3 where:
i is from 0 to 20; j is from 0 to 20, and 'i+j' is from 1 to 20; and
r is from 1 to 8; and p is from 3 to 6.

3. A urethane acrylate as claimed in either preceding claim 2, in which
Formula 2 is a divalent moiety of Formula 2a



Formula 2a

where m is from 2 to 12 and
Formula 3 is a divalent moiety of Formula 3a



Formula 3a

where n is from 1 to 8.

4. A urethane acrylate as claimed in any preceding claim, having a weight average molecular weight (M_w) of from about 3000 to about 6000 daltons.

5. A urethane acrylate as claimed in any preceding claim, having a viscosity of less than about 30,000 mPa.s.

6. A urethane acrylate as claimed in claim 5, having a viscosity of, less than about 20,000 mPa.s.

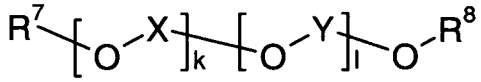
7. A urethane acrylate as claimed in claim 5, having a viscosity of, less than about 12,000 mPa.s.

8. A urethane acrylate prepared substantially as described in the Examples 1 to 6 herein.

9. A process for preparing a urethane acrylate as described in any preceding claim, the process comprising the step of reacting together

(a) Component A comprising at least one C_{2-15}hydrocarbyl diisocyanate isocyanurate;

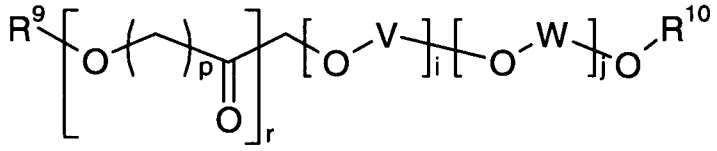
(b) Component B comprising at least one compound of Formula 2b



Formula 2b

where X, Y, k and l are as denoted in claim 1 for Formula 2, and R^7 and R^8 are suitable (meth)acrylate groups which are optionally the same.

(c) Component C comprising at least one compound of Formula 3b



Formula 3b

where V, W, i, j, p and r are as denoted in claim 1 for Formula 3, and R^9 and R^{10} are suitable (meth)acrylate groups which are optionally the same.