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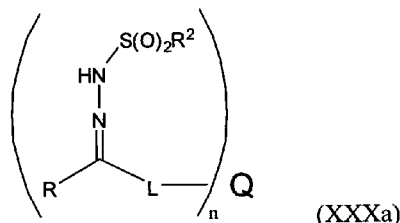
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(54) Title: CROSS-LINKABLE POLYMERS



(57) **Abstract:** The invention provides a functionalised compound which is a sulfonylhydrazone compound of formula (XXXa) wherein n is an integer equal to or greater than 3; L is a single bond or a linker group of formula (XII) as defined herein, R and R₂ are as defined herein, and Q is a polymer or a dendrimer. Further provided are the uses of the functionalised compound as a cross linking agent or as an adhesive. The invention further provides a process for cross linking or adhering a first substrate to a second substrate, which process comprises contacting the first and second substrates with a functionalised compound of the invention, and generating carbene reactive intermediate groups from the reactive intermediate precursor groups, so that carbene reactive intermediate groups react with the first and second substrates, thereby cross linking or adhering the first and second substrates. The resulting cross-linked products are also provided. The invention also provides an adhesive composition comprising the functionalised compound of the invention, a process for producing the functionalised compounds of the invention, and precursor compounds which are used in that process.

CROSS-LINKABLE POLYMERS

FIELD OF THE INVENTION

The invention relates to polymer compounds which bear chemically crosslinkable groups, and to processes for producing such compounds. In one aspect, the polymers are block co-polymers which are capable of forming phase domains. Crosslinking such compounds allows the production of thermally, hydrolytically and chemically stable cured materials.

Such materials show increased adhesive strength on inert, smooth or low surface energy materials, due to the highly reactive nature of the chemical crosslinker, and are suitable for use as flexible thermoset adhesives. The invention further relates to the use of the cross-linkable polymer compounds as cross-linking agents and as adhesives.

BACKGROUND TO THE INVENTION

Certain block co-polymers are capable of forming phase domains. The materials generally consist of a soft flexible portion and a hard inflexible portion. Materials such as this generally fall into the following four structural categories: (a) AB block copolymers; (b) ABA or BAB block copolymers, (c) $(AB)_n$ repeating block copolymers; and (d) multiarm polymers, such as triarm polymers, tetraarm polymers, dendrimers, and star polymers. These classes of polymers are illustrated schematically in Figs. 1(a), 1(b), 1(c) and 1(d) respectively, the soft, flexible portions being depicted as wavy lines and the hard, inflexible blocks as rectangles.

The most widely used examples of these phase domain block co-polymers are the styrene thermoplastic elastomers such as poly(styrene)-poly(butadiene)-poly(styrene) (SBS), poly(styrene)-poly(isoprene)-poly(styrene) (SIS), poly(styrene)-poly(butadiene/isoprene)-poly(styrene) (SIBS), poly(styrene)-poly(ethylene/butylene)-poly(styrene) (SEBS), poly(styrene)-poly(ethylene/propylene)-poly(styrene) (SEPS), and poly(styrene)-poly(ethylene/(ethylene/propylene))-poly(styrene) (SEEPS). These materials are widely used as hot melt and pressure sensitive adhesives.

These materials are thermoplastics which also have varying levels of elastomeric properties to them. The properties can be enhanced by the addition of additives such as tackifiers and blending with a second polymer. Multi-block polymers that form well known domains such as this can be termed "physically crosslinked".

One disadvantage of thermoplastic compositions containing only physically crosslinked co-polymers is that the domain behaviour of the materials breaks down when the individual blocks reach their glass transition temperature and, as a result, the upper working limit of these physically crosslinked materials is generally less than 100°C. Furthermore, physically crosslinked materials are susceptible to degradation by organic solvents and plasticisers limiting their use on certain materials such as polyvinyl chloride or in environments which encounter oils.

To overcome this limitation of physical crosslinking and to further improve the thermal and chemical stability of the polymer it is possible in certain cases to chemically crosslink the material, and by doing so it is possible to use these materials in a wider range of applications.

The chemical crosslinking process chemically links segments of different polymer strands together to form an extended three dimensional network. In such a cross-linked system the polymer is no longer a thermoplastic as it is prevented from returning to its original form by the three dimensional cross-linked network and as such is termed a thermoset polymer. Thermoset polymers are materials which undergo irreversible chemical cross linking on heating to form a high temperature stable material which is generally solid. The properties of the cured material vary and can range from brittle to elastomeric in nature. Other examples of thermoset materials are epoxies, silicones, polyurethanes and vulcanized elastomers or rubbers.

This chemical crosslinking of unsaturated block co-polymers enhances their mechanical, thermal and solvent stability at the expense of reducing the elastomeric properties of the system. In the case of fully saturated systems such as SEBS, SEPS and SEEPS, chemical crosslinking is possible by chemically grafting a reactive system onto one of the blocks which is capable of reacting with a chemical crosslinking agent.

Numerous methods are known for the chemical crosslinking of thermoplastic polymers together, most of which use a two or three component system.

Polymers which contain a block of un-saturation, such as SBS and SIS, can be chemical crosslinked together by two component reaction with sulphur in a vulcanization process or with peroxide and the un-saturated polymer. Such processes are well known to those skilled in the art and deliver materials which have higher temperature stability but reduced elasticity.

EP0227163 describes a chemical crosslinking system comprising a dimer of a benzocyclobutene derivative which on heating to above 200°C can thermally decompose and chemically crosslink to an unsaturated block in a polymer system. It is claimed that the system shows better thermal and hydrolytic stability than those obtained by chemical crosslinking with sulphur and peroxide. However, the operating temperature for curing, of above 200°C, precludes its use in applications where substrates that melt, or denature, above 200°C are used.

US5124405 relates to a tri-component chemical crosslinking system in which a polymer containing unsaturated blocks can be attacked chemically by an amino resin in the presence of a proton-donating acid catalyst. Reaction of the amino resin with the proton-donating acid catalyst leads to the formation of a carbocation, via a degradation mechanism, which can then react with unsaturated units on the polymer backbone to create a chemical crosslinking pathway. The procedure is carried out at between 93°C and 204°C, limiting its application.

US4556464 concerns chemically crosslinked systems in which di- or tri-acrylates can be used to cure selectively into an ABA block co-polymer at the A end groups. The A end groups consist of a random co-polymer of styrene and conjugated diene. Such an ABA system can be chemically crosslinked by the acrylates during activation with UV or electron beam irradiation.

US5446104 describes a star block co-polymer which contains epoxide end groups which can be used to crosslink the material.

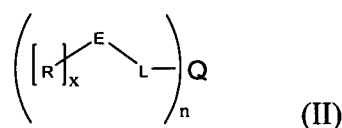
WO0192344 relates to a chemical crosslinking system that uses a styrene-hydrogenated diene block co-polymer which has previously had maleic anhydride grafted onto it via an extruder grafting process. This hybrid material is capable of reacting with aluminium acetylacetonate, which acts as a chemical crosslinker.

SUMMARY OF THE INVENTION

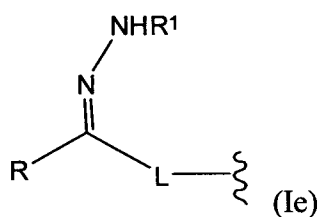
The inventors have provided a series of polymeric compounds which comprise multiple functionalities. The functionalities are carbene precursor groups which are readily convertible into carbene reactive intermediate groups, that can in turn react intramolecularly or with neighbouring polymer molecules, thereby cross-linking or curing the polymer. Due to their highly reactive nature, the reactive intermediate groups can also react with a wide variety of substrates, including inert, smooth or low-surface-energy bulk

materials, as well as nanoparticles, microparticles and individual compounds. The polymeric compounds are therefore suitable for use in a wide variety of applications, for instance as adhesives.

Accordingly, the invention provides a functionalised compound of formula (II), which functionalised compound comprises n carbene precursor groups which are the same or different, wherein n is an integer greater than or equal to 3:



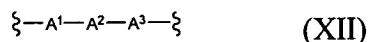
wherein x is 1, E is a group which is capable of being converted into a carbene reactive intermediate group, Q is a polymer or a dendrimer, and each of the $[\text{R}]_x\text{-E-L-}$ groups, which are the same or different, is a group of formula (1e)



wherein:

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} haloalkyl, C_{1-20} fluoroalkyl, C_{1-20} perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C_{1-10} alkylamino, $\text{di}(\text{C}_{1-10})$ alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C_{1-10} alkoxy, aryloxy, haloalkyl, thiol, C_{1-10} alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, $\text{tri}(\text{C}_{1-20}$ alkyl)silyl, $\text{aryldi}(\text{C}_{1-20}$ alkyl)silyl, $\text{diaryl}(\text{C}_{1-20}$ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R, wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

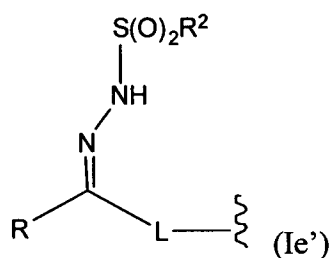
A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*\text{-C}_{1-20}$ alkylene-(O-C_{1-20}

alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²; and

R¹ is -S(O)₂R², wherein R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group.

Thus, the n carbene precursor groups, [R]_x-E-L-, are all sulfonylhydrazone groups of formula (1e')

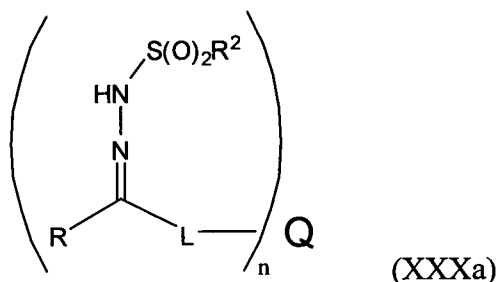


wherein L, R and R² are as defined above.

The ability to generate a carbene from a sulfonylhydrazone group without isolating the diazo group intermediate provides numerous advantages. Such sulfonylhydrazone groups are particularly advantageous because they are capable of being converted into a carbene reactive intermediate group, yet they are more stable than the diazo groups of formula (Ia) as defined herein. In particular, they act as a protected precursor to the carbene reactive intermediate and thereby allow a greater level of control over unwanted degradation of the functionalized compound of the invention, such as in transport or storage. Of particular significance is the decreased toxicity of a sulfonylhydrazone group

over a diazo group. Sulfonylhydrazone groups also offer a greater flexibility with regards to formulation as they are not degraded by carboxylic acids unlike diazo groups such as diazo esters, diazo ketones and alkyl or aryl diazos.

The functionalised compound of formula (II) of the invention is therefore a sulfonylhydrazone compound of formula (XXXa)

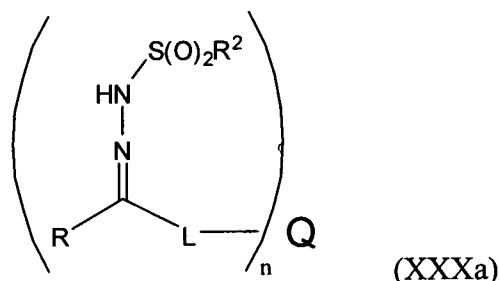


wherein

R, R², L, n and Q are as defined above.

In another aspect the invention provides a process for cross linking or adhering a first substrate to a second substrate, which first and second substrates are the same or different, which process comprises

(a) contacting the first and second substrates with a functionalised cross linking compound of the invention which is a sulfonylhydrazone compound of formula (XXXa)

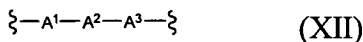


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryl di(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R, wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

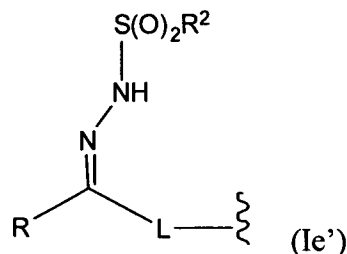
A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O) $_2$, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2-C_{1-20}$ alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2-C_{1-20}$ alkylene-O, * -arylene-O, * -heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O) $_2$, $^*-OC(O)$, $^*-N(R'')C(O)$, O, S, N(R''), $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2-C_{1-20}$ alkenylene and $^*-Z^2-C_{1-20}$ alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O) $_2$, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ;

R^2 is an unsubstituted or substituted C_{1-6} alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer; and

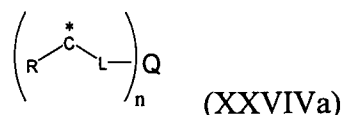
(b) generating carbene reactive intermediate groups from the n carbene precursor groups of formula (Ie')



wherein R, R² and L are as defined above, so that at least one carbene reactive intermediate group reacts with the first substrate and at least one other carbene reactive intermediate group reacts with the second substrate, thereby cross linking or adhering the first and second substrates.

The invention further provides a cross-linked or adhered product comprising:

- (a) a first substrate;
- (b) a second substrate; and
- (c) a cross linking moiety of formula (XXVIVa)



wherein

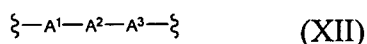
the first and second substrates are the same or different;

each * is a point of attachment of the cross linking moiety to the first substrate, the second substrate or to another moiety or molecule;

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

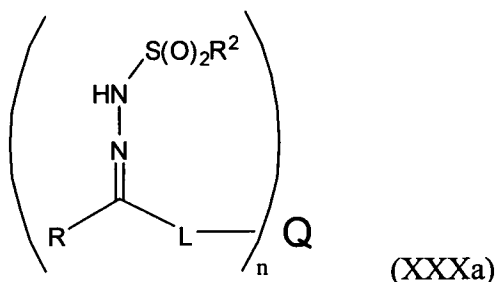
A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to

20, wherein Z^1 is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ; and

Q is a polymer or a dendrimer.

In another aspect, the invention provides a process for producing a functionalised compound which is a sulfonylhydrazone compound of formula (XXXa)

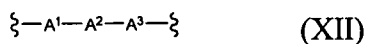


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryl di(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R, wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

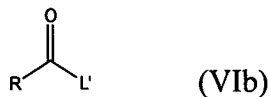
A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2-C_{1-20}$ alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2-C_{1-20}$ alkylene-O, $^*-$ arylene-O, $^*-$ heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O)₂, $^*-OC(O)$, $^*-N(R'')C(O)$, O, S, N(R''), $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2-C_{1-20}$ alkenylene and $^*-Z^2-C_{1-20}$ alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ;

R^2 is an unsubstituted or substituted C_{1-6} alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer;

which process comprises:

(a) treating a first compound, Q', which is a polymer or a dendrimer and which bears at least n functional groups, with at least one second compound of formula (VIb)

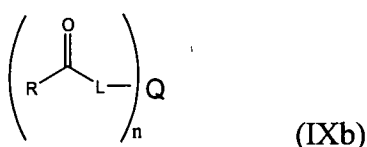


wherein:

L' is a leaving group or a reactive precursor to said group of formula (XII), wherein L' is reactable with a said functional group to couple the second compound to the first compound, and

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl,

thereby producing a third compound of formula (IXb):



wherein Q, L, R and n are as defined above; and

(b) treating the third compound with H₂N-N(H)S(O)₂R² in the presence of heat, wherein R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group, thereby producing said hydrazone compound of formula (XXXa).

BRIEF DESCRIPTION OF THE FIGURES

Fig. 1 is a schematic representation of (a) an AB block copolymer; (b) an ABA or BAB block copolymer, (c) an (AN)_n repeating block copolymer; (d) a multiarm or radial polymer (tri-arm polymer).

Fig. 2 is a schematic representation of the synthesis of triazine linked tosylhydrazone functionalised locust bean gum.

Fig. 3 is a schematic representation of the synthesis of ether linked tosylhydrazone functionalised locust bean gum.

Fig. 4 is a schematic representation of the synthesis of tosylhydrazone functionalised block copolymers containing polystyrene blocks.

DETAILED DESCRIPTION OF THE INVENTION

As used herein, a C₁₋₂₀ alkyl group is an unsubstituted or substituted, straight or branched chain saturated hydrocarbon radical having from 1 to 20 carbon atoms. Typically it is C₁₋₁₀ alkyl, for example methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl or decyl, or C₁₋₆ alkyl, for example methyl, ethyl, propyl, butyl, pentyl or hexyl, or C₁₋₄

alkyl, for example methyl, ethyl, i-propyl, n-propyl, t-butyl, s-butyl or n-butyl. In one embodiment, it is a C₂₋₂₀ alkyl group or, for instance, a C₃₋₂₀ alkyl or a C₄₋₂₀ alkyl group. When an alkyl group is substituted it typically bears one or more (e.g. one, two, three or four) substituents selected from substituted or unsubstituted C₁₋₂₀ alkyl; substituted or unsubstituted C₂₋₂₀ alkenyl; substituted or unsubstituted C₂₋₂₀ alkynyl; substituted or unsubstituted aryl; substituted or unsubstituted aralkyl; halo; cyano; keto; amino; C₁₋₁₀ alkylamino; di(C₁₋₁₀)alkylamino; arylamino; diarylamino; arylalkylamino; amido; acylamido; C₁₋₂₀ haloalkyl (e.g. -CF₃); ester; acyl; acyloxy; C₁₋₁₀ alkoxy; aryloxy; nitro; hydroxyl, carboxy; sulfonic acid; sulfonyl; sulphonamide; sulfhydryl (i.e. thiol, -SH); C₁₋₁₀ alkylthio; arylthio; tri(C₁₋₂₀ alkyl)silyl; aryldi(C₁₋₂₀ alkyl)silyl; diaryl(C₁₋₂₀ alkyl)silyl; and triarylsilyl.

Examples of substituted alkyl groups include C₁₋₂₀ haloalkyl, alkoxyalkyl and alkaryl groups. The term alkaryl, as used herein, pertains to a C₁₋₂₀ alkyl group in which at least one hydrogen atom (e.g., 1, 2, 3) has been replaced with an aryl group. Examples of such groups include, but are not limited to, benzyl (phenylmethyl, PhCH₂-), benzhydryl (Ph₂CH-), trityl (triphenylmethyl, Ph₃C-), phenethyl (phenylethyl, Ph-CH₂CH₂-), styryl (Ph-CH=CH-), cinnamyl (Ph-CH=CH-CH₂-).

Typically a substituted C₁₋₂₀ alkyl group carries 1, 2 or 3 substituents, for instance 1 or 2.

A C₁₋₂₀ haloalkyl group is a straight or branched chain saturated C₁₋₂₀ alkyl group in which at least one hydrogen atom has been replaced with a halogen atom, typically F, Cl or Br. In a C_n haloalkyl group, where n is from 1 to 20, the number of hydrogen atoms replaced with a halogen atom may be from n to (2n+1). The halogen atoms may be the same or different. C₁₋₂₀ haloalkyl groups include C₁₋₂₀ fluoroalkyl groups and C₁₋₂₀ perfluoroalkyl groups, as defined below. A C₁₋₂₀ haloalkyl group may have at least two halogen atoms or, for instance, at least three halogen atoms.

A C₁₋₂₀ fluoroalkyl group is a straight or branched chain saturated C₁₋₂₀ alkyl group in which at least one hydrogen atom has been replaced with a fluorine atom. In a C_n fluoroalkyl group, where n is from 1 to 20, the number of hydrogen atoms replaced with a fluorine atom may be from n to (2n+1). Thus, C₁₋₂₀ fluoroalkyl groups include C₁₋₂₀ perfluoroalkyl groups, in which all the hydrogen atoms that would otherwise have been present are replaced with a fluorine atom. Typically, a C₁₋₂₀ fluoroalkyl group has at least two fluorine atoms, more typically at least three fluorine atoms. Typically a C₁₋₂₀

fluoroalkyl group is a C₂₋₂₀ fluoroalkyl group, or for instance a C₃₋₂₀ fluoroalkyl group. Typically, a C₂₋₂₀ fluoroalkyl group has at least three fluorine atoms, more typically at least four fluorine atoms. Typically, a C₃₋₂₀ fluoroalkyl group has at least three fluorine atoms, more typically at least four fluorine atoms or, for instance, at least six fluorine atoms.

A C₁₋₂₀ perfluoroalkyl group is a straight or branched chain saturated perfluorinated hydrocarbon radical having from 1 to 20 carbon atoms. "Perfluorinated" in this context means completely fluorinated such that there are no carbon-bonded hydrogen atoms replaceable with fluorine. Typically it is C₁₋₁₂ perfluoroalkyl, for example trifluoromethyl (C₁), pentafluoroethyl (C₂), perfluoropropyl (C₃) (including perfluoro-*n*-propyl and perfluoro-*iso*-propyl), perfluorobutyl (C₄) (including perfluoro-*n*-butyl, perfluoro-*iso*-butyl, perfluoro-*sec*-butyl and perfluoro-*tert*-butyl), perfluoropentyl (C₅), perfluorohexyl (C₆), perfluoroheptyl (C₇), perfluorooctyl (C₈), perfluorononyl (C₉), perfluorodecyl (C₁₀), perfluoroundecyl (C₁₁) and perfluorododecyl (C₁₂), including straight chained and branched isomers thereof.

A C₁₋₂₀ hydrocarbon moiety is a straight-chained or branched, saturated or unsaturated hydrocarbon moiety having from 1 to 20 carbon atoms. A C₁₋₂₀ hydrocarbon moiety may be unsubstituted or substituted, the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Typically, when a C₁₋₂₀ hydrocarbon moiety is substituted, it is substituted by from one to four (e.g. one, two, three or four) substituents.

A tri(C₁₋₂₀ alkyl)silyl group represents a group of formula: -Si(R')(R'')(R''') wherein R', R'' and R''', which are the same or different, are unsubstituted or substituted, straight or branched chain C₁₋₂₀ alkyl groups as defined above.

A aryldi(C₁₋₂₀ alkyl)silyl group represents a group of formula: -Si(R')(R'')(R''') wherein R' and R'', which are the same or different, are unsubstituted or substituted, straight or branched chain C₁₋₂₀ alkyl groups as defined above, and wherein R''' is an unsubstituted or substituted aryl group.

A diaryl(C₁₋₂₀ alkyl)silyl group represents a group of formula: -Si(R')(R'')(R''') wherein R' is an unsubstituted or substituted, straight or branched chain C₁₋₂₀ alkyl group as defined above, and wherein R'' and R''', which are the same or different, are unsubstituted or substituted aryl groups.

A triarylsilyl group represents a group of formula: -Si(R')(R'')(R''') wherein R', R'' and R''', which are the same or different, are unsubstituted or substituted aryl groups.

A C₂₋₂₀ alkenyl group is a straight or branched group, which contains from 2 to 20 carbon atoms. One or more double bonds may be present in the alkenyl group, typically one double bond. A C₂₋₂₀ alkenyl group is typically ethenyl or a C₃₋₁₀ alkenyl group, i.e. a C₂₋₁₀ alkenyl group, more typically a C₂₋₆ alkenyl group. A C₃₋₁₀ alkenyl group is typically a C₃₋₆ alkenyl group, for example allyl, propenyl, butenyl, pentenyl or hexenyl. A C₂₋₄ alkenyl group is ethenyl, propenyl or butenyl. An alkenyl group may be unsubstituted or substituted by one to four (e.g. one, two, three or four) substituents, the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Where two or more substituents are present, these may be the same or different.

A C₂₋₂₀ alkynyl group is a straight or branched group which, unless otherwise specified, contains from 2 to 20 carbon atoms. One or more triple bonds, and optionally one or more double bonds may be present in the alkynyl group, typically one triple bond. A C₂₋₂₀ alkynyl group is typically ethynyl or a C₃₋₁₀ alkynyl group, i.e. a C₂₋₁₀ alkynyl group, more typically a C₂₋₆ alkynyl group. A C₃₋₁₀ alkynyl group is typically a C₃₋₆ alkynyl group, for example propynyl, butynyl, pentynyl or hexynyl. A C₂₋₄ alkynyl group is ethynyl, propynyl or butynyl. An alkynyl group may be unsubstituted or substituted by one to four substituents (e.g. one, two, three or four), the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Where two or more substituents are present, these may be the same or different.

An aryl ring is an unsubstituted or substituted aromatic ring of covalently linked carbon atoms. Typically, the aryl ring is a 5- or 6- membered aryl ring, examples of which include cyclopentadienyl (C_p) and phenyl. An aryl ring may be unsubstituted or substituted by, typically, one to five substituents (e.g. one, two, three, four or five), the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Where two or more substituents are present, these may be the same or different.

A heteroaryl ring is an unsubstituted or substituted heteroaromatic ring of covalently linked atoms including one or more heteroatoms. The one or more heteroatoms are typically selected from nitrogen, phosphorus, silicon, oxygen and sulfur (more commonly from nitrogen, oxygen and sulfur). A heteroaryl ring is typically a 5- or 6- membered heteroaryl ring containing at least one heteroatom selected from nitrogen, phosphorus, silicon, oxygen and sulfur (more commonly selected from nitrogen, oxygen and sulfur). It may contain, for example, 1, 2 or 3 heteroatoms. Examples of heteroaryl rings include pyridine, pyrazine, pyrimidine, pyridazine, furan, thiofuran, pyrazole, pyrrole,

oxazole, oxadiazole, isoxazole, thiadiazole, thiazole, isothiazole, imidazole and pyrazole. A heteroaryl ring may be unsubstituted or substituted by, typically, one to four substituents (e.g. one, two, three or four), the substituents, unless otherwise specified, being selected from those listed above for C₁₋₂₀ alkyl groups. Where two or more substituents are present, these may be the same or different.

A C₅₋₁₀ carbocyclic ring is an unsubstituted or substituted closed ring of from 5 to 10 covalently linked carbon atoms, which ring is saturated or unsaturated. Typically, the C₅₋₁₀ carbocyclic ring is not an aromatic ring. Typically the C₅₋₁₀ carbocyclic ring is a C₅₋₆ carbocyclic ring. The carbocyclic ring may be saturated or unsaturated. Thus, the term C₅₋₁₀ carbocyclic ring includes the sub-classes C₅₋₁₀ cycloalkyl ring, C₅₋₁₀ cycloalkenyl ring and C₅₋₁₀ cycloalkynyl ring. When a C₅₋₁₀ carbocyclic ring is substituted it typically bears one or more substituents selected from those listed above for C₁₋₂₀ alkyl groups. Examples of C₅₋₁₀ carbocyclic rings include, but are not limited to:

cyclopentane (C₅), cyclohexane (C₆), cycloheptane (C₇), methylcyclopropane (C₄), dimethylcyclopropane (C₅), methylcyclobutane (C₅), dimethylcyclobutane (C₆), methylcyclopentane (C₆), dimethylcyclopentane (C₇), methylcyclohexane (C₇), dimethylcyclohexane (C₈), menthane (C₁₀), cyclopentene (C₅), cyclopentadiene (C₅), cyclohexene (C₆), cyclohexadiene (C₆), methylcyclopropene (C₄), dimethylcyclopropene (C₅), methylcyclobutene (C₅), dimethylcyclobutene (C₆), methylcyclopentene (C₆), dimethylcyclopentene (C₇), methylcyclohexene (C₇), dimethylcyclohexene (C₈).

A C₅₋₁₀ heterocyclic ring is an unsubstituted or substituted closed ring of from 5 to 10 covalently linked atoms, which ring is saturated or unsaturated, wherein at least one of the ring atoms is a multivalent ring heteroatom, for example, nitrogen, phosphorus, silicon, oxygen, or sulfur (though more commonly nitrogen, oxygen, or sulfur). Typically, the C₅₋₁₀ heterocyclic ring is not an aromatic ring. Typically, the C₅₋₁₀ heterocyclic ring has from 1 to 4 heteroatoms, the remainder of the ring atoms are carbon. Typically, the C₅₋₁₀ heterocyclic ring is a C₅₋₆ heterocyclic ring in which from 1 to 4 of the ring atoms are ring heteroatoms, and the remainder of the ring atoms are carbon atoms. In this context, the prefixes C₅₋₁₀ and C₅₋₆ denote the number of ring atoms, or range of number of ring atoms. When a C₅₋₁₀ heterocyclic ring is substituted it typically bears one or more substituents selected from those listed above for C₁₋₂₀ alkyl groups.

Examples of monocyclic C₅₋₁₀ heterocyclic rings include, but are not limited to:

N₁: pyrrolidine (tetrahydropyrrole) (C₅), pyrroline (e.g., 3-pyrroline, 2,5-dihydropyrrole) (C₅), 2H-pyrrole or 3H-pyrrole (isopyrrole, isoazole) (C₅), piperidine (C₆), dihydropyridine (C₆), tetrahydropyridine (C₆), azepine (C₇);

O₁: oxolane (tetrahydrofuran) (C₅), oxole (dihydrofuran) (C₅), oxane (tetrahydropyran) (C₆), dihydropyran (C₆), pyran (C₆), oxepin (C₇);

S₁: thiolane (tetrahydrothiophene) (C₅), thiane (tetrahydrothiopyran) (C₆), thiepane (C₇);

O₂: dioxolane (C₅), dioxane (C₆), and dioxepane (C₇);

O₃: trioxane (C₆);

N₂: imidazolidine (C₅), pyrazolidine (diazolidine) (C₅), imidazoline (C₅), pyrazoline (dihydropyrazole) (C₅), piperazine (C₆);

N₁O₁: tetrahydrooxazole (C₅), dihydrooxazole (C₅), tetrahydroisoxazole (C₅), dihydroisoxazole (C₅), morpholine (C₆), tetrahydrooxazine (C₆), dihydrooxazine (C₆), oxazine (C₆);

N₁S₁: thiazoline (C₅), thiazolidine (C₅), thiomorpholine (C₆);

N₂O₁: oxadiazine (C₆);

O₁S₁: oxathiole (C₅) and oxathiane (thioxane) (C₆); and,

N₁O₁S₁: oxathiazine (C₆).

A C₃₋₂₀ carbocyclyl group is an unsubstituted or substituted monovalent moiety obtained by removing a hydrogen atom from an alicyclic ring atom of a carbocyclic ring of a carbocyclic compound, which moiety has from 3 to 20 carbon atoms (unless otherwise specified), including from 3 to 20 ring atoms. The carbocyclyl ring may be saturated or unsaturated. Thus, the term "carbocyclyl" includes the sub-classes cycloalkyl, cycloalkenyl and cycloalkynyl. Preferably, each ring has from 5 to 7 ring atoms. Examples of groups of C₃₋₂₀ carbocyclyl groups include C₃₋₁₀ carbocyclyl, C₅₋₇ carbocyclyl and C₅₋₆ carbocyclyl. When a C₃₋₂₀ carbocyclyl group is substituted it typically bears one or more substituents (typically one, two, three or four substituents) selected from those listed above for C₁₋₂₀ alkyl groups.

Examples of C₃₋₂₀ carbocyclyl groups include, but are not limited to, those derived from saturated monocyclic hydrocarbon compounds:

cyclopropane (C₃), cyclobutane (C₄), cyclopentane (C₅), cyclohexane (C₆), cycloheptane (C₇), methylcyclopropane (C₄), dimethylcyclopropane (C₅), methylcyclobutane (C₅), dimethylcyclobutane (C₆), methylcyclopentane (C₆),

dimethylcyclopentane (C₇), methylcyclohexane (C₇), dimethylcyclohexane (C₈), menthane (C₁₀);

unsaturated monocyclic hydrocarbon compounds:

cyclopropene (C₃), cyclobutene (C₄), cyclopentene (C₅), cyclopentadiene (C₅), cyclohexene (C₆), cyclohexadiene (C₆), methylcyclopropene (C₄), dimethylcyclopropene (C₅), methylcyclobutene (C₅), dimethylcyclobutene (C₆), methylcyclopentene (C₆), dimethylcyclopentene (C₇), methylcyclohexene (C₇), dimethylcyclohexene (C₈);

saturated polycyclic hydrocarbon compounds:

thujane (C₁₀), carane (C₁₀), pinane (C₁₀), bornane (C₁₀), norcarane (C₇), norpinane (C₇), norbornane (C₇), adamantane (C₁₀), decalin (decahydronaphthalene) (C₁₀);

unsaturated polycyclic hydrocarbon compounds: camphene (C₁₀), limonene (C₁₀), pinene (C₁₀);

polycyclic hydrocarbon compounds having an aromatic ring:

indene (C₉), indane (e.g., 2,3-dihydro-1H-indene) (C₉), tetraline (1,2,3,4-tetrahydronaphthalene) (C₁₀), acenaphthene (C₁₂), fluorene (C₁₃), phenalene (C₁₃), 5,5,8,8-tetramethyl tetraline (C₁₄), acephenanthrene (C₁₅), aceanthrene (C₁₆), cholanthrene (C₂₀).

Further examples of C₃₋₂₀ carbocyclyl groups include C₃₋₂₀ halocarbocyclyl groups, C₃₋₂₀ fluorocarbocyclyl groups, C₃₋₂₀ perfluorocarbocyclyl groups and C₃₋₁₀ cycloalkyl groups.

A C₃₋₂₀ halocarbocyclyl group is a C₃₋₂₀ carbocyclyl group in which at least one hydrogen atom has been replaced with a halogen atom, typically F, Cl or Br. The halogen atoms may be the same or different. C₃₋₂₀ halocarbocyclyl groups include C₃₋₂₀ fluorocarbocyclyl groups and C₃₋₂₀ perfluorocarbocyclyl groups, as defined below. A C₃₋₂₀ halocarbocyclyl group may have at least two halogen atoms or, for instance, at least three or at least four, at least five or at least six halogen atoms.

A C₃₋₂₀ fluorocarbocyclyl group is a C₃₋₂₀ carbocyclyl group in which at least one hydrogen atom has been replaced with a fluorine atom. C₃₋₂₀ fluorocarbocyclyl groups include C₃₋₂₀ perfluorocarbocyclyl groups, as defined below. A C₃₋₂₀ fluorocarbocyclyl group may have at least two fluorine atoms or, for instance, at least three or at least four, at least five or at least six fluorine atoms.

A C₃₋₂₀ perfluorocarbocyclyl group a perfluorinated C₃₋₂₀ carbocyclyl group. “Perfluorinated” in this context means completely fluorinated such that there are no carbon-bonded hydrogen atoms replaceable with fluorine.

A C₃₋₁₀ cycloalkyl group or moiety is a 3- to 10- membered unsubstituted or substituted group or moiety, typically a 3-to 6-membered group or moiety, which may be a monocyclic ring or which may consist of two or more fused rings. Examples of C₃₋₁₀ cycloalkyl groups or moieties include cyclopropane (C₃), cyclobutane (C₄), cyclopentane (C₅), cyclohexane (C₆), cycloheptane (C₇), methylcyclopropane (C₄), dimethylcyclopropane (C₅), methylcyclobutane (C₅), dimethylcyclobutane (C₆), methylcyclopentane (C₆), dimethylcyclopentane (C₇), methylcyclohexane (C₇), dimethylcyclohexane (C₈), menthane (C₁₀), thujane (C₁₀), carane (C₁₀), pinane (C₁₀), bornane (C₁₀), norcarane (C₇), norpinane (C₇), norbornane (C₇), adamantane (C₁₀) and decalin (decahydronaphthalene) (C₁₀).

A C₃₋₂₀ heterocyclyl group is an unsubstituted or substituted monovalent, monocyclic, bicyclic or tricyclic moiety obtained by removing a hydrogen atom from a ring atom of a heterocyclic compound, which moiety has from 3 to 20 ring atoms (unless otherwise specified), of which from 1 to 10 are ring heteroatoms. Preferably, each ring has from 3 to 7 ring atoms, of which from 1 to 4 are ring heteroatoms. When a C₃₋₂₀ heterocyclyl group is substituted it typically bears one or more substituents selected from those listed above for C₁₋₂₀ alkyl groups. Typically a substituted C₃₋₂₀ heterocyclyl group carries 1, 2 or 3 substituents, for instance 1 or 2.

Examples of groups of heterocyclyl groups include C₃₋₂₀ heterocyclyl, C₅₋₂₀ heterocyclyl, C₃₋₁₅ heterocyclyl, C₅₋₁₅ heterocyclyl, C₃₋₁₂ heterocyclyl, C₅₋₁₂ heterocyclyl, C₃₋₁₀ heterocyclyl, C₅₋₁₀ heterocyclyl, C₃₋₇ heterocyclyl, C₅₋₇ heterocyclyl, and C₅₋₆ heterocyclyl.

Examples of monocyclic C₃₋₂₀ heterocyclyl groups include, but are not limited to, those derived from:

N₁: aziridine (C₃), azetidine (C₄), pyrrolidine (tetrahydropyrrole) (C₅), pyrroline (e.g., 3-pyrroline, 2,5-dihydropyrrole) (C₅), 2H-pyrrole or 3H-pyrrole (isopyrrole, isoazole) (C₅), piperidine (C₆), dihydropyridine (C₆), tetrahydropyridine (C₆), azepine (C₇);

O₁: oxirane (C₃), oxetane (C₄), oxolane (tetrahydrofuran) (C₅), oxole (dihydrofuran) (C₅), oxane (tetrahydropyran) (C₆), dihydropyran (C₆), pyran (C₆), oxepin (C₇);

S₁: thiirane (C₃), thietane (C₄), thiolane (tetrahydrothiophene) (C₅), thiane (tetrahydrothiopyran) (C₆), thiepane (C₇);

O₂: dioxolane (C₅), dioxane (C₆), and dioxepane (C₇);

O₃: trioxane (C₆);

N₂: imidazolidine (C₅), pyrazolidine (diazolidine) (C₅), imidazoline (C₅), pyrazoline (dihydropyrazole) (C₅), piperazine (C₆);

N₁O₁: tetrahydrooxazole (C₅), dihydrooxazole (C₅), tetrahydroisoxazole (C₅), dihydroisoxazole (C₅), morpholine (C₆), tetrahydrooxazine (C₆), dihydrooxazine (C₆), oxazine (C₆);

N₁S₁: thiazoline (C₅), thiazolidine (C₅), thiomorpholine (C₆);

N₂O₁: oxadiazine (C₆);

O₁S₁: oxathiole (C₅) and oxathiane (thioxane) (C₆); and,

N₁O₁S₁: oxathiazine (C₆).

Examples of C₃₋₂₀ heterocyclyl groups which are also aryl groups are described below as heteroaryl groups.

An aryl group is a substituted or unsubstituted, monocyclic or bicyclic aromatic group which typically contains from 6 to 14 carbon atoms, preferably from 6 to 10 carbon atoms in the ring portion. Examples include phenyl, naphthyl, indenyl and indanyl groups. An aryl group is unsubstituted or substituted. When an aryl group as defined above is substituted it typically bears one or more substituents (for instance, one, two, three, four or five substituents) selected from those listed above for C₁₋₂₀ alkyl groups. A substituted aryl group may be substituted in two positions with a single unsubstituted or substituted C₁₋₆ alkylene group, or with a bidentate group represented by the formula -X-C₁₋₆ alkylene, or -X-C₁₋₆ alkylene-X-, wherein X is selected from O, S and NR, and wherein R is H, aryl or C₁₋₆ alkyl. Thus a substituted aryl group may be an aryl group fused with a cycloalkyl group or with a heterocyclyl group. A further example of a substituted aryl group is a C₆₋₁₀ perfluoroaryl group.

A C₆₋₁₀ perfluoroaryl group is a perfluorinated aryl group which contains from 6 to 10 carbon atoms in the ring portion. "Perfluorinated" in this context means completely fluorinated such that there are no carbon-bonded hydrogen atoms replaceable with fluorine. Typically it is pentafluorophenyl.

The term aralkyl as used herein, pertains to an aryl group in which at least one hydrogen atom (e.g., 1, 2, 3) has been substituted with a C₁₋₂₀ alkyl group. Examples of such groups include, but are not limited to, tolyl (from toluene), xylyl (from xylene), mesityl (from mesitylene), and cumenyl (or cumyl, from cumene), and duryl (from durene).

The ring atoms of an aryl group may include one or more heteroatoms, as in a heteroaryl group. Such an aryl group (a heteroaryl group) is a substituted or unsubstituted mono- or bicyclic heteroaromatic group which typically contains from 6 to 10 atoms in the ring portion including one or more heteroatoms. It is generally a 5- or 6-membered ring, or two fused rings each of which is the same or different and typically independently selected from a 5-membered ring and a 6-membered ring, containing at least one heteroatom selected from O, S, N, P, Se and Si. It may contain, for example, 1, 2 or 3 heteroatoms. Examples of heteroaryl groups include pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, furanyl, thienyl, pyrazolidinyl, pyrrolyl, oxazolyl, oxadiazolyl, isoxazolyl, thiadiazolyl, thiazolyl, isothiazolyl, imidazolyl, pyrazolyl, quinolyl and isoquinolyl. A heteroaryl group may be unsubstituted or substituted, for instance, as specified above for aryl. Typically it carries 0, 1, 2 or 3 substituents.

A C₁₋₂₀ alkylene group is an unsubstituted or substituted bidentate moiety obtained by removing two hydrogen atoms, either both from the same carbon atom, or one from each of two different carbon atoms, of a hydrocarbon compound having from 1 to 20 carbon atoms (unless otherwise specified), which may be aliphatic or alicyclic, and which may be saturated, partially unsaturated, or fully unsaturated. Thus, the term "alkylene" includes the sub-classes alkenylene (C₁₋₂₀ alkenylene), alkynylene (C₁₋₂₀ alkynylene), cycloalkylene, etc. Typically it is C₁₋₁₀ alkylene, or C₁₋₆ alkylene. Typically it is C₁₋₄ alkylene, for example methylene, ethylene, i-propylene, n-propylene, t-butylene, s-butylene or n-butylene. It may also be pentylene, hexylene, heptylene, octylene and the various branched chain isomers thereof. An alkylene group may be unsubstituted or substituted, for instance, as specified above for alkyl. Typically a substituted alkylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

In this context, the prefixes (e.g., C₁₋₄, C₁₋₇, C₁₋₁₀, C₂₋₇, C₃₋₇, etc.) denote the number of carbon atoms, or range of number of carbon atoms. For example, the term "C₁₋₄alkylene," as used herein, pertains to an alkylene group having from 1 to 4 carbon atoms. Examples of groups of alkylene groups include C₁₋₄ alkylene ("lower alkylene"), C₁₋₇ alkylene and C₁₋₁₀ alkylene.

Examples of linear saturated C₁₋₇ alkylene groups include, but are not limited to, -(CH₂)_n- where n is an integer from 1 to 7, for example, -CH₂- (methylene), -CH₂CH₂- (ethylene), -CH₂CH₂CH₂- (propylene), and -CH₂CH₂CH₂CH₂- (butylene).

Examples of branched saturated C₁₋₇ alkylene groups include, but are not limited to, -CH(CH₃)-, -CH(CH₃)CH₂-, -CH(CH₃)CH₂CH₂-, -CH(CH₃)CH₂CH₂CH₂-, -CH₂CH(CH₃)CH₂-, -CH₂CH(CH₃)CH₂CH₂-, -CH(CH₂CH₃)-, -CH(CH₂CH₃)CH₂-, and -CH₂CH(CH₂CH₃)CH₂-.

Examples of linear partially unsaturated C₁₋₇ alkylene groups include, but is not limited to, -CH=CH- (vinylene), -CH=CH-CH₂-, -CH₂-CH=CH₂-, -CH=CH-CH₂-CH₂-, -CH=CH-CH₂-CH₂-CH₂-, -CH=CH-CH=CH-, -CH=CH-CH=CH-CH₂-, -CH=CH-CH=CH-CH₂-CH₂-, -CH=CH-CH₂-CH=CH-, and -CH=CH-CH₂-CH₂-CH=CH-.

Examples of branched partially unsaturated C₁₋₇ alkylene groups include, but is not limited to, -C(CH₃)=CH-, -C(CH₃)=CH-CH₂-, and -CH=CH-CH(CH₃)-

Examples of alicyclic saturated C₁₋₇ alkylene groups include, but are not limited to, cyclopentylene (e.g., cyclopent-1,3-ylene), and cyclohexylene (e.g., cyclohex-1,4-ylene).

Examples of alicyclic partially unsaturated C₁₋₇ alkylene groups include, but are not limited to, cyclopentenylene (e.g., 4-cyclopenten-1,3-ylene), cyclohexenylene (e.g., 2-cyclohexen-1,4-ylene; 3-cyclohexen-1,2-ylene; 2,5-cyclohexadien-1,4-ylene). These are examples of C₅₋₆ cycloalkylene groups.

An example of a substituted C₁₋₂₀ alkylene group is a C₁₋₂₀ perfluoroalkylene group. A C₁₋₂₀ perfluoroalkylene group is a perfluorinated C₁₋₂₀ alkylene group. "Perfluorinated" in this context means completely fluorinated such that there are no carbon-bonded hydrogen atoms replaceable with fluorine.

C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, C₁₋₂₀ alkyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl and C₁₋₂₀ perfluoroalkyl groups as defined herein are either uninterrupted or interrupted by one or more heteroatoms or heterogroups, such as S, O or N(R'') wherein R'' is H, C₁₋₆ alkyl or aryl (typically phenyl), or by one or more arylene groups. The arylene groups are typically phenylene, but may be perfluoroarylene groups, for instance tetrafluorophenylene. The phrase "optionally interrupted" as used herein thus refers to a C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, C₁₋₂₀ alkyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl or C₁₋₂₀ perfluoroalkyl group, as defined above, which is uninterrupted or which is interrupted between adjacent carbon atoms by a heteroatom such as oxygen or sulfur, by a heterogroup such as N(R'') wherein R'' is H, aryl or C₁₋₆ alkyl, or by an arylene group. For instance, a C₁₋₂₀ alkyl group such as n-butyl may be interrupted by the heterogroup N(R'') as follows: -CH₂N(R'')CH₂CH₂CH₃, -CH₂CH₂N(R'')CH₂CH₃, or -CH₂CH₂CH₂N(R'')CH₃. Similarly, an alkylene group such as n-butylene may be interrupted by the heterogroup N(R'') as

follows: $-\text{CH}_2\text{N}(\text{R}'')\text{CH}_2\text{CH}_2\text{CH}_2-$, $-\text{CH}_2\text{CH}_2\text{N}(\text{R}'')\text{CH}_2\text{CH}_2-$, or $-\text{CH}_2\text{CH}_2\text{CH}_2\text{N}(\text{R}'')\text{CH}_2-$. Typically an interrupted group, for instance an interrupted C_{1-10} alkylene or C_{1-20} alkyl group, is interrupted by 1, 2 or 3 heteroatoms or heterogroups, or by 1, 2 or 3 arylene (typically phenylene) groups. More typically, an interrupted group, for instance an interrupted C_{1-10} alkylene or C_{1-20} alkyl group, is interrupted by 1 or 2 heteroatoms or heterogroups, or by 1 or 2 arylene (typically phenylene) groups. For instance, a C_{1-20} alkyl group such as n-butyl may be interrupted by 2 heterogroups $\text{N}(\text{R}'')$ as follows: $-\text{CH}_2\text{N}(\text{R}'')\text{CH}_2\text{N}(\text{R}'')\text{CH}_2\text{CH}_3$.

An arylene group is an unsubstituted or substituted bidentate moiety obtained by removing two hydrogen atoms, one from each of two different aromatic ring atoms of an aromatic compound, which moiety has from 5 to 14 ring atoms (unless otherwise specified). Typically, each ring has from 5 to 7 or from 5 to 6 ring atoms. An arylene group may be unsubstituted or substituted, for instance, as specified above for aryl. Typically a substituted heteroarylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

In this context, the prefixes (e.g., C_{5-20} , C_{6-20} , C_{5-14} , C_{5-7} , C_{5-6} , etc.) denote the number of ring atoms, or range of number of ring atoms, whether carbon atoms or heteroatoms. For example, the term " C_{5-6} arylene," as used herein, pertains to an arylene group having 5 or 6 ring atoms. Examples of groups of arylene groups include C_{5-20} arylene, C_{6-20} arylene, C_{5-14} arylene, C_{6-14} arylene, C_{6-10} arylene, C_{5-12} arylene, C_{5-10} arylene, C_{5-7} arylene, C_{5-6} arylene, C_5 arylene, and C_6 arylene.

The ring atoms may be all carbon atoms, as in "carboarylene groups" (e.g., C_{6-20} carboarylene, C_{6-14} carboarylene or C_{6-10} carboarylene).

Examples of C_{6-20} arylene groups which do not have ring heteroatoms (i.e., C_{6-20} carboarylene groups) include, but are not limited to, those derived from the compounds discussed above in regard to aryl groups, e.g. phenylene, and also include those derived from aryl groups which are bonded together, e.g. phenylene-phenylene (diphenylene) and phenylene-phenylene-phenylene (triphenylene).

Alternatively, the ring atoms may include one or more heteroatoms, as in "heteroarylene groups" (e.g., C_{5-10} heteroarylene). A heteroarylene group may be unsubstituted or substituted, for instance, as specified above for aryl. Typically a substituted heteroarylene group carries 1, 2 or 3 substituents, for instance 1 or 2.

Examples of heteroarylene groups include, but are not limited to, those derived from the compounds discussed above in regard to heteroaryl groups. Examples of heteroarylene groups include bidentate groups derived from pyridine, pyrazine, pyrimidine, pyridazine, furan, thiofuran, pyrazole, pyrrole, oxazole, oxadiazole, isoxazole, thiadiazole, thiazole, isothiazole, imidazole and pyrazole.

A perfluoroarylene group is a perfluorinated arylene group. "Perfluorinated" in this context means completely fluorinated such that there are no carbon-bonded hydrogen atoms replaceable with fluorine. Typically it is tetrafluorophenylene.

As used herein the term halo is a group selected from -F, -Cl, -Br, and -I.

As used herein the term keto represents a group of formula: =O

As used herein the term nitro represents a group of formula: -NO₂

As used herein the term cyano represents a group of formula: -CN

As used herein the term hydroxyl represents a group of formula: -OH

As used herein the term thiol represents a group of formula: -SH

As used herein the term sulfonyl represents a group of formula: -S(O)₂R' wherein R' is a C₁₋₁₀ alkyl group, preferably a C₁₋₆ alkyl group, as defined previously.

As used herein the term acyl represents a group of formula: -C(=O)R, wherein R is an acyl substituent, for example, a substituted or unsubstituted C₁₋₂₀ alkyl group, a substituted or unsubstituted C₃₋₂₀ heterocyclyl group, or a substituted or unsubstituted aryl group. Examples of acyl groups include, but are not limited to, -C(=O)CH₃ (acetyl), -C(=O)CH₂CH₃ (propionyl), -C(=O)C(CH₃)₃ (t-butyryl), and -C(=O)Ph (benzoyl, phenone).

As used herein the term acyloxy (or reverse ester) represents a group of formula: -OC(=O)R, wherein R is an acyloxy substituent, for example, substituted or unsubstituted C₁₋₂₀ alkyl group, a substituted or unsubstituted C₃₋₂₀ heterocyclyl group, or a substituted or unsubstituted aryl group, typically a C₁₋₆ alkyl group. Examples of acyloxy groups include, but are not limited to, -OC(=O)CH₃ (acetoxyl), -OC(=O)CH₂CH₃, -OC(=O)C(CH₃)₃, -OC(=O)Ph, and -OC(=O)CH₂Ph.

As used herein the term ester (or carboxylate, carboxylic acid ester or oxycarbonyl) represents a group of formula: -C(=O)OR, wherein R is an ester substituent, for example, a substituted or unsubstituted C₁₋₂₀ alkyl group, a substituted or unsubstituted C₃₋₂₀ heterocyclyl group, or a substituted or unsubstituted aryl group (typically a phenyl group).

Examples of ester groups include, but are not limited to, $-C(=O)OCH_3$, $-C(=O)OCH_2CH_3$, $-C(=O)OC(CH_3)_3$, and $-C(=O)OPh$.

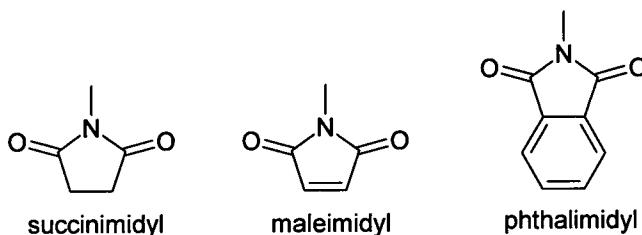
As used herein the term amino represents a group of formula $-NH_2$. The term C_1 - C_{10} alkylamino represents a group of formula $-NHR'$ wherein R' is a C_1 - C_{10} alkyl group, preferably a C_1 - C_6 alkyl group, as defined previously. The term di(C_1 - C_{10})alkylamino represents a group of formula $-NR'R''$ wherein R' and R'' are the same or different and represent C_1 - C_{10} alkyl groups, preferably C_1 - C_6 alkyl groups, as defined previously. The term arylamino represents a group of formula $-NHR'$ wherein R' is an aryl group, preferably a phenyl group, as defined previously. The term diarylamino represents a group of formula $-NR'R''$ wherein R' and R'' are the same or different and represent aryl groups, preferably phenyl groups, as defined previously. The term arylalkylamino represents a group of formula $-NR'R''$ wherein R' is a C_1 - C_{10} alkyl group, preferably a C_1 - C_6 alkyl group, and R'' is an aryl group, preferably a phenyl group.

As used herein the term amido represents a group of formula: $-C(=O)NR'R''$, wherein R' and R'' are independently H or amino substituents, as defined for di(C_1 - C_{10})alkylamino groups. Examples of amido groups include, but are not limited to, $-C(=O)NH_2$, $-C(=O)NHCH_3$, $-C(=O)N(CH_3)_2$, $-C(=O)NHCH_2CH_3$, and $-C(=O)N(CH_2CH_3)_2$, as well as amido groups in which R' and R'' , together with the nitrogen atom to which they are attached, form a heterocyclic structure as in, for example, piperidinocarbonyl, morpholinocarbonyl, thiomorpholinocarbonyl, and piperazinocarbonyl.

As used herein, the terms "carboxy", "carboxyl" and "carboxylic acid" each represent a group of the formula: $-C(=O)OH$, or $-COOH$. As would be understood by the skilled person, a carboxylic acid group (for instance, when employed in the present invention) can exist in protonated and deprotonated forms (for example, $-C(=O)OH$ and $-C(=O)O^-$), and in salt forms (for example, $-C(=O)O^-X^+$, wherein X^+ is a monovalent cation).

As used herein the term acylamido represents a group of formula: $-NR^xC(=O)R^y$, wherein R^x is an amide substituent, for example, hydrogen, a C_1 - C_{20} alkyl group, a C_3 - C_{20} heterocyclyl group, an aryl group, preferably hydrogen or a C_1 - C_{20} alkyl group, and R^y is an acyl substituent, for example, a C_1 - C_{20} alkyl group, a C_3 - C_{20} heterocyclyl group, or an aryl group, preferably hydrogen or a C_1 - C_{20} alkyl group. Examples of acylamide groups include, but are not limited to, $-NHC(=O)CH_3$, $-NHC(=O)CH_2CH_3$, $-NHC(=O)Ph$, $-NHC(=O)C_{15}H_{31}$ and $-NHC(=O)C_9H_{19}$. Thus, a substituted C_1 - C_{20} alkyl group may

comprise an acylamido substituent defined by the formula -NHC(=O)-C_{1-20} alkyl, such as $\text{-NHC(=O)C}_{15}\text{H}_{31}$ or $\text{-NHC(=O)C}_9\text{H}_{19}$. R^x and R^y may together form a cyclic structure, as in, for example, succinimidyl, maleimidyl, and phthalimidyl:



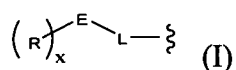
A C_{1-10} alkylthio group is a said C_{1-10} alkyl group, preferably a C_{1-6} alkyl group, attached to a thio group. An arylthio group is an aryl group, preferably a phenyl group, attached to a thio group.

A C_{1-20} alkoxy group is a said substituted or unsubstituted C_{1-20} alkyl group attached to an oxygen atom. A C_{1-10} alkoxy group is a said substituted or unsubstituted C_{1-10} alkyl group attached to an oxygen atom. A C_{1-6} alkoxy group is a said substituted or unsubstituted C_{1-6} alkyl group attached to an oxygen atom. A C_{1-4} alkoxy group is a substituted or unsubstituted C_{1-4} alkyl group attached to an oxygen atom. Said C_{1-20} , C_{1-10} , C_{1-6} and C_{1-4} alkyl groups are optionally interrupted as defined herein. Examples of C_{1-4} alkoxy groups include, -OMe (methoxy), -OEt (ethoxy), -O(nPr) (n-propoxy), -O(iPr) (isopropoxy), -O(nBu) (n-butoxy), -O(sBu) (sec-butoxy), -O(iBu) (isobutoxy), and -O(tBu) (tert-butoxy). Further examples of C_{1-20} alkoxy groups are -O(Adamantyl) , $\text{-O-CH}_2\text{-Adamantyl}$ and $\text{-O-CH}_2\text{-CH}_2\text{-Adamantyl}$. An aryloxy group is a substituted or unsubstituted aryl group, as defined herein, attached to an oxygen atom. An example of an aryloxy group is -OPh (phenoxy).

As used herein, the term “sulfonic acid” represents a group of the formula: $\text{-S(=O)}_2\text{OH}$. As would be understood by the skilled person, a sulfonic acid group can exist in protonated and deprotonated forms (for example, $\text{-S(=O)}_2\text{OH}$ and $\text{-S(=O)}_2\text{O}^-$), and in salt forms (for example, $\text{-S(=O)}_2\text{O}^-\text{X}^+$, wherein X^+ is a monovalent cation).

As used herein, the term “sulfonamide” represents a group of formula: $\text{-S(=O)}_2\text{NH}_2$.

The present invention provides a functionalised compound of formula (II), as defined above, which comprises n carbene precursor groups of the following formula:

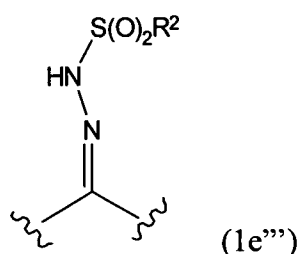


which are the same or different, wherein n is an integer equal to or greater than 3, E is

group which is capable of being converted into a carbene reactive intermediate group, x is 1, and R and L are as defined above. These n reactive intermediate precursor groups of formula (I) are attached to a polymer or a dendrimer, Q.

The term “carbene precursor group”, as used herein, means a latent reactive group which is capable of being converted into a carbene reactive intermediate group by a chemical process or by the application of energy, wherein the carbene reactive intermediate group is capable of further reaction. The “application of energy” may for instance involve the application of thermal energy (i.e. heating) or irradiation, although any suitable source of energy can be used.

An example of a carbene precursor group, E, which is capable of being converted into a carbene reactive intermediate is a sulfonylhydrazone group of formula (1e’’’):



wherein R^2 is an unsubstituted or substituted C_{1-6} alkyl group or an unsubstituted or substituted aryl group.

Typically, R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl, di(C_{1-6} alkyl)amino, hydroxyl, nitro, cyano or methoxy.

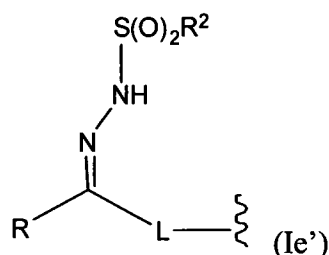
More typically, R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or di(C_{1-6} alkyl)amino.

Typically, R^1 is $-\text{S(O)}_2\text{R}^2$ wherein R^2 is phenyl substituted with C_{1-6} alkyl. More typically, R^1 is $-\text{S(O)}_2\text{R}^2$ wherein R^2 is phenyl substituted with methyl (i.e. tolyl). Thus, in one embodiment, R^1 is a tosyl group. In another embodiment, R^1 is H.

Such sulfonylhydrazone groups are “carbene precursor groups”, because they are capable of conversion into carbene reactive intermediates. Conversion of the sulfonylhydrazone group into the carbene reactive intermediate is achieved by treatment with a base followed by the application of energy, typically by heating or by irradiation. Any suitable base may be used, for instance an organic base such as a trialkyl amine (e.g. triethylamine) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). Alternatively an inorganic base may be used, such as an alkali metal hydroxide, e.g. sodium, lithium or potassium

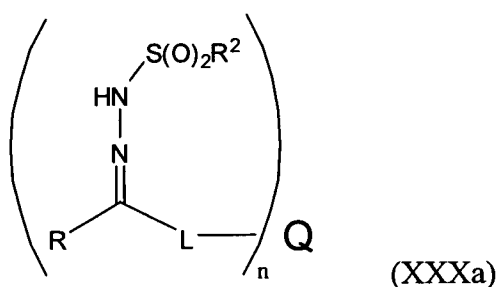
hydroxide. The decomposition of the sulfonylhydrazone to the carbene is thought to occur by elimination of R^1 , to form a diazo intermediate group, and subsequent elimination of dinitrogen to form the reactive carbene intermediate. In the present invention, E is a sulfonylhydrazone group of formula (1e'') as defined above.

Thus, in the present invention, the n carbene precursor groups, $[R]_x-E-L$ -, are all groups of the following formula (1e')



wherein L, R and R^2 are as defined above.

The functionalised compound of formula (II) of the invention is therefore a sulfonylhydrazone compound of formula (XXXa)

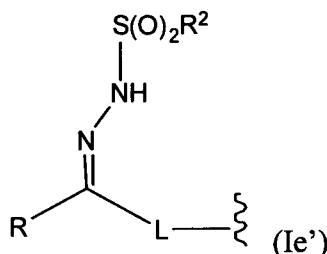


wherein

R, R^2 , L, n and Q are as defined above.

The ability to generate a carbene from a sulfonylhydrazone group without isolating the diazo group intermediate provides numerous advantages. Such sulfonylhydrazone groups are particularly advantageous because they are capable of being converted into a carbene reactive intermediate group, yet they are more stable than the diazo groups of formula (Ia). In particular, they act as a protected precursor to the carbene reactive intermediate and thereby allow a greater level of control over unwanted degradation of the functionalized compound of the invention, such as in transport or storage. Of particular significance is the decreased toxicity of a sulfonylhydrazone group over a diazo group. Sulfonylhydrazone groups also offer a greater flexibility with regards to formulation as they are not degraded by carboxylic acids unlike diazo groups such as diazo esters, diazo ketones and alkyl or aryl diazos.

The groups L, R and R^2 may differ from one group of formula (1e')



to the next in the functionalised compound of the invention of formula (XXXa). For instance, the functionalised compound may comprise a first group of formula (1e') and a second group of formula (1e'), wherein the groups R^2 , the linker groups (or single bonds) L, and/or the terminal groups R are different in the first and second groups of formula (1e'). Typically, however, R^2 is the same in all of the carbene precursor groups of formula (1e') in the functionalised compound. Similarly, L is typically the same in all of the carbene precursor groups of formula (1e') in the functionalised compound. Similarly, R is typically the same terminal group in all of the precursor groups of formula (1e') in the compound.

The number of reactive intermediate precursor groups in the functionalised compound, n, is an integer equal to or greater than 3.

In another embodiment, n is greater than or equal to 4.

In one embodiment, n is an integer of from 3 to 50 or from 4 to 50, more typically an integer of from 3 to 20, from 3 to 10, from 4 to 20, or from 4 to 10, or an integer of 3, 4 or 5.

In another embodiment, however, n is an integer of from 3 to 500, or from 4 to 500, and is more typically an integer of from 3 to 200, from 4 to 200, from 3 to 100, or from 10 to 100, for instance from 10 to 50.

In yet another embodiment, n is an integer equal to or greater than 50, for instance equal to or greater than 100. Thus, n may be an integer of from 50 to 1,000,000, from 50 to 100,000, from 50 to 10,000, from 50 to 5,000, or from 50 to 1,000. More typically, in this embodiment, n is an integer of from 50 to 1,000.

The reactivity of the functionalised compound of the invention and its derived carbene reactive intermediate can be modified by including electron releasing or electron withdrawing groups on the aromatic aryl or heteroaryl ring of the terminal group R. In addition, the solubility of the functionalised compound and its derived carbene reactive intermediate can be modified by including groups of a given hydrophilicity or lipophilicity on the aromatic ring. Thus, in the functionalised compounds of the invention, each R

group is selected from aryl and heteroaryl, which aryl or heteroaryl is unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

More typically, R is phenyl which is unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

In the functionalised compounds of the invention, each L, which is the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2$ - C_{1-20} alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2$ - C_{1-20} alkylene-O, * -arylene-O, * -heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O)₂, $^*-OC(O)$, $^*-N(R'')C(O)$, O, S, N(R''), $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2$ - C_{1-20} alkenylene and $^*-Z^2$ - C_{1-20} alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 .

In one embodiment, A^1 is an unsubstituted or substituted arylene group. For instance, A^1 may be an unsubstituted or substituted phenylene group, more typically an unsubstituted phenylene group.

A^2 may be an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-)_m wherein m is 1 to 20, $^*-Z^1$ - C_{1-20} alkylene, $^*-Z^1$ - C_{1-20} perfluoroalkylene and $^*-Z^1$ - C_{1-20} alkylene-(O- C_{1-20} alkylene-)_m wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl. More typically, A^2 is C_{1-10} alkylene or $^*-C_{1-6}$ alkylene-(O- C_{2-4} alkylene-)_m wherein m is 1 to 20 and wherein * is the point of attachment of A^2 to A^1 .

Typically, however A^2 is a single bond.

A^1 may be a phenylene group, typically an unsubstituted phenylene group, and A^2 is C_{1-10} alkylene or $^*-C_{1-6}$ alkylene-(O- C_{2-4} alkylene-)_m wherein m is 1 to 20 and wherein * is the point of attachment of A^2 to A^1 .

A^3 may be a single bond, O, C(O), $^*-OC(O)$ or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, arylene, heteroarylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, * -arylene-O and * -heteroarylene-O, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 .

A^3 may be a single bond, O, C(O), $^*-OC(O)$ or an unsubstituted or substituted group selected from $^*-O$ -arylene, $^*-O$ -heteroarylene, $^*-O$ -arylene-O and $^*-O$ -heteroarylene-O wherein * is the point of attachment of A^3 to A^2 . A^3 may be a single bond,

O, or an unsubstituted or substituted group selected from *-O-arylene, *-O-heteroarylene, *-O-arylene-O and *-O-heteroarylene-O wherein * is the point of attachment of A^3 to A^2 . Typically, A^3 is a single bond, O, or an unsubstituted or substituted group selected from *-O-heteroarylene and *-O-heteroarylene-O wherein * is the point of attachment of A^3 to A^2 .

More typically, however A^3 is a single bond.

Q is a polymer or a dendrimer. The polymer or dendrimer is functionalised with said n carbene precursor groups of formula (1e') in said compound of formula (XXXa). As is shown in formula (XXXa), each of the n reactive intermediate precursor groups is bonded to the polymer or dendrimer, Q, via the group L of the reactive intermediate precursor group, which may be a linking group or a single bond. When L is a group of formula (XII) as defined above, each of the n reactive intermediate precursor groups is typically bonded to the polymer or dendrimer, Q, via group A^3 of said group of formula (XII).

As is described in further detail below, the functionalised compounds of formula (II) may be synthesised by coupling the carbene precursor groups (or carbonyl precursors thereto) to a polymer or dendrimer Q' by reaction between a functional group on the linker moiety of the carbene precursor group (or on the carbonyl precursor) with functional groups, $-A^4-X^2$ on Q'. Thus, the polymer or dendrimer Q of the compound of formula (XXXa) is typically attached to the groups L of the n reactive intermediate precursor groups via n linker groups of formula A^4 .

Accordingly, Q is typically a polymer or a dendrimer which comprises n linker groups of formula A^4 , each of which is attached to a group L, wherein n is an integer equal to or greater than 2. Each individual A^4 is the same as or different from the others and is independently selected from a single bond, $-Z^3$ -arylene-*, $-Z^3$ -heteroarylene-*, $-Z^3$ -C₁₋₂₀ alkylene-*, arylene, heteroarylene, C₁₋₂₀ alkylene, $-Z^3$ -arylene-O-*, $-Z^3$ -heteroarylene-O-*, $-Z^3$ -C₁₋₂₀ alkylene-O-*, arylene-O-*, heteroarylene-O-*, C₁₋₂₀ alkylene-O-*, -C(O)-*, S(O)₂, -OC(O)-*, -N(R'')C(O)-*, O, S, N(R''), -C(O)O-*, -C(O)N(R'')-*, -S(O)₂O-*, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, $-Z^3$ -C₁₋₂₀ alkenylene-* and $-Z^3$ -C₁₋₂₀ alkynylene-*, wherein Z^3 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A^4 to L.

In one embodiment, each A^4 is arylene.

In one embodiment, Q is a dendrimer, which dendrimer comprises n surface groups which are linker groups of formula A⁴ as defined above. The n linker groups A⁴ are the same as or different from one another and bonded to the n L groups of the reactive intermediate precursor groups of formula (I). Any suitable dendrimer structure may be employed. When Q is a dendrimer, n is typically an integer of from 3 to 500, or from 4 to 500, and is more typically an integer of from 3 to 200, or from 4 to 200, from 3 to 100, or from 4 to 100, or from 10 to 100, for instance from 10 to 50.

When Q comprises a polymer, the polymer may be a linear polymer, a graft polymer, branched polymer or a hyperbranched polymer. The polymer may for instance be a homopolymer or a copolymer. The co-polymer may be a ter-polymer or any other multiple combination polymer. Suitable copolymers include polystyrene-*co*-butadiene, for instance.

Also covered are different polymer architectures, including but not limited to graft polymers, branched polymers; block copolymers, for instance, SBS rubber (Kraton), or EO-PO-EO (Pluronic); star polymers (Tetronic); or hyperbranched polymers (PEI).

Polymers of different molecular weight ranges are also covered, from small macromers with a repeat unit length of a dimer, to polymers with a molecular weight of millions. The degree of polymerisation, D_p, of the polymer (i.e. the polymer molecular weight divided by the molecular weight of the repeat unit) may be from 2 to 100,000,000.

Polymers with different polydispersity indexes are also covered, from polymers produced from living polymerisation, such as anionic, atom-transfer radical polymerisation (ATRP) or Reversible addition fragmentation transfer (RAFT) polymerisation, with a PDI approaching 1, to those produced from step-growth or chain-growth polymerisation where the PDI can be >3.

Typically, the polymer employed is either soluble or dispersable.

When Q comprises a polymer, the polymer may be a homo-polymer or a copolymer.

In one embodiment, when Q comprises a polymer, the polymer is selected from any of the polymers listed in the following paragraph and their copolymers. Thus, the polymer may be a homopolymer comprising any of the following polymers, or a copolymer which comprises the monomeric units of any one or more of the following polymers:

Condensation polymers and Addition polymers. Polysaccharides, including but not limited to chitin, guar gums, gum arabic, galactomannans, for instance locust bean gum

(LBG). Proteins, including but not limited to Keratin. Polyesters, including but not limited to Nylon, polyethylene terephthalate (PET) and polyoxyethylene terephthalate (POET). Polyethers, including but not limited to polypropylene glycol (PPG), polyethylene glycol (PEG), Polyethylene oxide (PEO). Polyolefins, including but not limited to polyethylene (PE), polypropylene (PP), and co-polymers thereof. Polyolefin co-polymers. Polyacrylates and polymethacrylates, including but not limited to polyacrylic acid (PAA) polymethacrylic acid (PMAA), Poly2-dimethylamino methacrylate (PDMAEMA), Poly-2-hydroxyethyl methacrylate (PHEMA), acrylonitrile. Polystyrene. Thermoplastic elastomers, including but not limited to, Polybutadiene, Polyisoprene, SBS rubber and SIS rubber. Polycarbonates. Polyetheretherketone (PEEK). Polyetherimides. Polyimides. Polysulfones. Poly vinyl chloride (PVC). Polysilanes. Polysiloxanes. Polyureas. Polyurethanes. Polylactic acid. Polyvinylidene chloride. Fluoro-polymers, including but not limited to PTFE (polytetrafluoroethylene), PFA (perfluoroalkoxy polymer resin), fluorinated ethylene-propylene and PVDF (Kynar). Polyethylene imines.

When Q comprises a polymer, the polymer may be a salt of any of the polymers described herein.

In a preferred embodiment, Q is a block-co-polymer which is capable of forming phase domains. Any suitable block structure may be employed such as linear, branched, star or dendritic as depicted in Figure 1.

Polymers of different molecular weight ranges are also covered, from small macromers with a repeat unit length of a dimer, to polymers with a molecular weight of millions. The degree of polymerisation, D_p , of the polymer (i.e. the polymer molecular weight divided by the molecular weight of the repeat unit) may be from 2 to 100,000,000.

Polymers with different polydispersity indexes are also covered, from polymers produced from living polymerisation, such as anionic, atom-transfer radical polymerisation (ATRP) or Reversible addition fragmentation transfer (RAFT) polymerisation, with a PDI approaching 1, to those produced from step-growth or chain-growth polymerisation where the PDI can be >3 .

Typically, the polymer employed is either soluble or dispersable.

In one embodiment, when Q comprises a block-co-polymer, the blocks of the co-polymer are selected from any of the polymers listed in the following paragraph and their copolymers. Thus, the block-co-polymer comprises the monomeric units of any one or more of the following polymers:

Condensation polymers and Addition polymers. Polysaccharides, including but not limited to chitin, guar gums, gum arabic, galactomannans, for instance locust bean gum (LBG). Proteins, including but not limited to Keratin. Polyesters, including but not limited to Nylon, polyethylene terephthalate (PET), polyoxyethylene terephthalate (POET) or a copolymer of polyethylene terephthalate and polyoxyethylene terephthalate (PET-POET). Polyethers, including but not limited to polypropylene glycol (PPG), polyethylene glycol (PEG), Polyethylene oxide (PEO). Polyolefins, including but not limited to polyethylene (PE), polypropylene (PP), and co-polymers thereof. Polyolefin co-polymers. Polyacrylates and polymethacrylates, including but not limited to polyacrylic acid (PAA) polymethacrylic acid (PMAA), Poly2-dimethylamino methacrylate (PDMAEMA), Poly-2-hydroxyethyl methacrylate (PHEMA), acrylonitrile. Polystyrene. Thermoplastic elastomers, including but not limited to, Polybutadiene, Polyisoprene, SBS rubber and SIS rubber. Polycarbonates. Polyetheretherketone (PEEK). Polyetherimides. Polyimides. Polysulfones. Poly vinyl chloride (PVC). Polysilanes. Polysiloxanes. Polyureas. Polyurethanes. Polylactic acid. Polyvinylidene chloride. Fluoro-polymers, including but not limited to PTFE (polytetrafluoroethylene), PFA (perfluoroalkoxy polymer resin), fluorinated ethylene-propylene and PVDF (Kynar), Polyethylene imines.

Typically, the polymer is one that has a functionality $-A^4-X^2$ as defined herein, for instance an OH, NH, SH or aryl (typically phenyl) functionality that allows single step transformation to introduce the reactive intermediate precursor groups of formula (I) onto the polymer.

In one embodiment, Q comprises a polysaccharide, a polyester, polystyrene or a polystyrene block.

Typically, when Q comprises a polymer, n is an integer equal to or greater than 50, for instance equal to or greater than 100. Thus, n may be an integer of from 50 to 1,000,000, from 50 to 100,000, from 50 to 10,000, from 50 to 5,000, or from 50 to 1,000. More typically, in this embodiment, n is an integer of from 50 to 1,000.

In one embodiment of the functionalised compound of the invention, L is a group of formula (XII) as defined above, in which A^3 is a single bond.

In one embodiment, L itself is a single bond. Typically, in this embodiment, each L is attached to a phenyl group of Q.

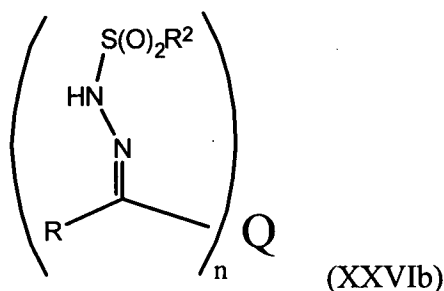
Typically, in this embodiment, Q is a polymer or dendrimer bearing phenyl groups, more typically a polymer bearing phenyl groups, for instance polystyrene.

Typically, when L is a single bond, Q comprises at least n aryl or heteroaryl rings, wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring of Q. The single bond, L, thereby bonds the aryl or heteroaryl ring directly to the carbon atom of the carbene precursor group (i.e. the carbon atom that is also bonded to R in the functionalised compound of the invention). In this embodiment Q is a polymer or dendrimer that comprises said n aryl or heteroaryl rings. Typically, said aryl or heteroaryl rings are aryl rings. Usually, said aryl rings are phenyl rings. Many examples of polymers and copolymers that comprise aryl rings are described herein and include, for instance, polystyrene.

More typically, when L is a single bond, Q is a polymer which comprises at least n aryl or heteroaryl rings, wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring, thereby bonding the aryl or heteroaryl ring directly to the carbon atom which is bonded to R. Typically, said aryl or heteroaryl rings are aryl rings. Typically, said aryl rings are phenyl rings.

Thus, in some embodiments of the functionalised compound of the invention, L is a single bond and Q is a polymer which comprises at least n aryl or heteroaryl rings, wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring, thereby bonding the aryl or heteroaryl ring directly to the carbon atom which is bonded to R. Typically, said aryl or heteroaryl rings are aryl rings. Typically, said aryl rings are phenyl rings.

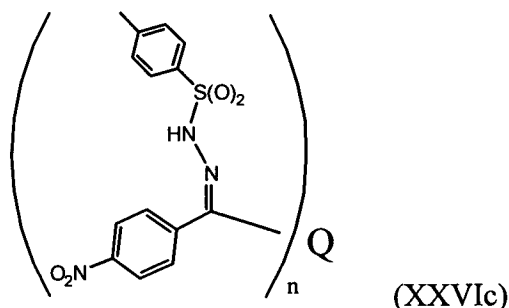
In another embodiment, the functionalised compound is a compound of formula (XXVIb)



wherein Q, R, R² and n are as defined hereinbefore. R may for instance be phenyl or nitrophenyl. Typically in this embodiment, Q is a polymer or dendrimer bearing aryl or heteroaryl groups, more typically phenyl groups, wherein the carbon atom of the diazomethane group is bonded directly to said aryl or heteroaryl groups. More typically, in this embodiment, Q is polystyrene. Or, Q can be a polymer which comprises polystyrene blocks or a copolymer comprising styrene monomer units (a styrene copolymer). Typically,

the carbon atoms of the sulfonylhydrazone groups are bonded to phenyl groups of said polystyrene. Typically the number of sulfonylhydrazone groups bonded to the polymer Q is from 0.5 % to 100% of the number of said aryl or hetroaryl groups on the backbone. More typically the number of sulfonylhydrazone groups is from 0.5 % to 50 % of the number of said aryl or hetroaryl groups.

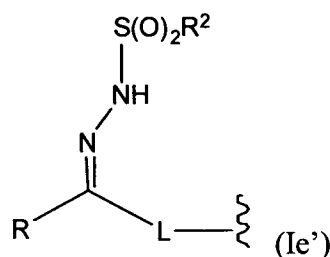
In one embodiment the compound is of formula (XXVIc)



wherein n is as defined hereinbefore, but is typically an integer equal to or greater than 50, and Q is polystyrene or a copolymer comprising styrene monomer units (a styrene copolymer). Alternatively, Q can be a polymer which comprises polystyrene blocks. Each sulfonylhydrazone group in the compound of formula (XXVIc) is typically bonded to a phenyl group of said polystyrene or said copolymer comprising polystyrene.

The present invention is particularly concerned with embodiments in which Q is a polymer which is capable of forming phase domains.

More particularly, the invention is concerned with embodiments in which Q , within the functionalised compound, is a block copolymer or dendrimer which comprises one or more “hard” polymer blocks, A , and one or more “soft” polymer blocks, B , wherein the n carbene precursor groups of formula (Ie’)



are predominantly attached to one or more of the hard blocks. A “hard” polymer block is defined as a polymer chain (or chains) having a glass transition temperature (T_g) that is significantly above ambient temperature. Such hard copolymer blocks include, but are not limited to homopolymers such as polystyrene; they can also include statistical copolymers.

A hard polymer block should ideally have a T_g which is equal to or greater than 40°C, preferably equal to or greater than 60°C. A “soft” polymer block, on the other hand, is defined as a polymer chain (or chains) having a T_g that is below ambient temperature. These can include, but are not limited to, homopolymers such as polyethylene oxide, and polydienes (e.g. polybutadiene, polyisoprenes, natural rubber). They can also include statistical copolymers such as ethylene-co-propylene. Soft polymer blocks normally have a T_g which is equal to or less than 20°C, preferably equal to or less than 0°C.

A hard polymer block, as defined above, is frequently referred to herein as a thermoplastic polymer block, A, or A¹. A soft polymer block, as defined above, is on the other hand frequently referred to herein as an elastomeric polymer block, B, or B¹.

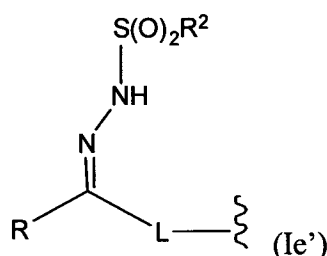
By attaching the reactive precursor groups predominantly to the hard blocks of such copolymers (as opposed to the soft elastomeric block), the inventors have provided a series of novel, one-component block multiphase co-polymers which are capable of forming phase domains and also chemically crosslinking preferentially through the hard block portion of the polymer. Such systems show higher temperature stability without impacting on the elasticity of the polymer, greater resistance to solvents and plasticisers, and no hydrolytic instability. Furthermore, due to the highly reactive nature of the intermediates generated from the reactive intermediate precursor functionalities, E, an increase in the adhesive strength of the materials can be observed on inert, low surface energy and smooth materials without the need for surface priming or promoting. The inventors have thereby provided a series of thermally stable, crosslinkable, and elastomeric polymers which can be used in a wide variety of applications due to their high adhesive strength.

The block copolymer or dendrimer Q, in this embodiment, may be a linear or branched block copolymer, a star block co-polymer, a radial block-copolymer or a dendrimer which comprises such A and B blocks. Typically the hard blocks A comprise blocks of alkenyl arenes such as polystyrene. The soft, rubbery blocks, on the other hand, typically comprise blocks of polymerised olefins, polymerised ethylene oxide, polymerised conjugated dienes (which are either hydrogenated subsequently, to form substantially saturated B blocks, or retained in their unsaturated form). Such polymers, comprising combinations of one or more hard, thermoplastic “A” blocks and one or more soft, elastomeric “B” blocks, are thermoplastics which have varying levels of elastomeric properties and are typically capable of forming phase domains. Many such polymers are available commercially from companies such as Kraton and BASF (Pluronic products).

Accordingly, in one embodiment of the the functionalised compound of the present invention, Q is a block copolymer or dendrimer, which block copolymer or dendrimer comprises one or more linear or branched thermoplastic polymer blocks, A, which are the same or different, and one or more linear or branched elastomeric polymer blocks, B, which are the same or different.

The n reactive intermediate precursor groups are predominantly attached to one or more of the hard blocks, A, as opposed to the one or more elastomeric blocks, B.

Accordingly, in one embodiment, the majority of the n carbene precursor groups of formula (Ie')



present in the functionalised compound are bonded to the one or more thermoplastic polymer blocks A. In other words, typically, more than 50% of said n carbene precursor groups of formula (Ie') are bonded to said one or more thermoplastic polymer blocks A. More typically, at least 60% of said n carbene precursor groups of formula (Ie') are bonded to said one or more thermoplastic polymer blocks A. Even more typically, at least 70% of said n carbene precursor groups of formula (Ie') are bonded to said one or more thermoplastic polymer blocks A. Even more typically, at least 80% of said n carbene precursor groups of formula (Ie') are bonded to said one or more thermoplastic polymer blocks A. Even more typically, at least 90% of said n carbene precursor groups of formula (Ie') are bonded to said one or more thermoplastic polymer blocks A. Even more typically, each of said n carbene precursor groups of formula (Ie') is bonded to said one or more thermoplastic polymer blocks A. As explained above, this ensures that the functionalised compound is capable of chemically crosslinking preferentially through the hard block portion of the copolymer; accordingly, on curing, the compound retains the useful elastomeric, rubbery properties provided by the one or more soft blocks, B.

Typically, Q is a block copolymer or dendrimer, which block copolymer or dendrimer is capable of forming phase domains.

Typically, Q is a multiphase copolymer.

IUPAC defines a phase domain as “a region of a material that is uniform in chemical composition and physical state” and a multiphase copolymer as “a copolymer comprising separate phase-separated domains”.

Typically, in this embodiment, Q is a block copolymer having the structure $A_z-(B-A)_y-B_x$, wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20, provided that the sum of z, y and z is equal to or greater than 2. Each “A” is a linear or branched thermoplastic polymer block, and each “B” is a linear or branched elastomeric polymer block. More typically, the block copolymer has the structure A-B-A, B-A-B, A-B, or $(A-B)_m$, wherein m is an integer from 1 to 20. Even more typically, Q is a block copolymer having the structure A-B-A, wherein each A is a linear or branched thermoplastic polymer block, and each B is a linear or branched elastomeric polymer block.

Alternatively, Q may be a dendrimer or a radial block copolymer, which dendrimer or radial block copolymer is of the formula (Xa):



wherein:

q is an integer of from 3 to 100;

each P, which is the same or different, is a polymer arm having the structure $A_z-(B-A)_y-B_x$, wherein each A, which is the same or different, is a linear or branched thermoplastic polymer block and each B, which is the same or different, is a linear or branched elastomeric polymer block, and wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20; provided that in each polymer arm P, the sum of z, y and z is equal to or greater than 1 and provided that, in at least one of said polymer arms P, the sum of z, y and z is equal to or greater than 2; and

Core is a core moiety of the dendrimer or radial block copolymer of formula (Xa), to which each of the polymer arms P is attached.

Such dendrimers or a radial block copolymers of formula (Xa) may be asymmetric or symmetric, given that each polymer arm P may be the same or different.

Dendrimers or a radial block copolymers of formula (Xa) may be produced as described in US 5,446,104, by coupling the polymer arms P to a central core moiety in a coupling process. The coupling agents used are typically polyfunctional coupling agents or monomers. Coupling agents such as divinyl benzene may (a) polymerise or oligomerise, as well as (b) react with the living chain ends of the polymer arms, P. The results of these two types of reactions is the formation of a star-shaped polymer or dendrimer having from 3 to

100, more typically up to 40 or 50, arms attached to the central core, which core is composed principally of the coupling agent.

Accordingly, in one embodiment, the group Core, in the dendrimer or radial block copolymer of formula (Xa), comprises an oligomer or polymer formed from a polyfunctional coupling monomer. Typically, the polyfunctional coupling monomer is an aryl ring substituted with from 2 to 4 unsubstituted or substituted C₂₋₂₀ alkenyl groups. More typically, the polyfunctional coupling monomer is a divinyl substituted aryl ring, preferably *para*-divinyl benzene or *meta*-divinyl benzene.

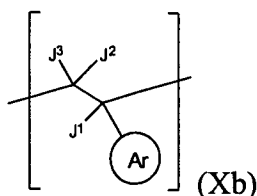
In another embodiment, the Core is formed from one of the blocks A or B. Accordingly, in one embodiment, the group Core, in the dendrimer or radial block copolymer of formula (Xa), comprises a linear or branched thermoplastic polymer block, A¹, and/or a linear or branched elastomeric polymer block, B¹. For instance, Core may comprise a polymer of formula A¹_z-(B¹-A¹)_y-B¹_x, wherein each A¹ is a linear or branched thermoplastic polymer block and each B¹ is a linear or branched elastomeric polymer block, and wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20 provided that the sum of z, y and x is equal to or greater than 1.

Typically, and irrespective of whether the block copolymer Q is a block copolymer, radial block copolymer or dendrimer, each of said one or more thermoplastic polymer blocks A comprises unsubstituted or substituted aryl groups attached to a polymer backbone. Typically, the unsubstituted or substituted aryl groups are phenyl groups, as in polystyrene. However, other aryl groups may be suitable, for instance naphthyl groups. Usually, each of the carbene precursor groups of formula (Ie'), which is bonded to said one or more blocks A, is bonded to an aryl group in said one or more blocks A.

Typically, the polymer backbone of said one or more blocks A, to which the aryl groups are attached, comprises, or is, a saturated aliphatic hydrocarbon chain. Usually, each of the aryl groups is attached to said backbone by a single bond (e.g. as in a polystyrene block). Alternatively, the aryl groups may be fused to a C₅₋₁₀ carbocyclic ring which forms part of said backbone (e.g. as in a polyindene block).

The one or more linear or branched "hard" thermoplastic blocks, A, within the polymer or dendrimer Q, may be defined as follows:

Typically, each of said one or more linear or branched thermoplastic polymer blocks, A, comprises monomer units of formula (Xb):



wherein

Ar is an unsubstituted or substituted aryl group; and

J^1 , J^2 and J^3 , which are the same or different, are independently selected from H, unsubstituted or substituted C_{1-10} alkyl, halo, unsubstituted or substituted C_{1-10} alkoxy, amino, unsubstituted or substituted C_{1-10} alkylamino, unsubstituted or substituted di(C_{1-10})alkylamino, unsubstituted or substituted arylamino, unsubstituted or substituted diarylamino, unsubstituted or substituted arylalkylamino, unsubstituted or substituted C_{2-10} alkenyl, unsubstituted or substituted aryl and unsubstituted or substituted heteroaryl, wherein said unsubstituted or substituted C_{1-10} alkyl is optionally interrupted by $N(R'')$, O, S or arylene wherein R'' is H, C_{1-6} alkyl or aryl;

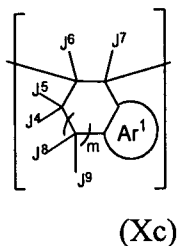
wherein each of the reactive intermediate precursor groups $[R]_x-E-L-$ which is bonded to said one or more blocks A, is bonded to a group Ar.

Typically, Ar is an unsubstituted or substituted phenyl group, more typically an unsubstituted phenyl group. In another embodiment, however, Ar is an unsubstituted or substituted naphthyl group.

Typically, J^1 , J^2 and J^3 are independently selected from hydrogen, unsubstituted or substituted C_{1-10} alkyl, halo, unsubstituted or substituted C_{1-10} alkoxy, and unsubstituted or substituted aryl. Usually, however, J^1 , J^2 and J^3 are each hydrogen.

Typically, therefore, Ar is a phenyl group and J^1 , J^2 and J^3 are each hydrogen.

In another embodiment, each of said one or more linear or branched thermoplastic polymer blocks, A, comprises monomer units of formula (Xc)



wherein

Ar^1 is an unsubstituted or substituted aryl group;

m is 0 or an integer from 1 to 6; and

J^4 , J^5 , J^6 , J^7 , J^8 and J^9 which are the same or different, are independently selected from H, unsubstituted or substituted C_{1-10} alkyl, halo, unsubstituted or substituted C_{1-10} alkoxy, amino, unsubstituted or substituted C_{1-10} alkylamino, unsubstituted or substituted di(C_{1-10})alkylamino, unsubstituted or substituted arylamino, unsubstituted or substituted diarylamino, unsubstituted or substituted arylalkylamino, unsubstituted or substituted C_{2-10} alkenyl, unsubstituted or substituted aryl and unsubstituted or substituted heteroaryl, wherein said unsubstituted or substituted C_{1-10} alkyl is optionally interrupted by $N(R'')$, O, S or arylene wherein R'' is H, C_{1-6} alkyl or aryl;

wherein each of the reactive intermediate precursor groups $[R]_x-E-L-$ which is bonded to said one or more blocks A, is bonded to a group Ar^1 .

Typically, Ar is an unsubstituted or substituted phenyl ring, more typically an unsubstituted phenyl ring.

Usually, J^4 , J^5 , J^6 , J^7 , J^8 and J^9 are independently selected from hydrogen, unsubstituted or substituted C_{1-10} alkyl, halo, unsubstituted or substituted C_{1-10} alkoxy, and unsubstituted or substituted aryl. Usually, however, J^4 , J^5 , J^6 , J^7 , J^8 and J^9 are each hydrogen.

Typically, therefore, Ar^1 is a phenyl ring and J^4 , J^5 , J^6 , J^7 , J^8 and J^9 are each hydrogen.

Typically, m is 0.

Typically, when said one or more linear or branched thermoplastic polymer blocks, A, comprise monomer units of formula (Xb) or (Xc) as defined above, each of said blocks comprises at least 80 weight % of said monomer units. More typically, each of said blocks comprises at least 90 weight % of said monomer units of formula (Xb) or (Xc). In one embodiment, each of said blocks A consists essentially of said monomer units of formula (Xb) or (Xc).

In one embodiment, each of said one or more linear or branched thermoplastic polymer blocks, A, in the block copolymer or dendrimer Q, is a homopolymer block which comprises monomer units of formula (Xb) or (Xc) as defined above. Such "A" blocks include poly(styrene) and poly(indene) blocks.

In another embodiment, each of said one or more linear or branched thermoplastic polymer blocks, A, is a random copolymer block, which comprises co-monomer units of formula (Xb) or (Xc) as defined above, and co-monomer units derived from an additional co-monomer. The additional co-monomer may for instance be a conjugated diene having

from 4 to 24 carbon atoms, or a conjugated diene of formula (Xd) as defined herein. Such “A” blocks include poly(styrene-isoprene) and poly(styrene-butadiene), and are described in US 4,556,464.

In another embodiment, the one or more linear or branched thermoplastic polymer blocks, A, in the block copolymer or dendrimer Q, are selected from: (i) homopolymer blocks which comprise monomer units of formula (Xb) or (Xc) as defined above, and (ii) random copolymer blocks, which comprise co-monomer units of formula (Xb) or (Xc) as defined above, and co-monomer units derived from an additional co-monomer. The additional co-monomer may for instance be a conjugated diene having from 4 to 24 carbon atoms, or a conjugated diene of formula (Xd) as defined herein.

Typically, each of said one or more linear or branched thermoplastic polymer blocks, A, in the block copolymer or dendrimer Q, comprises poly(indene) or a poly(C₁₋₆ alkenyl-aryl). For the avoidance of doubt, a poly(C₁₋₆ alkenyl-aryl) is a polymer of a monomer which consists of an aryl group as defined herein bonded to a polymerisable C₁₋₆ alkenyl group.

Typically, the monomer is styrene, and the thermoplastic polymer blocks, A, in the block copolymer or dendrimer Q, therefore comprise poly(styrene).

Typically, in this embodiment, each of said blocks comprises at least 80 weight % of poly(styrene). More typically, each of said blocks comprises at least 90 weight % of poly(styrene). In one embodiment, each of said blocks A consists essentially of poly(styrene).

In another embodiment, each of said one or more linear or branched thermoplastic polymer blocks, A, in the block copolymer or dendrimer Q, comprises a random copolymer of a C₁₋₆ alkenyl-aryl monomer, for instance styrene, and a conjugated diene monomer, which conjugated diene monomer has from 4 to 24 carbon atoms. Preferably, the C₁₋₆ alkenyl-aryl monomer is styrene. Preferably, the conjugated diene is as further defined hereinbelow. Such copolymer “A” blocks include poly(styrene-isoprene) and poly(styrene-butadiene), and are described in US 4,556,464.

The one or more linear or branched “soft” elastomeric blocks, B, within the polymer or dendrimer Q, may be defined as follows:

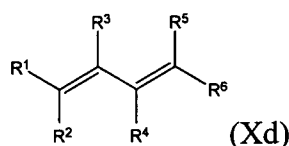
Each of the one or more “soft” elastomeric blocks, B, may be any suitable elastomeric polymer block. Suitable elastomeric blocks include, for instance, polymers or copolymers comprising polymerised olefins, polymers or copolymers comprising

polymerised ethylene oxide, polymers or copolymers comprising conjugated diene monomers, and ethylene-propylene-diene terpolymers (EPDMs), but and any other polymer block which imparts elastomeric properties may be employed.

Typically, however, each of said elastomeric polymer blocks, B, comprises a polymer or copolymer of one or more conjugated diene monomers. Such polymers or copolymers blocks of conjugated diene monomers may be prepared in the absence or presence of hydrogenation. Whether or not hydrogenation is performed determines the degree of unsaturation in the resulting polymer or copolymer block. Typically, the block is prepared in the absence of hydrogenation and is therefore an unsaturated polymer or copolymer of one or more conjugated diene monomers. Such blocks include poly(isoprene) and poly(butadiene). Alternatively, however, the block may be prepared in the presence of hydrogenation, and is thereby converted into a saturated elastomeric block B, such as poly(ethylene/butylene) or poly(ethylene/propylene). Elastomeric polymers comprising hydrogenated polymers of conjugated diene monomers are described in WO 01/92344 (Kraton Polymers Research, B.V.).

Accordingly, in one embodiment, each of said one or more linear or branched elastomeric polymer blocks, B, which are the same or different, comprises a polymer or copolymer of one or more conjugated diene monomers, or a hydrogenated polymer or copolymer of one or more conjugated diene monomers.

Typically, the one or more conjugated diene monomers are selected from conjugated diene monomers of formula (Xd)



wherein R^1 , R^2 , R^3 , R^4 , R^5 and R^6 , which are the same or different, are independently selected from H, unsubstituted or substituted C_{1-20} alkyl, unsubstituted or substituted C_{2-20} alkenyl and unsubstituted or substituted aryl. More typically, R^1 , R^2 , R^3 , R^4 , R^5 and R^6 , which are the same or different, are independently selected from H, unsubstituted or substituted C_{1-20} alkyl, and unsubstituted or substituted aryl.

More typically, the one or more conjugated diene monomers have from 4 to 24 carbon atoms.

In one embodiment, the one or more conjugated diene monomers are selected from 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-

butadiene, 2-propyl-1,3-butadiene, 2-butyl-1,3-butadiene, 2-pentyl-1,3-butadiene (2-amyl-1,3-butadiene), 2-hexyl-1,3-butadiene, 2-heptyl-1,3-butadiene, 2-octyl-1,3-butadiene, 2-nonyl-1,3-butadiene, 2-decyl-1,3-butadiene, 2-dodecyl-1,3-butadiene, 2-tetradecyl-1,3-butadiene, 2-hexadecyl-1,3-butadiene, 2-isoamyl-1,3-butadiene and 2-phenyl-1,3-butadiene; and from: 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 6-methylene-2,7-octadiene, 1,3-nonyldiene, 1,3-decyldiene, and 1,3-dodecyldiene and the 2-methyl, 2,3-dimethyl, 2-ethyl, 2-propyl, 2-butyl, 2-pentyl, 2-hexyl, 2-heptyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 2-tetradecyl, 2-hexadecyl, 2-isoamyl and 2-phenyl derivatives thereof.

Usually, the one or more conjugated diene monomers are 1,3-butadiene, isoprene, or a mixture thereof.

Accordingly, in one embodiment, each of said one or more linear or branched elastomeric polymer blocks, B, which are the same or different, comprises poly(butadiene), poly(isoprene), poly(butadiene-co-isoprene), or a hydrogenated derivative thereof.

Said hydrogenated derivatives thereof include poly(ethylene/butylene), poly(ethylene/propylene) and poly(ethylene/ethylene/propylene).

In one embodiment, Q is selected from poly(styrene)-poly(butadiene)-poly(styrene) (SBS), poly(styrene)-poly(isoprene)-poly(styrene) (SIS), poly(styrene)-poly(butadiene/isoprene)-poly(styrene) (SIBS), poly(styrene)-poly(ethylene/butylene)-poly(styrene) (SEBS), poly(styrene)-poly(ethylene/propylene)-poly(styrene) (SEPS), and poly(styrene)-poly(ethylene/ethylene/propylene)-poly(styrene) (SEEPS). Such polymers are commercially available, for instance from Kraton. Typically, in this embodiment, the majority of the n carbene precursor groups of formula (Ie'), are bonded to the poly(styrene) "A" blocks. More typically, at least 60% of said n carbene precursor groups of formula (Ie') are bonded to the poly(styrene) blocks. Even more typically, at least 70% of said n carbene precursor groups of formula (Ie') are bonded to the poly(styrene) blocks. Even more typically, each of said n carbene precursor groups of formula (Ie') is bonded to the poly(styrene) blocks.

L is usually a single bond in this embodiment, and therefore each hydrazone group of formula (Ie) is bonded directly to Q.

Generally, when Q, in the functionalised compounds of the invention of formula (XXXa), comprises a polymer whose backbone bears aryl or heteroaryl groups, wherein the reactive intermediate precursor groups are attached to the polymer or dendrimer via such

aryl or heteroaryl groups, the number of reactive intermediate precursor groups, n , is typically from 0.5 % to 100 % of the number of said aryl or heteroaryl groups in Q. More typically, the number of reactive intermediate precursor groups, n , is from 0.5 % to 50 % of the number of said aryl or heteroaryl groups in Q. Typically, therefore, not all of the aryl or heteroaryl groups on the polymer backbone within Q bear a reactive intermediate precursor group.

The multiple carbene precursor groups of formula (Ie') of the functionalised compounds of the invention of formula (XXXa) can be readily converted into reactive carbene intermediate groups, which can in turn react with and bond to a wide variety of substrates, including individual molecules and bulk materials.

The reactive carbene intermediate groups are typically generated by a thermal process, but can be generated chemically or by irradiation. Typically, the reactive carbene intermediate groups are generated by thermal irradiation, for instance by heating. This heat might be applied to the functionalised compound externally, but may also be as a result of another process, for example, extrusion. Alternatively, the reactive intermediate groups may be generated by electromagnetic radiation, for instance by UV, microwave or laser irradiation, or by ultrasonic irradiation.

Since the functionalised compounds of the invention bear at least 3 reactive intermediate precursor groups which can be converted into reactive intermediate groups, one molecule of the functionalised compound can react with two or more molecules or particles of a substrate compound, B, to form a cross link between the molecules or particles of B. Similarly, a molecule of the compound can form a cross link between two or more different compounds, e.g. compounds C and D. The functionalised compound can also react with itself intermolecularly, i.e. with other molecules of the functionalised compound. In some cases, the functionalised compound can also react with itself intramolecularly. Thus, a bulk sample of the functionalised compound can react both with itself and with any other material or materials with which it is brought into contact, to form a cross-linked network that bonds the materials together. For instance, a bulk layer of a functionalised compound of the invention may be applied between two substrates, E and F, and the reactive intermediate precursor groups of the functionalised compound may then be converted into reactive intermediate groups, thereby causing the functionalised compound to react with itself intermolecularly and to react with the surfaces of the two substrates,

thereby forming a cross-linked network between E and F, bonding the two substrates together.

Such substrates may be in any suitable physical form, for instance in the form of a solution or suspension of the substrate, or in the form of a solid film, layer, sheet or board. Alternatively, the substrates may be in powder form, or in the form of pellets, beads, particles, nanoparticles or microparticles. The pellets, beads or particles may be macroscopic particles, i.e. visible to the naked eye, or microscopic particles. Thus, the particles could be microparticles or nanoparticles.

Accordingly, the invention provides the use of a functionalised compound of the invention, as defined herein, as a cross linking agent.

The invention further provides the use of a functionalised compound of the invention, as defined herein, as an adhesive.

The functionalised compound may, for instance, be used as a thermoset adhesive, a hot melt adhesive, a laminating adhesive or an assembly adhesive.

The invention further provides the use of a functionalised compound of the invention as defined herein as an agent for producing a chemically-bound three-dimensional network on or within a substrate.

Typically, Q, in the functionalised compound used as an adhesive, is a block copolymer or dendrimer as defined herein which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n reactive intermediate precursor groups are bonded to said one or more thermoplastic polymer blocks A. Such compounds are particularly suitable for use as thermoset adhesives.

The adhesive properties of the functionalised compounds of the invention may be enhanced by the addition of additives such as tackifiers and further polymers.

Accordingly, in another aspect, the invention provides an adhesive composition comprising a functionalised compound of the invention.

Typically, Q, in the functionalised compound employed in the adhesive composition, is a block copolymer or dendrimer as defined herein which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n reactive carbene intermediate precursor groups are bonded to said one or more thermoplastic

polymer blocks A. Such compounds are particularly suitable for use as thermoset adhesives.

Typically, the adhesive composition comprises one or more further components or additives.

The one or more additives may for instance include an adhesion promoting or tackifying resin that is compatible with the functionalised compound. A common tackifying resin is a diene-olefin copolymer of piperylene and 2-methyl-2-butene having a softening point of about 95 °C. This resin is available commercially and is prepared by the cationic polymerization of 60% piperylene, 10% isoprene, 5% cyclopentadiene, 15% 2-methyl-2-butene and about 10% dimer, as taught in U.S. Pat. No. 3,577,398. Other tackifying resins of the same general type may be employed in which the resinous copolymer comprises 20-80 weight percent of piperylene and 80-20 weight percent of 2-methyl-2-butene. The resins normally have softening points (ring and ball) between about 80 °C and about 115 °C.

Other adhesion promoting resins which are also useful in the adhesive composition of the invention include hydrogenated rosins, esters of rosins, polyterpenes, terphenol resins and polymerized mixed olefins, lower softening point resins and liquid resins. An example of a liquid resin is Adtac LV from Hercules. To obtain good thermo-oxidative and color stability, it is preferred that the tackifying resin be a saturated resin, e.g., a hydrogenated dicyclopentadiene resin or a hydrogenated polystyrene or polyalphamethylstyrene resin. The amount of adhesion promoting resin employed varies from about 20 to about 400 parts by weight per hundred parts rubber (phr), preferably between about 70 to about 350 phr. The selection of the particular tackifying agent is, in large part, dependent upon the specific functionalised compound of the invention employed in the respective adhesive composition.

The adhesive composition of the instant invention may contain plasticizers, such as rubber extending plasticizers, or compounding oils or organic or inorganic pigments and dyes. Rubber compounding oils are well-known in the art and include both high saturates content oils and high aromatics content oils. Preferred plasticizers are highly saturated oils. The amounts of rubber compounding oil employed in the invention composition can vary from 0 to about 100 phr, and preferably between about 0 to about 60 phr.

Further optional components of the present invention are stabilizers which inhibit or retard heat degradation, oxidation, skin formation and color formation. Stabilizers are

typically added in order to protect against heat degradation and oxidation during the preparation, use and high temperature storage of the adhesive composition.

Combinations of primary and secondary antioxidants are preferred. Such combinations include sterically hindered phenolics with phosphites or thioethers, such as hydroxyphenylpropionates with aryl phosphates or thioethers, or amino phenols with aryl phosphates. Specific examples of useful antioxidant combinations include 3-(3,5-di-*t*-butyl-4-hydroxyphenyl)-propionate)methane (Irganox 1010 from Ciba-Geigy) with tris(nonylphenyl)phosphite (Polyguard HR from Uniroyal), Irganox 1010 with bis(2,4-di-*t*-butyl)pentaerythritol disphosphite (Ultranox 626 from Borg-Wagner), 4-((4,6-bis(octylthio)-s-triazin-2-yl)amino)-2,6-di-*t*-butylphenol (Irganox 565) with Polygard HR, and Irganox 565 with Ultranox 626.

Additional stabilizers known in the art may also be incorporated into the adhesive composition. These may be for protection during the life of the article against, for example, oxygen, ozone and ultraviolet radiation. However, these additional stabilizers should be compatible with the essential stabilizers mentioned herein-above and their intended function as taught herein.

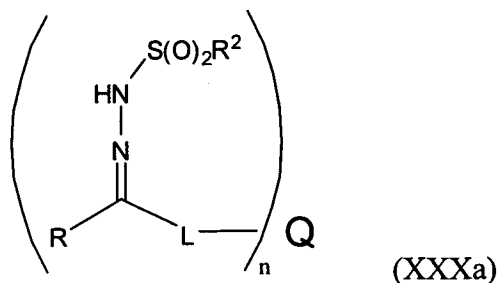
One or more solvents may also be present in the adhesive composition.

The adhesive compositions of the present invention may be prepared by blending the components at an elevated temperature until a homogeneous blend is obtained. The resultant adhesives may then be used in a wide variety of applications.

The sulfonylhydrazone functionalised compounds of the invention of formula (XXXa) can be used to cross link or adhere two or more substrates, which two or more substrates may be the same or different.

Accordingly, the invention provides a process for cross linking or adhering a first substrate to a second substrate, which first and second substrates are the same or different, which process comprises

(a) contacting the first and second substrates with a functionalised cross linking compound which is a sulfonylhydrazone compound of formula (XXXa)

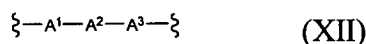


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

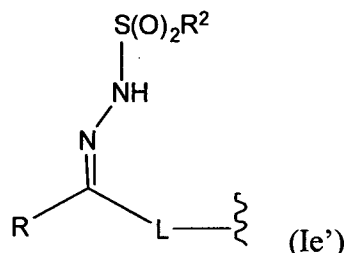
A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

R^2 is an unsubstituted or substituted C_{1-6} alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer; and

(b) generating carbene reactive intermediate groups from the n carbene precursor groups of formula (Ie')



wherein R, R^2 and L are as defined above, so that at least one carbene reactive intermediate group reacts with the first substrate and at least one other carbene reactive intermediate group reacts with the second substrate, thereby cross linking or adhering the first and second substrates.

Q in the functionalised cross linking compound is a polymer or a dendrimer. Typically, the polymer or dendrimer is one which is capable of forming a phase domain structure.

The functionalised cross linking compound may be any functionalised compound of formula (XXXa) of the invention as further defined herein.

Typically, Q, in the functionalised cross linking compound used in the process of the invention for cross linking or adhering a first substrate to a second substrate, is a block copolymer or dendrimer as defined herein which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n reactive intermediate precursor groups are bonded to said one or more thermoplastic polymer blocks A. Such compounds are particularly suitable for use as thermoset adhesives.

As the skilled person will appreciate, in the process of the invention for cross linking or adhering a first substrate to a second substrate, typically some of the reactive intermediate groups react with the first and second substrates and others react with other molecules of the cross linking compound itself. The reactive intermediate groups of the cross linking compound can also react intramolecularly, with other groups or blocks within the same cross linking compound.

In step (a), the first and second substrates may be contacted with the functionalised cross linking compound by any suitable method, depending on the physical forms of the first and second substrates. For instance, when the first and second substrates are both in particulate form, the particles may for instance be mixed with the functionalised cross linking compound to form a substantially homogeneous mixture. Alternatively, when the first and second substrates are both layers or sheets, the first and second substrates may be contacted with the functionalised cross linking compound by (i) applying a layer of the functionalised cross linking compound onto the first substrate, and (ii) subsequently applying a layer of the second substrate onto the functionalised cross linking compound. In another embodiment, the first and second substrates may be contacted with the functionalised cross linking compound by applying a mixture of the second substrate and the functionalised cross linking compound to the first substrate.

The functionalised cross linking compound may be applied as the neat compound or in solution. Any suitable solvent may be used for the functionalised cross linking compound. Such suitable solvents include but are not limited to alcohols. For instance, the solvent may be methanol, methyl ethyl ketone, toluene or anisole.

The first or second substrate may for instance be contacted with the functionalised cross linking compound by dip coating, spray coating, rolling, printing or co-extrusion. The dip coating, spray coating, rolling, printing or co-extrusion may be performed in solution or otherwise. Thus, the dip coating, spray coating, rolling, printing or co-extrusion may be performed using a solution of the functionalised cross linking compound or using the neat functionalised cross linking compound. Similarly, the dip coating, spray coating, rolling, printing or co-extrusion may be carried out using the neat first or second substrate or using a suitable solution of the first or second substrate.

In step (b) of the process of the present invention for cross linking or adhering a first substrate to a second substrate, the generated reactive intermediate groups may react with the surfaces of both the first and second substrates. In this context, the term “surface” means either the whole of the surface of the substrate in question or only a portion of the surface of the substrate.

The reactive intermediate groups are typically generated by a thermal process, but may be generated chemically or by irradiation. Typically, the reactive intermediate groups are generated by thermal irradiation, for instance by heating. This heat might be applied externally, but may also be as a result of another process, for example, extrusion.

Alternatively, the reactive intermediate may be generated by electromagnetic radiation, for instance by UV, microwave or laser irradiation, or by ultrasonic irradiation. Some of these techniques, including laser and UV irradiation, are suitable for generation of the reactive intermediate selectively, i.e. on only a portion of the surface of the first or second substrate.

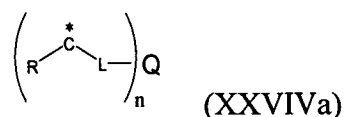
In one embodiment, the reactive intermediate groups are generated by heating the functionalised cross linking compound to a temperature of from 50 °C to 300 °C, more typically to a temperature of from 50 °C to 200 °C.

In one embodiment, only a portion of the surface of the first substrate is cross linked to a second substrate. For example, the surface of the first substrate may be modified in certain areas only, to form specific a “pattern” of cross linking. In this way, the two-dimensional shape of the resulting cross linked product may be controlled. This may be useful in the design of printed circuit boards, for example, where the cross linking of metal to substrate is only desired in certain specific places.

In one embodiment, the reactive carbene intermediate groups are generated selectively, i.e. only on certain portions of the surface of the first substrate. In this way, only the particular regions of the surface on which the reactive intermediate has been generated become cross linked to the second substrate. This is known as “selective activation”, and can be used to form specific a “pattern” of cross linking.

The invention also provides a cross-linked or adhered product comprising:

- (a) a first substrate;
- (b) a second substrate; and
- (c) a cross linking moiety of formula (XXVIVa)



wherein

the first and second substrates are the same or different;

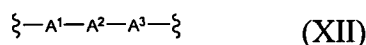
each * is a point of attachment of the cross linking moiety to the first substrate, the second substrate or to another moiety or molecule;

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy,

amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryl di(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²; and

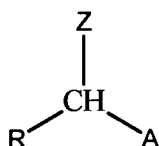
Q is a polymer or a dendrimer.

Typically, each * is a point of attachment of the cross linking moiety to the first substrate, the second substrate, or to the same cross linking moiety of formula (XXVIVa) (intramolecular cross-linking) or another cross linking moiety of formula (XXVIVa) (intermolecular cross-linking). However, as the skilled person will appreciate, some of the carbon atoms may be bonded to molecules of other compounds too, if such other

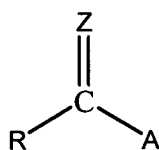
compounds were present in the reaction mixture when the crosslinked or adhered product was formed.

Various different modes of binding of the cross linking moiety of formula (XXVIVa) to the first and second substrates or to the same (intramolecular) or another (intermolecular) cross linking moiety of formula (XXVIVa) are possible via the carbene carbon atom marked “*”. Possible bonding modes include those described below:

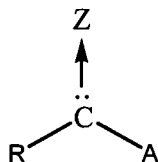
The point of attachment of the cross linking moiety of formula (XXVIVa) to the first and second substrates, or to the same or another cross linking moiety of formula (XXVIVa), is depicted “*”. Thus, in the cross-linked product of the invention as defined above, the carbon atom marked “*” is bonded to the first or second substrate, or to the same or another cross linking moiety of formula (XXVIVa). As the skilled person would understand, various different modes of binding of the cross linking moiety of formula (XXVIVa) to the substrates, or to the same or another cross linking moiety of formula (XXVIVa), are possible via that carbon atom. For instance, the bond between the carbon atom marked “*” and an atom “Z” of the first or second substrate (or an atom “Z” of the same or another cross linking moiety of formula XXVIVa) may be a single covalent bond, in which case that carbon atom is also bonded to another atom or group (for example a hydrogen atom), as follows:



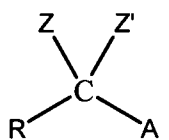
Alternatively, the bond between the carbon atom marked “*” and an atom “Z” of the first or second substrate (or an atom “Z” of the same or another cross linking moiety of formula XXVIVa) may be a double bond, as follows:



Alternatively, the bond between the carbon atom marked “*” and an atom “Z” of the first or second substrate (or an atom “Z” of the same or another cross linking moiety of formula XXVIVa) may be a dative bond (also known as a coordinate bond), in which both electrons are provided by the carbon atom, as follows:



Alternatively, the carbon atom marked “*” may be bonded to two atoms, “Z” and “Z’”, of the first or second substrate (or to two atoms, “Z” and “Z’”, of the same or another cross linking moiety of formula (XXVIVa); or to one atom, “Z”, of the first or second substrate and to another atom, “Z’”, of the same or another cross linking moiety of formula (XXVIVa) wherein the bonds between the carbon atom marked “*” and the atoms Z and Z’ are both single bonds, as follows:



In the cross-linked product of the invention as defined above, R, L and Q may be as further defined hereinbefore. In one embodiment of the cross-linked product of the invention, Q is a block copolymer or dendrimer as defined herein which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n carbene precursor groups of formula (Ie’) are bonded (via L) to said one or more thermoplastic polymer blocks A.

The first and second substrates which are crosslinked or adhered in accordance with the present invention may be the same material or two different materials. Each substrate may be any natural or synthetic substrate which is capable of reaction with a carbene reactive intermediate group generated from a diazo-functionalised cross linking compound as defined above, for instance from a diazo-functionalised compound of formula (II). Thus, a huge variety of first and second substrates may cross linked or adhered in accordance with the present invention.

The first and second substrates, which are the same or different, may for instance be independently selected from any of the following materials:

- natural or synthetic polymers including but not limited to cellulose, polyglycosides, polypeptides, polyacrylates, polyacrylics, polyamides, polyimides, polycarbonates, polyesters, epoxy resins, polyethers, polyketones, polyolefins, rubbers, polystyrenics, polysulfones, polyurethanes, polyvinyls and their co-polymers;

- polyesters, polyacrylates, polyolefins, polyamides, polyimides, polysulfones and epoxy resins, homopolymers and copolymers of ethylene, propylene, styrene, PET (polyethylene terephthalate) or EPDM (ethylene propylene diene monomer);

- homopolymers and copolymers, for instance a block copolymers;
- thermoplastic resins and thermosetting resins;
- inorganic materials including but not limited to metals, metal alloys, metal salts, silica, glasses, alumina, titania, and allotropes of carbon such as diamond, diamond-like carbon, graphite, fullerenes and nanotubes;
- nanoparticles and microparticles;
- C₆₀ and nanotubes, for instance carbon nanotubes;
- textiles and paper.

The first substrate, or the second substrate, may comprise any two or more of the above-listed materials.

The first and second substrates may be in any suitable physical form, and may be in the same form as one another or in different forms from one another. Suitable forms include film, layer, sheet or board, powder form, pellet form or in the form of beads, particles, nanoparticles or microparticles, fibers, yarns or cords. The pellets, beads or particles may be macroscopic particles, i.e. visible to the naked eye, or microscopic particles. Thus, the particles could be microparticles or nanoparticles.

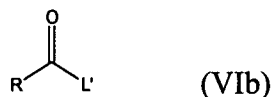
In one embodiment of the process of the invention for cross linking or adhering a first substrate to a second substrate, or of the cross-linked or adhered product of the invention, the first substrate is a first polymer and the second substrate is a second polymer. The first and second polymers, which may be the same or different, may be independently selected from any of those listed above.

In one embodiment the first polymer is a hydrophilic polymer, for instance poly(ethyleneimine). In another embodiment the first polymer is a hydrophobic polymer, for instance poly(tetrafluoroethylene). The second polymer may be a polyester or a poly(alkylene) (for instance polyethylene or polypropylene). In one embodiment, the second polymer is selected from poly(ethylene terephthalate) and polypropylene.

In one embodiment the first polymer is an epoxy resin. In another embodiment, the first polymer is an epoxy resin and the second polymer is an epoxy resin.

Functionalised compounds of the invention may be produced by the process of the invention as defined above for producing a functionalised compound of formula (XXXa).

Step (a) of the process comprises: process comprises: (a) treating a first compound, Q', which is a polymer or a dendrimer and which bears at least n functional groups, with at least one second compound of formula (VIb)



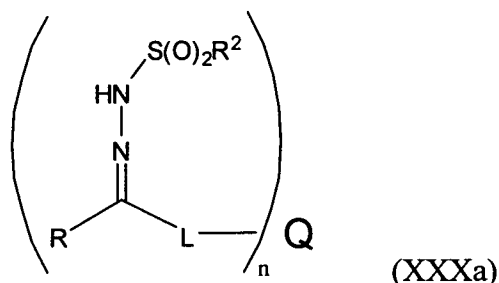
wherein:

L' is a leaving group or a reactive precursor to said group of formula (XII), wherein L' is reactable with a said functional group to couple the second compound to the first compound, and

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

Typically, the first compound, Q', which bears at least n functional groups (or n functional groups, in one embodiment) is treated with at least n equivalents of the at least one second compound of formula (VIb). As the skilled person will appreciate, however, functionalised compounds which comprise n carbene precursor groups of formula (Ie') all of which are the same can be synthesised by treating said first compound with at least n equivalents of a single second compound of formula (VIb). In contrast, functionalised compounds which comprise n carbene precursor groups of formula (Ie') not all of which are the same can be synthesised by treating said first compound with more than one type of second compound of formula (VIb). For instance, the first compound which bears at least n functional groups (or n functional groups, in one embodiment) can be treated with less than n equivalents of one compound of formula (VIb) and with less than n equivalents of another compound of formula (VIb), provided that the total number of equivalents of the compounds of formula (VIb) is at least n, to produce a functionalised compound of the invention comprising two different types of carbene precursor groups of formula (Ie').

The functionalised compound produced by the process of the invention is a sulfonylhydrazone compound of formula (XXXa)

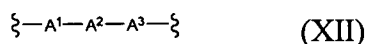


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} haloalkyl, C_{1-20} fluoroalkyl, C_{1-20} perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C_{1-10} alkylamino, di(C_{1-10})alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C_{1-10} alkoxy, aryloxy, haloalkyl, thiol, C_{1-10} alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C_{1-20} alkyl)silyl, aryldi(C_{1-20} alkyl)silyl, diaryl(C_{1-20} alkyl)silyl and triarylsilyl;

each L , which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R , wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^{*-}C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^{*-}Z^1$ - C_{1-20} alkylene, $^{*-}Z^1$ - C_{1-20} perfluoroalkylene, $^{*-}Z^1$ -arylene, $^{*-}Z^1$ -heteroarylene and $^{*-}Z^1$ - C_{1-20} alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O) $_2$, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from $^{*-}Z^2$ -arylene, $^{*-}Z^2$ -heteroarylene, $^{*-}Z^2$ - C_{1-20} alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^{*-}Z^2$ -arylene-O, $^{*-}Z^2$ -heteroarylene-O, $^{*-}Z^2$ - C_{1-20} alkylene-O, $^{*-}$ arylene-O, $^{*-}$ heteroarylene-

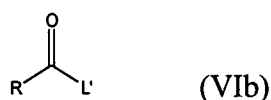
O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer;

and the process comprises:

(a) treating a first compound, Q', which is a polymer or a dendrimer and which bears at least n functional groups, with at least one second compound of formula (VIb)

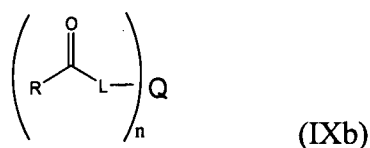


wherein:

L' is a leaving group or a reactive precursor to said group of formula (XII), wherein L' is reactable with a said functional group to couple the second compound to the first compound, and

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl,

thereby producing a third compound of formula (IXb):

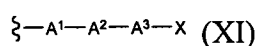


wherein Q, L, R and n are as defined above; and

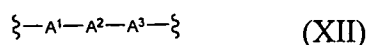
(b) treating the third compound with H₂N-N(H)S(O)₂R² in the presence of heat, wherein R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group, thereby producing said hydrazone compound of formula (XXXa).

The reaction conditions employed for step (a) depend on the particular standard coupling chemistry which is used to couple or react Q' with the leaving group or reactive precursor to said group of formula (XII), denoted L', in the compound of formula (VIb). The coupling chemistry employed will of course depend on the particular terminal functional groups of Q' and L' that are reacted together (which include functional groups of formulae $-A^4-X^2$ and $-A^3-X$ respectively, as defined hereinbefore) but standard coupling chemistry can be used. For instance, when Q' is a polymer which comprises aryl (e.g. phenyl or indenyl) substituents (such as polystyrene, or a block copolymer containing polystyrene or polyindene blocks), a compound of formula (VIb) in which L' is halo can be coupled to those phenyl ring substituents by a Friedel Crafts Acylation. Such a reaction is used in the synthesis of the tosyl hydrazone-functionalised polystyrene block copolymers in Example 3 hereinbelow. Alternatively, the coupling of the Q' functional groups to the L' group in the compound of formula (VIb) can be achieved by reaction between a triazine moiety derived from cyanuric chloride and a hydroxyl group; such a reaction is used in the synthesis of the triazine-linked diazomethane locust bean gum compound (6) in the Examples hereinbelow. Alternatively, a reaction between an alkyl halide moiety and a hydroxyl group may be employed, as is used in the synthesis of the ether-linked diazomethane locust bean gum compound (9) in the Examples hereinbelow. Alternatively, an esterification-type reaction may be employed, such as a standard esterification reaction between an -OH group and a carboxylic acid group, or a reaction between an -OH group and an activated carboxylic acid moiety such as an acyl halide or an acid anhydride moiety. Many other types of standard coupling reactions can however be employed, such as for instance the coupling of an amino group or a thiol group to a carboxylic acid or acyl halide group, or the reaction of a functional group with an alkene or an alkyne group. Such standard coupling reactions are well known in the art and are described, for instance, in "Advanced Organic Chemistry; Reactions, Mechanisms, and Structure", Jerry March, Fourth Edition, 1992, Wiley Interscience.

Typically, in the process of the invention for producing a functionalised compound, L' is a group of formula (XI)



and L is a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl;

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

and, in the group of formula (XI):

X is H, a halo group or a leaving group,

provided that when A³ is a single bond, *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene or S(O)₂, X is other than H and provided that when A³ is O, S, N(R''), -C(O)O-*, -C(O)N(R'')-* or -S(O)₂O-*, X is other than a halo group.

In one embodiment of the process of the invention for producing a functionalised compound, A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, C(O), S(O)₂, *-OC(O) and *-N(R'')C(O), wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²; and, in the group of formula (XI), X is halo or a leaving group.

In one embodiment, L is a single bond and L' is a leaving group. More typically, L' is halo. Even more typically, L' is chloro.

The groups L' react with the n functional groups of said first compound, Q'. As explained hereinbefore, typically, Q' has n functionalities $-A^4-X^2$ as defined herein, for instance an OH, NH, SH or aryl (typically phenyl) functionalities, that allow single step transformation to introduce the carbene precursor functionalities (or precursors thereof) onto Q. In one embodiment, all of said n functional groups are the same. Typically, when Q is a polymer or dendrimer, each $-A^4-X^2$ functionality is an aryl group.

Typically, in the process of the invention for producing a functionalised compound, both Q and Q' comprise a polymer or dendrimer, wherein the polymer is a linear polymer, a branched polymer, a hyperbranched polymer, a homopolymer, a copolymer or a block copolymer. The polymer may comprise a polysaccharide or a polyester or polystyrene, for instance.

In one embodiment, Q' is a polymer or a dendrimer which bears n functional groups which are n aryl or heteroaryl groups, and wherein Q is a polymer or dendrimer comprising n linker groups which are arylene or heteroarylene groups, wherein each of said arylene or heteroarylene groups is attached to L.

The present invention is particularly concerned with embodiments in which Q, within in the functionalised compound, is a block copolymer or dendrimer which comprises one or more "hard" thermoplastic polymer blocks, A, and one or more "soft" elastomeric polymer blocks, B, wherein the n carbene precursor groups defined herein of formula (Ie') are predominantly attached to one or more of the hard A blocks.

The inventors have found that such compounds may be synthesised by first reacting a compound of formula (VIb), as defined above, with a block copolymer or dendrimer Q' which comprises one or more thermoplastic polymer blocks, A, and one or more elastomeric polymer blocks, B, and n functional groups. Typically, the n functional groups are aryl groups, more typically phenyl groups or phenyl rings. Importantly, more than 50% (and typically more than 60%, more than 70%, more than 80% or more than 90%) of the n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A as opposed to the elastomeric blocks, B. Accordingly, when the compound of formula (VIb) reacts with the n functional groups of Q', the n carbene precursor groups defined herein of formula (Ie') are predominantly introduced into the hard "A" blocks.

Accordingly, in one embodiment of the process of the invention for producing a functionalised compound, Q and Q' comprise a block copolymer or dendrimer, which block copolymer or dendrimer comprises one or more linear or branched thermoplastic polymer

blocks, A, and one or more linear or branched elastomeric polymer blocks, B. Usually, more than 50% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

More typically, at least 60% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

Even more typically, at least 70% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

Even more typically, at least 80% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

Even more typically, at least 90% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

In one embodiment, each of said n functional groups of Q' is bonded to said one or more thermoplastic polymer blocks A.

In one embodiment, when L is a single bond and L' is a leaving group, said n functional groups of Q' are n aryl or heteroaryl rings, wherein Q comprises said n aryl or heteroaryl rings and wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring of Q, thereby bonding the aryl or heteroaryl ring directly to the carbon atom which is bonded to R.

In another embodiment, when L is a single bond and L' is a leaving group, Q' is a polymer and said n functional groups of Q' are n aryl rings, wherein Q is a polymer which comprises said n aryl rings and wherein each L which is single bond is attached directly to a said aryl ring of Q, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

In one embodiment, L is a single bond, L' is a leaving group, Q' is a polymer and said n functional groups of Q' are n aryl rings, and Q is a polymer which comprises said n aryl rings, wherein each L which is single bond is attached directly to a said aryl ring of Q, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

The block copolymer or dendrimer Q' which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B may be as further defined herein.

Typically, said n functional groups of Q' are aryl groups, preferably phenyl groups. Such groups are readily reacted with compounds of formula (VIb) in which L' is a leaving

group, for instance a halo group. In particular, acyl chloride compounds of formula (VIb) may react with the n aryl functional groups of Q' by Fridel-Crafts Acylation.

Accordingly, L' is usually a leaving group, for instance a halo group, and each L of the functionalised compound is a single bond. Typically, L' is a halo group, and is preferably a chloro group. Accordingly, the coupling reaction between Q' and the compound of formula (VIb) in step (a) as defined above is typically a Friedel-Crafts Acylation. Such a reaction is well known in the art and is described, for instance, in "Advanced Organic Chemistry; Reactions, Mechanisms, and Structure", Jerry March, Fourth Edition, 1992, Wiley Interscience. A synthesis Example is outlined hereinbelow in Example 3. Typically, the Friedel-Crafts Acylation is carried out in solution in the presence of aluminium trichloride.

Once the polymer or dendrimer Q' has been treated with the second compound of formula (VIb), then the process of the invention further comprises the step of converting the carbonyl to the carbene precursor functionality of formula (Ie'), i.e. the sulfonylhydrazone functionality. This involves converting a ketone compound, into a sulfonylhydrazone compound.

Conversion of the ketone compound into the corresponding hydrazone compound is achieved by treating the ketone compound with $\text{H}_2\text{N}-\text{N}(\text{H})\text{S}(\text{O})_2\text{R}^2$ in the presence of heat, wherein R^2 is as defined above. Typically, the ketone compound is treated with $\text{H}_2\text{N}-\text{N}(\text{H})\text{S}(\text{O})_2\text{R}^2$ in the presence of heat and a solvent. Any suitable solvent may be employed, for instance a polar protic solvent such as an alcohol (e.g. methanol, ethanol), or an aprotic solvent, for instance toluene. The reaction is carried out with heating, typically at the reflux temperature of the solvent used. For example, when the solvent is ethanol the reaction is suitably carried out at a temperature of 78 °C or higher, e.g. at a temperature of 80 °C.

Conversion of the hydrazone compound, in which Y is $\text{H}_2\text{N}-\text{N}(\text{H})\text{S}(\text{O})_2\text{R}^2$, into the corresponding diazomethane compound, in which Y is $\text{N}=\text{N}$, is achieved by elimination. The elimination is typically achieved by treating the sulfonylhydrazone compound with a basic compound such as an inorganic salt or a trialkylamine compound. Usually, the inorganic salt is lithium hydroxide, sodium hydroxide or potassium hydroxide. Usually, the trialkylamine compound is triethylamine. Typically, the treatment of the tosyl hydrazone compound with the trialkylamine compound is carried out in the presence of a solvent. The solvent used is suitably a polar protic solvent such as an alcohol, for instance methanol or water. The treatment can be carried out with the tosyl hydrazone compound either in phase

with the base, as a biphasic mixture or as a suspension of tosyl hydrazone compound in a basic solution.

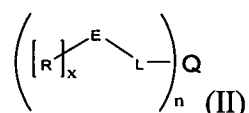
The block copolymer or dendrimer starting materials, Q', which comprise one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, are well known in the art. Such compounds are commercially available and/or obtainable by routine methods.

Block copolymers of formula $A_z-(B-A)_y-B_x$, having thermoplastic, aryl-containing "A" blocks as defined in formula (Xb) or (Xc) herein, and elastomeric "B" blocks comprising diolefin monomer units, can be synthesised as described in US 5,124,405, US 4,556,464, and WO 01/92344.

Furthermore, dendrimers and a radial block copolymers of formula (Xa) may be produced as described in US 5,446,104. Such polymers are made by coupling polymer arms using a polyfunctional coupling agent or coupling monomer. A preferred coupling agent is a polyalkenyl aromatic coupling agent such as those described in US 4,010,226, US 4,391,949 and US 4,444,953. US 5,104,921 contains a complete description of such polyalkenyl aromatic compounds at columns 12 and 13. Divinyl aromatic hydrocarbons containing up to 26 carbon atoms per molecule are preferred and particularly divinyl benzene in either its meta or para isomer and commercial divinyl benzene which is a mixture of said isomers is also quite satisfactory. The coupling agent is preferably added to the living polymer after the polymerization is substantially complete. The amount of coupling agent varies between wide limits but preferably at least one equivalent is used per equivalent of unsaturated living polymer. The coupling reaction is generally carried out in the same solvent as for the polymerization reaction. The temperature varies between wide limits, for example, from 25 to 90 °C.

Further aspects of the disclosure

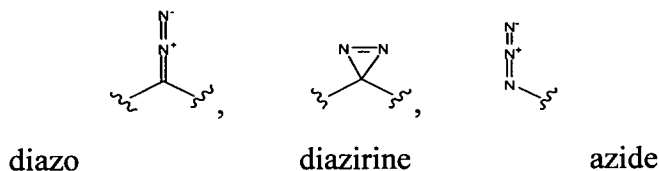
In a broader aspect, disclosed herein is a functionalised compound of formula (II), which functionalised compound comprises n reactive intermediate precursor groups which are the same or different, wherein n is an integer greater than or equal to 2:



wherein x is 0 or 1, L is a single bond or a linker group, R is a terminal group and E is a reactive intermediate precursor functionality, and wherein Q is a polymer or a dendrimer.

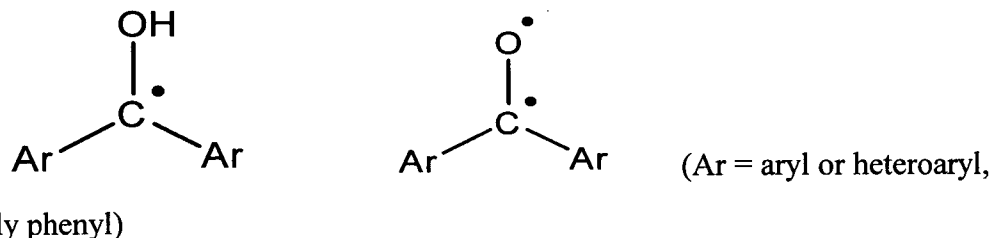
The term “reactive intermediate precursor functionality”, as used herein, means a latent reactive group which is capable of being converted into a reactive intermediate group by a chemical process or by the application of energy, wherein the reactive intermediate group is capable of further reaction. The “application of energy” may for instance involve the application of thermal energy (i.e. heating) or irradiation, although any suitable source of energy can be used.

Examples of reactive intermediate precursor functionalities, E, include, but are not limited to the following groups:

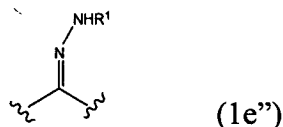


Thus, in one embodiment, E is a diazo, diazirine or azide group.

Diazo and diazirine groups are “carbene precursor groups”, i.e. are capable of conversion into carbene reactive intermediates, whereas azide groups are “nitrene precursor groups”, i.e. are capable of conversion into nitrene reactive intermediates. Carbonyl groups based around a benzophenone scaffold on the other hand are precursors which are capable of being converted into organic radical reactive intermediates, for instance into any of the following reactive intermediates:



A further example of a reactive intermediate precursor functionality, E, is a hydrazone group of formula (1e’):



wherein R¹ is H or –S(O)₂R², wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino.

Typically, R¹ is –S(O)₂R² wherein R² is phenyl substituted with C₁₋₆ alkyl. More typically, R¹ is –S(O)₂R² wherein R² is phenyl substituted with methyl (i.e. tolyl). Thus, in one embodiment, R¹ is a tosyl group. In another embodiment, R¹ is H.

Such hydrazone groups are “carbene precursor groups”, because they are capable of conversion into carbene reactive intermediates. When R^1 is H this conversion may be achieved by oxidation of the hydrazone to a diazomethane followed by the application of energy, typically by heating or by irradiation. When R^1 is $-S(O)_2R^2$ conversion of the N sulfonylhydrazone group into the carbene reactive intermediate is achieved by treatment with sulfonyl hydrazine with a base followed by the application of energy, typically by heating or by irradiation. The decomposition of the sulfonyl hydrazone to the carbene is thought to occur by elimination of R^1 , to form a diazo intermediate group, and subsequent elimination of dinitrogen to form the reactive carbene intermediate.

Accordingly, in one embodiment, E is a hydrazone group of formula (1e”) as defined above.

In another embodiment, E is a diazo group, diazirine group, azide group or a hydrazone group of formula (1e”) as defined above.

As the skilled person will appreciate, whether x is 0 or 1 depends on the valency of the atom to which L and, when present, R, are attached. When that atom is a carbon atom (as it is in diazo, diazirine and hydrazone groups), x is 1, whereas when that atom is nitrogen (as it is in azide groups), x is 0.

Typically, the reactive intermediate employed is a carbene reactive intermediate, a nitrene reactive intermediate or a benzophenone radical. Thus, typically, each of the reactive intermediate precursor functionalities, E, is selected from: a group which is capable of being converted into a carbene reactive intermediate group; a group which is capable of being converted into a nitrene reactive intermediate group; and a group which is capable of being converted into a benzophenone radical.

Typically, the n reactive intermediate precursor groups of formula (I) are selected from:

carbene precursor groups, wherein x, L and R are as defined above and E is a group which is capable of being converted into a carbene reactive intermediate group;

nitrene precursor groups, wherein x, L and R are as defined above and E is a group which is capable of being converted into a nitrene reactive intermediate group; and

benzophenone radical precursor groups, wherein x, L and R are as defined above and E is a group which is capable of being converted into a benzophenone radical.

More typically, the n reactive intermediate precursor groups of formula (I) are selected from:

carbene precursor groups, wherein x, L and R are as defined above and E is a group which is capable of being converted into a carbene reactive intermediate group;

nitrene precursor groups, wherein x, L and R are as defined above and E is a group which is capable of being converted into a nitrene reactive intermediate group; and

benzophenone radical precursor groups, wherein x is 1, L comprises an unsubstituted or substituted arylene group (typically an unsubstituted or substituted phenylene group) bonded to the carbonyl carbon atom, R is an unsubstituted or substituted aryl group (typically an unsubstituted or substituted phenyl group), and E is a carbonyl group or another group which is capable of being converted into a benzophenone radical.

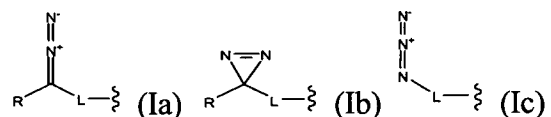
In another embodiment, the n reactive intermediate precursor groups are selected from:

carbene precursor groups, wherein x, L and R are as defined in claim 1 and E is a group which is capable of being converted into a carbene reactive intermediate group;

nitrene precursor groups, wherein x, L and R are as defined in claim 1 and E is a group which is capable of being converted into a nitrene reactive intermediate group; and

organic radical precursor groups, wherein x, L and R are as defined in claim 1 and E is a group which is capable of being converted into an organic radical.

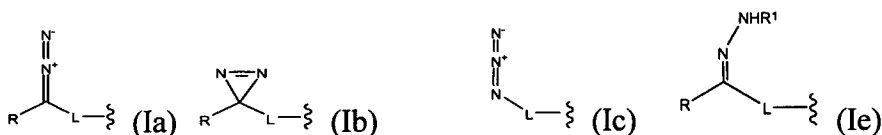
In one embodiment, the n reactive intermediate precursor groups of formula (I), which are the same or different, are selected from groups of the following formulae (Ia), (Ib) and (Ic):



wherein R and L are as defined above.

Typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia), diazirine groups of formula (Ib) or azide groups of formula (Ic). More typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia) or diazirine groups of formula (Ib). Even more typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia).

In another embodiment, the n reactive intermediate precursor groups of formula (I), which are the same or different, are selected from groups of the following formulae (Ia), (Ib), (Ic) and (Ie):



wherein R and L are as defined above and, in the group of formula (Ie), R^1 is H or $-\text{S}(\text{O})_2\text{R}^2$, wherein R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or $\text{di}(\text{C}_{1-6}$ alkyl)amino.

Typically, R^1 is $-\text{S}(\text{O})_2\text{R}^2$ wherein R^2 is phenyl substituted with C_{1-6} alkyl. More typically, R^1 is $-\text{S}(\text{O})_2\text{R}^2$ wherein R^2 is phenyl substituted with methyl (i.e. tolyl). Thus, in one embodiment, R^1 is a tosyl group. In another embodiment, R^1 is H.

Typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia), diazirine groups of formula (Ib), azide groups of formula (Ic), or hydrazone groups of formula (Ie). More typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia), diazirine groups of formula (Ib), or hydrazone groups of formula (Ie). Even more typically, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia) or hydrazone groups of formula (Ie). In one embodiment, the n reactive intermediate precursor groups of formula (I) are diazo groups of formula (Ia). In another embodiment, the n reactive intermediate precursor groups of formula (I) are hydrazone groups of formula (Ie).

The functionalised compound as defined above comprises n reactive intermediate precursor groups of formula (I) which are the same or different. Thus, although each of the n reactive intermediate precursor groups falls within the formula (I) definition, the reactive intermediate precursor functionalities, E, the linker groups (or single bonds) L, the integer x and/or the terminal groups R when present, may differ from one reactive intermediate precursor group to the next in the functionalised compound. For instance, the functionalised compound may comprise a first reactive intermediate precursor group of formula (I) and a second reactive intermediate precursor group of formula (I), wherein the reactive intermediate precursor functionalities, E, the linker groups (or single bonds) L, the integer x and/or the terminal groups R are different in the first and second reactive intermediate precursor groups. Typically, however, E is the same reactive intermediate precursor functionality in all of the precursor groups in the functionalised compound. Similarly, L is typically the same in all of the precursor groups in the functionalised compound. Similarly, R is typically the same terminal group in all of the precursor groups in the compound, and/or x is the same integer in all of those groups.

The number of reactive intermediate precursor groups in the functionalised compound, n , is an integer equal to or greater than 2.

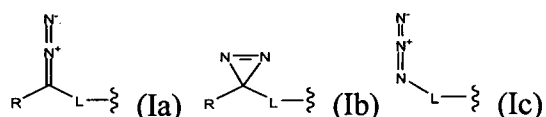
Typically, however, n is greater than or equal to 3. In another embodiment, n is greater than or equal to 4.

In one embodiment, n is an integer of from 2 to 50 or from 3 to 50, more typically an integer of from 2 to 20, from 2 to 10, from 3 to 20, or from 3 to 10, or an integer of 2, 3, 4 or 5.

In another embodiment, however, n is an integer of from 2 to 500, or from 3 to 500, and is more typically an integer of from 2 to 200, from 3 to 200, from 2 to 100, from 3 to 100, or from 10 to 100, for instance from 10 to 50.

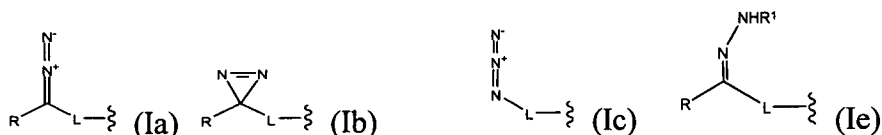
In yet another embodiment, n is an integer equal to or greater than 50, for instance equal to or greater than 100. Thus, n may be an integer of from 50 to 1,000,000, from 50 to 100,000, from 50 to 10,000, from 50 to 5,000, or from 50 to 1,000. More typically, in this embodiment, n is an integer of from 50 to 1,000.

The reactive intermediate precursor functionalities, E , the linker groups (or single bonds) L , the terminal groups R , and the integer x may differ from one reactive intermediate precursor group to the next in the functionalised compound, but are typically the same. Typically, each of the n reactive intermediate precursor functionalities, E , which are the same or different, is independently selected from: a group which is capable of being converted into a carbene reactive intermediate group; a group which is capable of being converted into a nitrene reactive intermediate group; and a group which is capable of being converted into an organic radical. In one embodiment, each of the $[R]_x-E-L$ groups in the functionalised compound of formula (II), which are the same or different, are independently selected from groups of the following formulae (Ia), (Ib) and (Ic):



wherein R and L are as defined above.

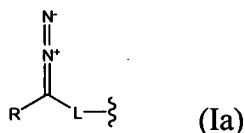
In one embodiment, each of the $[R]_x-E-L$ groups in the functionalised compound of formula (II), which are the same or different, are selected from groups of the following formulae (Ia), (Ib), (Ic) and (Ie):



wherein R and L are as defined above and, in the group of formula (Ie), R¹ is H or -S(O)₂R², wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino.

Typically, the [R]_x-E-L- groups in the functionalised compound of formula (II) are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib), azide groups of formula (Ic) and hydrazone groups of formula (Ie). In another embodiment, the [R]_x-E-L- groups in the functionalised compound of formula (II) are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib) and azide groups of formula (Ic). More typically, the [R]_x-E-L- groups in the functionalised compound of formula (II) are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib) and hydrazone groups of formula (Ie). In another embodiment, the [R]_x-E-L- groups in the functionalised compound of formula (II) are selected from diazo groups of formula (Ia) and diazirine groups of formula (Ib). In one embodiment, the [R]_x-E-L- groups in the functionalised compound of formula (II) are diazo groups of formula (Ia). In another embodiment, the [R]_x-E-L- groups in the functionalised compound of formula (II) are hydrazone groups of formula (Ie).

Accordingly, disclosed herein is a diazo-functionalised compound, which diazo-functionalised compound comprises n carbene precursor groups of formula (Ia) which are the same or different, wherein n is an integer equal to or greater than 2 (but may be as further defined herein):

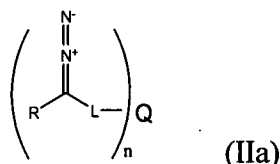


wherein L is a single bond or a linker group and R is a terminal group.

The diazo-functionalised compound defined above comprises n carbene precursor groups of formula (I) which are the same or different. Thus, although each of the n carbene precursor groups falls within the formula (I) definition, the linker groups (or single bonds) L, and/or the terminal groups R, may differ from one carbene precursor group to the next in the diazo-functionalised compound. For instance, the diazo-functionalised compound may comprise a first carbene precursor group of formula (I) and a second carbene precursor group of formula (I), wherein the terminal groups R and/or the linker groups (or single bonds) L are different in the first and second carbene precursor groups. Typically, however, L is the same in all of the carbene precursor groups in the diazo-functionalised

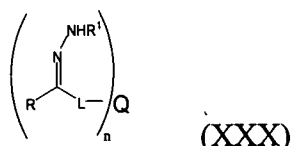
compound. Similarly, R is typically the same terminal group in all of the carbene precursor groups in the compound.

The diazo-functionalised compound is a compound of formula (IIa)



wherein n is an integer equal to or greater than 2 (but may be as further defined herein); L is a single bond or a linker group; R is a terminal group; and Q is polymer or a dendrimer. Again, the linker groups (or single bonds) L, and the terminal groups R, may differ from one carbene precursor group to the next in the diazo-functionalised compound, but are typically the same.

In another embodiment, the functionalised compound is a hydrazone compound of formula (XXX)



wherein:

n is an integer equal to or greater than 2;

each L, which is the same or different, is a single bond or a linker group;

each R, which is the same or different, is a terminal group;

R¹ is H or -S(O)₂R², wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino; and Q is a polymer or a dendrimer.

Typically, R¹ is -S(O)₂R² wherein R² is phenyl substituted with C₁₋₆ alkyl. More typically, R¹ is -S(O)₂R² wherein R² is phenyl substituted with methyl (i.e. tolyl). Thus, in one embodiment, R¹ is a tosyl group. In another embodiment, R¹ is H.

each R group is typically selected from hydrogen, aryl, heteroaryl, C₁₋₂₀ perfluoroalkyl, C₁₋₁₀ alkoxy, aryloxy, di(C₁₋₁₀)alkylamino, alkylarylamino, diarylamino, C₁₋₁₀ alkylthio, arylthio and CR'₃, wherein each R' is independently selected from a halogen atom, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, heteroaryl, C₃₋₂₀ carbocyclyl, C₃₋₂₀ heterocyclyl, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl, triarylsilyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl and C₁₋₂₀ alkyl, which C₁₋₂₀ alkyl and

C₁₋₂₀ perfluoroalkyl are optionally interrupted by N(R''), O, S or arylene wherein R'' is H, C₁₋₆ alkyl or aryl;

provided that when R is aryl or heteroaryl said aryl or heteroaryl may be unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

More typically, R is phenyl which is unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

Each L, which may be the same or different, may be a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R (or to the nitrene nitrogen atom when E is a nitrene precursor group, such as an azide), wherein A¹ is a single bond or an unsubstituted or substituted group selected from arylene, heteroarylene, C₁₋₂₀ perfluoroalkylene, *-O-C₁₋₂₀ alkylene, *-O-C₁₋₂₀ perfluoroalkylene, *-O-arylene, *-O-heteroarylene, *-N(R'')-C₁₋₂₀ alkylene, *-N(R'')-C₁₋₂₀ perfluoroalkylene, *-N(R'')-arylene, *-N(R'')-heteroarylene, *-S-C₁₋₂₀ alkylene, *-S-C₁₋₂₀ perfluoroalkylene, *-S-arylene, *-S-heteroarylene, *-C(R')₂-C₁₋₂₀ alkylene, *-C(R')₂-C₁₋₂₀ perfluoroalkylene, *-C(R')₂-arylene, *-C(R')₂-heteroarylene and C₁₋₂₀ alkylene, wherein each R' is independently selected from a halogen atom, C₁₋₁₀ haloalkyl, C₁₋₁₀ fluoroalkyl, C₁₋₁₀ perfluoroalkyl, aryl, heteroaryl, C₃₋₁₀ carbocyclyl, C₃₋₁₀ heterocyclyl, tri(C₁₋₁₀ alkyl)silyl, aryldi(C₁₋₁₀ alkyl)silyl, diaryl(C₁₋₁₀ alkyl)silyl, triarylsilyl, C₂₋₁₀ alkenyl, C₂₋₁₀ alkynyl and C₁₋₁₀ alkyl, wherein * is the point of

attachment of A^1 to the carbon atom bonded to R, wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by $N(R'')$, O, S or arylene, and wherein R'' is H, C_{1-6} alkyl or aryl;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O) $_2$, $N(R'')$, C(O)O, OC(O), C(O) $N(R'')$ and $N(R'')$ C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by $N(R'')$, O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2-C_{1-20}$ alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2-C_{1-20}$ alkylene-O, * -arylene-O, * -heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O) $_2$, $^*-OC(O)$, $^*-N(R'')$ C(O), O, S, $N(R'')$, $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2-C_{1-20}$ alkenylene and $^*-Z^2-C_{1-20}$ alkynylene, wherein Z^2 is selected from O, S, $N(R'')$, C(O), S(O), S(O) $_2$, C(O)O, OC(O), C(O) $N(R'')$ and $N(R'')$ C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 .

Typically, however A^1 is a single bond.

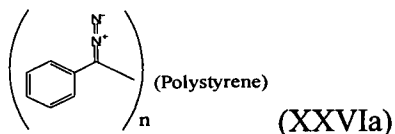
In one embodiment A^1 , A^2 and A^3 are all single bonds, which means that L is itself a single bond. Thus, in some embodiments, L is a single bond and each of the reactive intermediate precursor functionalities, E, is bonded directly to Q.

In one embodiment, of the broader aspect, the functionalised compound is of formula (XXIIIa)



wherein Q and n are as defined hereinbefore. Typically in this embodiment, Q is a polymer or dendrimer bearing aryl or heteroaryl groups, more typically phenyl groups, wherein the carbon atom of the diazomethane group is bonded directly to said aryl or heteroaryl groups. More typically, in this embodiment, Q is polystyrene. Typically, the carbon atoms of the diazomethane groups are bonded to phenyl groups of said polystyrene.

In another embodiment of this broad aspect, the functionalised compound is a compound of formula (XXVIa)



wherein n is an integer equal to or greater than 50.

The functionalised compounds of the broader aspects of the invention as defined above may be as further defined herein for the functionalised compounds of the invention.

Embodiments are disclosed in which Q , within the functionalised compound, is a block copolymer or dendrimer which comprises one or more “hard” polymer blocks, A , and one or more “soft” polymer blocks, B , wherein the n reactive intermediate precursor groups defined herein, $[R]_x-E-L-$, are predominantly attached to one or more of the hard blocks. Thus, the majority of the n reactive intermediate precursor groups, $[R]_x-E-L-$, present in the functionalised compound may be bonded to the one or more thermoplastic polymer blocks A . In other words, typically, more than 50% of said n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to said one or more thermoplastic polymer blocks A . More typically, at least 60% of said n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to said one or more thermoplastic polymer blocks A . Even more typically, at least 70% of said n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to said one or more thermoplastic polymer blocks A . Even more typically, at least 80% of said n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to said one or more thermoplastic polymer blocks A . Even more typically, at least 90% of said n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to said one or more thermoplastic polymer blocks A . Even more typically, each of said n reactive intermediate precursor groups, $[R]_x-E-L-$, is bonded to said one or more thermoplastic polymer blocks A .

Typically, each of the reactive intermediate precursor groups $[R]_x-E-L-$ which is bonded to said one or more blocks A , is bonded to a group Ar in a unit of formula (Xb) as defined herein.

Typically, each of the reactive intermediate precursor groups $[R]_x-E-L-$ which is bonded to said one or more blocks A , is bonded to a group Ar^1 in a unit of formula (Xc) as defined herein.

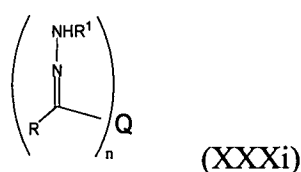
In one embodiment, Q is selected from poly(styrene)-poly(butadiene)-poly(styrene) (SBS), poly(styrene)-poly(isoprene)-poly(styrene) (SIS), poly(styrene)-poly(butadiene/isoprene)-poly(styrene) (SIBS), poly(styrene)-poly(ethylene/butylene)-

poly(styrene) (SEBS), poly(styrene)-poly(ethylene/propylene)-poly(styrene) (SEPS), and poly(styrene)-poly(ethylene/ethylene/propylene)-poly(styrene) (SEEPS). Such polymers are commercially available, for instance from Kraton. Typically, in this embodiment, the majority of the n reactive intermediate precursor groups, $[R]_x-E-L-$, are bonded to the poly(styrene) "A" blocks. More typically, at least 60% of said n reactive intermediate precursor groups are bonded to the poly(styrene) blocks. Even more typically, at least 70% of said n reactive intermediate precursor groups are bonded to the poly(styrene) blocks. Even more typically, each of said n reactive intermediate precursor groups is bonded to the poly(styrene) blocks.

Typically, when Q is a block copolymer or dendrimer as defined above, which comprises one or more linear or branched thermoplastic polymer blocks, A , and one or more linear or branched elastomeric polymer blocks, B , the n reactive intermediate precursor groups, $[R]_x-E-L-$, are hydrazone groups of formula (Ie). Such hydrazone groups are advantageous because they are capable of being converted into a carbene reactive intermediate group, yet they are generally more stable than the diazo groups of formula (Ia).

Furthermore, L is usually a single bond in this embodiment, and therefore each hydrazone group of formula (Ie) is bonded directly to Q .

Accordingly, in one embodiment, the functionalised compound of the invention is a compound of formula (XXXi) which comprises n reactive intermediate precursor groups which are hydrazone groups:



wherein:

n is an integer equal to or greater than 2;

each R , which is the same or different, is a terminal group;

R^1 is H or $-S(O)_2R^2$, wherein R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or di(C_{1-6} alkyl)amino; and

Q is a block copolymer or dendrimer, which block copolymer or dendrimer comprises one or more linear or branched thermoplastic polymer blocks, A , which are the same or different, and one or more linear or branched elastomeric polymer blocks, B , which are the same or different,

wherein more than 50% of said n hydrazone groups, $(R)(R^1HN-N=)C-$, are bonded to said one or more linear or branched thermoplastic polymer blocks A.

Typically, in this embodiment, more than 80% of said n hydrazone groups, $(R)(R^1HN-N=)C-$, are bonded to said one or more linear or branched thermoplastic polymer blocks A. Typically, R is an unsubstituted or substituted aryl group. More typically, R is an unsubstituted or substituted phenyl group. Even more typically, R is nitro-substituted phenyl. Typically, R^1 is tosyl. The blocks A and B may be as further defined herein. Typically, however, Q is selected from poly(styrene)-poly(butadiene)-poly(styrene) (SBS), poly(styrene)-poly(isoprene)-poly(styrene) (SIS), poly(styrene)-poly(butadiene/isoprene)-poly(styrene) (SIBS), poly(styrene)-poly(ethylene/butylene)-poly(styrene) (SEBS), poly(styrene)-poly(ethylene/propylene)-poly(styrene) (SEPS), and poly(styrene)-poly(ethylene/ethylene/propylene)-poly(styrene) (SEEPS).

Typically the number of hydrazone groups bonded to the polymer, Q, is from 0.5 % to 100 % of the number of aryl or heteroaryl groups on the polymer backbone of Q. More typically the number of hydrazone groups bonded to the polymer Q is from 0.5 % to 50 % of the number aryl or heteroaryl groups on the backbone of polymer Q.

More generally, when Q, in the functionalised compounds of the invention, comprises a polymer whose backbone bears aryl or heteroaryl groups, wherein the reactive intermediate precursor groups are attached to the polymer or dendrimer via such aryl or heteroaryl groups, the number of reactive intermediate precursor groups, n , is typically from 0.5 % to 100 % of the number of said aryl or heteroaryl groups in Q. More typically, the number of reactive intermediate precursor groups, n , is from 0.5 % to 50 % of the number of said aryl or heteroaryl groups in Q. Typically, therefore, not all of the aryl or heteroaryl groups on the polymer backbone within Q bear a reactive intermediate precursor group.

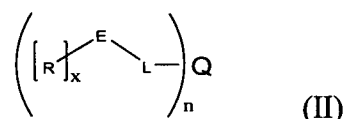
The multiple reactive intermediate precursor groups of the functionalised compounds of the invention can be readily converted into reactive intermediate groups, which can in turn react with and bond to a wide variety of substrates, including individual molecules and bulk materials.

The reactive intermediate groups are typically generated by a thermal process and/or by an irradiation process, but can be generated chemically. Typically, the reactive intermediate groups are generated by thermal irradiation, for instance by heating, especially when the groups are diazo groups and the reactive intermediate is a carbene reactive

intermediate. This heat might be applied to the functionalised compound externally, but may also be as a result of another process, for example, extrusion. Alternatively, the reactive intermediate groups may be generated by electromagnetic radiation, for instance by UV, microwave or laser irradiation, or by ultrasonic irradiation.

Thus, in another broad aspect, disclosed herein is a process for cross linking a first substrate to a second substrate, which first and second substrates are the same or different, which process comprises

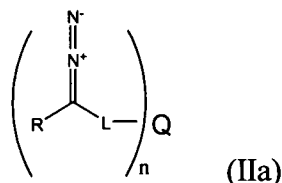
(a) contacting the first and second substrates with a functionalised cross linking compound of formula (II), which functionalised cross linking compound comprises n reactive intermediate precursor groups which are the same or different, wherein n is an integer greater than or equal to 2:



wherein x is 0 or 1, L is a single bond or a linker group, R is a terminal group and E is a reactive intermediate precursor functionality, and wherein Q is a polymer or a dendrimer; and

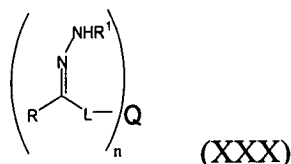
(b) generating reactive intermediate groups from said reactive intermediate precursor groups, so that at least one reactive intermediate group reacts with the first substrate and at least one other reactive intermediate group reacts with the second substrate, thereby cross linking the first and second substrates.

In one embodiment, the functionalised cross linking compound used in the process of the invention for cross linking or adhering a first substrate to a second substrate is a diazo-functionalised compound of formula (IIa)



wherein n is an integer equal to or greater than 2; L is a single bond or a linker group; R is a terminal group; and Q is a polymer or a dendrimer.

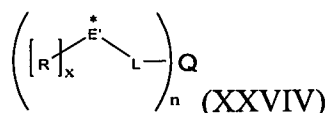
In another embodiment, the functionalised cross linking compound used in the process of the invention for cross linking or adhering a first substrate to a second substrate is a hydrazone-functionalised compound of formula (XXX)



wherein n is an integer greater than or equal to 2; each L, which is the same or different, is a single bond or a linker group; each R, which is the same or different, is a terminal group; R¹ is H or -S(O)₂R², wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino; and Q is a polymer or a dendrimer.

In another broad aspect, disclosed is a cross-linked product comprising:

- (a) a first substrate;
- (b) a second substrate; and
- (c) a cross linking moiety of formula (XXVIV)



wherein

the first and second substrates are the same or different,

E' is a carbon or nitrogen atom;

each * is a point of attachment of the cross linking moiety to the first substrate, the second substrate or to another moiety or molecule;

n is an integer equal to or greater than 2;

x is 1 when E' is carbon and x is 0 when E' is nitrogen;

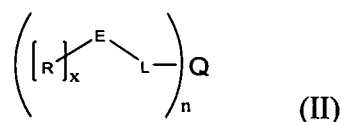
each L, which is the same or different, is a single bond or a linker group;

each R, which is the same or different, is a terminal group; and

Q is a polymer or a dendrimer.

In one embodiment of the cross-linked product of the invention, Q is a block copolymer or dendrimer as defined herein which comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n [R]_x-E'-L-groups are bonded (via L) to said one or more thermoplastic polymer blocks A.

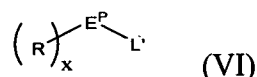
In another broad aspect, provided herein is a process for producing a functionalised compound of formula (II), which functionalised compound comprises n reactive intermediate precursor groups which are the same or different, wherein n is an integer greater than or equal to 2:



wherein x is 0 or 1, L is a single bond or a linker group, R is a terminal group and E is a reactive intermediate precursor functionality, and wherein Q is a polymer or a dendrimer,

the process comprising:

(a) treating a first compound, Q' , which is a polymer or a dendrimer and which bears n functional groups, with at least one second compound of formula (VI)

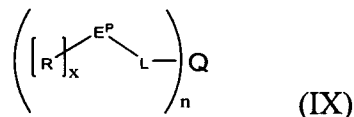


wherein:

L' is a leaving group or a reactive precursor to said linker group, wherein L' is reactable with a said functional group to couple the second compound to the first compound,

R is said terminal group and x is 0 or 1, and

E^{P} is said reactive intermediate precursor functionality E or a precursor thereto, thereby producing a third compound which is of formula (IX):



wherein L is said single bond or linker group, R is said terminal group, x is 0 or 1, and E^{P} is as defined above, which third compound is said functionalised compound of formula (II) when E^{P} is said reactive intermediate precursor functionality E ; provided that:

when E^{P} is a precursor to said reactive intermediate precursor functionality E , the process further comprises:

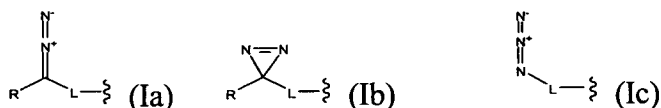
(b) converting the E^{P} groups of said third compound into reactive intermediate precursor groups, E , thereby producing said functionalised compound of formula (II).

Typically, the first compound, Q' , which bears at least n functional groups (or n functional groups, in one embodiment) is treated with at least n equivalents of the at least one second compound of formula (VI). As the skilled person will appreciate, however, functionalised compounds which comprise n reactive intermediate precursor groups of formula (I) all of which are the same can be synthesised by treating said first compound with at least n equivalents of a single second compound of formula (VI). In contrast,

functionalised compounds which comprise n reactive intermediate precursor groups of formula (I) not all of which are the same can be synthesised by treating said first compound with more than one type of second compound of formula (VI). For instance, the first compound which bears at least n functional groups (or n functional groups, in one embodiment) can be treated with less than n equivalents of one compound of formula (VI) and with less than n equivalents of another compound of formula (VI), provided that the total number of equivalents of the compounds of formula (VI) is at least n , to produce a functionalised compound of the invention comprising two different types of reactive intermediate precursor groups of formula (I).

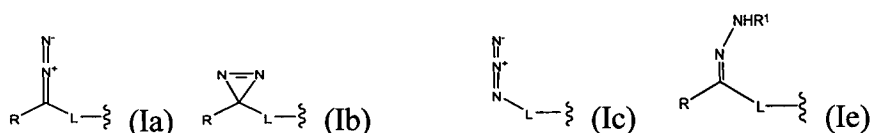
Typically, each of the n reactive intermediate precursor functionalities, E, which are the same or different, is independently selected from: a group which is capable of being converted into a carbene reactive intermediate group; a group which is capable of being converted into a nitrene reactive intermediate group; and a group which is capable of being converted into an organic radical.

In one embodiment, each of the $[R]_x-E-L$ groups in the functionalised compound of formula (II), which are the same or different, are independently selected from groups of the following formula (Ia), (Ib) and (Ic):



wherein R and L are as defined above.

In another embodiment, each of the $[R]_x-E-L$ groups in the functionalised compound of formula (II), which are the same or different, are independently selected from groups of the following formula (Ia), (Ib), (Ic) and (Ie):



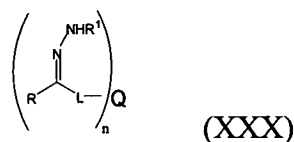
wherein R and L are as defined above and, in the group of formula (Ie), R^1 is H or $-\text{S}(\text{O})_2R^2$, wherein R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or $\text{di}(C_{1-6}$ alkyl)amino.

Typically, the $[R]_x-E-L$ groups in the functionalised compound of the invention of formula (II) are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib) and azide groups of formula (Ic). More typically, the $[R]_x-E-L$ groups in the

functionalised compound of formula (II) are selected from diazo groups of formula (Ia) and diazirine groups of formula (Ib).

In another embodiment, the $[R]_x$ -E-L- groups in the functionalised compound of the invention of formula (II) are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib), azide groups of formula (Ic), and hydrazone groups of formula (Ie). More typically, the $[R]_x$ -E-L- groups are selected from diazo groups of formula (Ia), diazirine groups of formula (Ib), and hydrazone groups of formula (Ie). Even more typically, the $[R]_x$ -E-L- groups are selected from diazo groups of formula (Ia) or hydrazone groups of formula (Ie). In one embodiment, the $[R]_x$ -E-L- groups are diazo groups of formula (Ia). In another embodiment, the $[R]_x$ -E-L- groups are hydrazone groups of formula (Ie).

Thus, in one embodiment, the hydrazone-functionalised compound produced by the process of the invention is a compound of formula (XXX)



wherein:

n is an integer greater than or equal to 2;

each L, which is the same or different, is a single bond or a linker group;

each R_i , which is the same or different, is a terminal group;

R¹ is H or -S(O)₂R², wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino; and

Q is a polymer or a dendrimer;

and the process comprises:

(a) treating a first compound, Q', which is a polymer or a dendrimer and which bears at least n functional groups, with at least one second compound of formula (VIb)



wherein:

L' is a leaving group or a reactive precursor to said linker group, wherein L' is reactable with a said functional group to couple the second compound to the first compound, and

R is said terminal group,

thereby producing a third compound of formula (IXb):

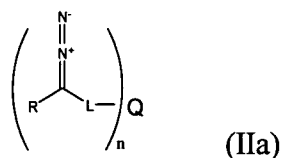


wherein Q, L, R and n are as defined above; and

(b) treating the third compound with $\text{H}_2\text{N}-\text{NHR}^1$ in the presence of heat, wherein R^1 is H or $-\text{S}(\text{O})_2\text{R}^2$ and wherein R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or $\text{di}(\text{C}_{1-6}$ alkyl)amino, thereby producing said hydrazone compound of formula (XXX).

In another embodiment, the $[\text{R}]_x\text{-E-L-}$ groups in the functionalised compound of the invention of formula (II) are diazo groups of formula (Ia).

Thus, in one embodiment, the diazo-functionalised compound produced by the process of the invention is a compound of formula (IIa)



wherein:

n is an integer equal to or greater than 2;

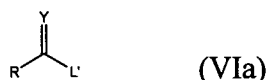
each L is a single bond or a linker group;

each R is a terminal group; and

Q is a polymer or a dendrimer;

and the process comprises:

(a) treating a first compound, Q', which is a polymer or a dendrimer and which bears n functional groups, with at least one second compound of formula (VIa)



wherein:

L' is a leaving group or a reactive precursor to said linker group, wherein L' is reactable with a said functional group to couple the second compound to the first compound,

R is said terminal group, and

Y is $\text{N}=\text{N}$, O or $\text{N}-\text{NHR}^1$, wherein R^1 is H or $-\text{S}(\text{O})_2\text{R}^2$ and wherein R^2 is C_{1-6} alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C_{1-6} alkyl or $\text{di}(\text{C}_{1-6}$ alkyl)amino,

thereby producing a third compound of formula (IXa):



wherein Q, L, R, Y and n are as defined above, which third compound is said diazo-functionalised compound when Y is N=N;

provided that:

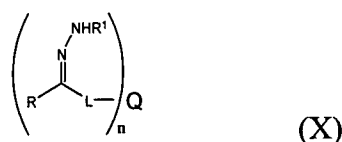
- when Y is N-NHR¹, the process further comprises:

(b) converting the Y groups of said third compound, by oxidation or elimination, into diazo groups, thereby producing said diazo-functionalised compound of formula (IIa); and

provided that:

- when Y is O, the process further comprises:

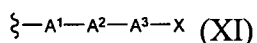
(b) treating the third compound with H₂N-NHR¹ in the presence of heat, wherein R¹ is as defined above, thereby producing a fourth compound of formula (X):



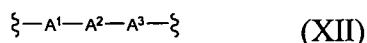
wherein Q, L, R, R¹ and n are as defined above; and

(c) converting the N-NHR¹ groups of said fourth compound, by oxidation or elimination, into diazo groups, thereby producing said diazo-functionalised compound of formula (IIa).

Typically, in the process for producing a functionalised compound, L' is a group of formula (XI)



and L is a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is a single bond or an unsubstituted or substituted group selected from arylene, heteroarylene, C₁₋₂₀ perfluoroalkylene, *-O-C₁₋₂₀ alkylene, *-O-C₁₋₂₀ perfluoroalkylene, *-O-arylene, *-O-heteroarylene, *-N(R'')-C₁₋₂₀ alkylene, *-N(R'')-C₁₋₂₀ perfluoroalkylene, *-N(R'')-arylene, *-N(R'')-heteroarylene, *-S-C₁₋₂₀ alkylene, *-S-C₁₋₂₀ perfluoroalkylene, *-S-arylene, *-S-heteroarylene, *-C(R')₂-C₁₋₂₀ alkylene, *-C(R')₂-C₁₋₂₀ perfluoroalkylene, *-C(R')₂-arylene, *-C(R')₂-heteroarylene and C₁₋₂₀ alkylene, wherein each R' is independently selected from a halogen atom, C₁₋₁₀ haloalkyl, C₁₋₁₀ fluoroalkyl, C₁₋₁₀ perfluoroalkyl, aryl, heteroaryl,

C₃₋₁₀ carbocyclyl, C₃₋₁₀ heterocyclyl, tri(C₁₋₁₀ alkyl)silyl, aryldi(C₁₋₁₀ alkyl)silyl, diaryl(C₁₋₁₀ alkyl)silyl, triarylsilyl, C₂₋₁₀ alkenyl, C₂₋₁₀ alkynyl and C₁₋₁₀ alkyl, wherein * is the point of attachment of A¹ to the carbon atom bonded to R, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein R'' is H, C₁₋₆ alkyl or aryl;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl;

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

and, in the group of formula (XI):

X is H, a halo group or a leaving group,

provided that when A³ is a single bond, *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene or S(O)₂, X is other than H and provided that when A³ is O, S, N(R''), -C(O)O-*, -C(O)N(R'')-* or -S(O)₂O-*, X is other than a halo group.

In one embodiment of the process, A¹, A² and A³ are a single bond and, therefore, L is a single bond and L' is X. Typically, L' is halo or a leaving group. More typically, L' is halo. Even more typically, L' is chloro.

Once the polymer or dendrimer Q' has been treated with the second compound of formula (VI), (VIa) or (VIb), then depending on the nature of E^P / Y, the process of the invention may further comprise the step(s) of converting the precursor E^P to the reactive intermediate precursor functionality, E. This may involve converting a ketone compound,

in the case where Y in formula (VIa) or (VIb) is O, into a hydrazone compound, and optionally converting the resulting hydrazone compound, when Y is N-NHR¹ into the corresponding diazo compound. Thus, in the process of the invention for producing a hydrazone compound of formula (XXX), the process may further comprise the step of converting the ketone compound of formula (IXb) into the corresponding hydrazone compound.

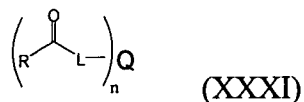
Conversion of the ketone compound into the corresponding hydrazone compound is achieved by treating the ketone compound with H₂N-NHR¹ in the presence of heat, wherein R¹ is as defined above. Typically, the ketone compound is treated with H₂N-NHR¹ in the presence of heat and a solvent. Any suitable solvent may be employed, for instance a polar protic solvent such as an alcohol (e.g. methanol, ethanol), or an aprotic solvent, for instance toluene. The reaction is carried out with heating, typically at the reflux temperature of the solvent used. For example, when the solvent is ethanol the reaction is suitably carried out at a temperature of 78 °C or higher, e.g. at a temperature of 80 °C.

Conversion of the hydrazone compound, in which Y is N-NHR¹, into the corresponding diazomethane compound, in which Y is N=N, is achieved by oxidation or elimination. In the cases where R¹ is -S(O)₂R², wherein R² is as defined above, an elimination reaction is performed. The elimination is typically achieved by treating the hydrazone compound with a basic compound such as an inorganic salt or a trialkylamine compound. Usually, the inorganic salt is lithium hydroxide, sodium hydroxide or potassium hydroxide. Usually, the trialkylamine compound is triethylamine. Typically, the treatment of the tosyl hydrazone compound with the trialkylamine compound is carried out in the presence of a solvent. The solvent used is suitably a polar protic solvent such as an alcohol, for instance methanol or water. The treatment can be carried out with the tosyl hydrazone compound either in phase with the base, as a biphasic mixture or as a suspension of tosyl hydrazone compound in a basic solution.

In the case where R¹ is H, an oxidation reaction is performed. Any suitable oxidant can be used to convert the hydrazone compound, in which Y is N-NH₂, into the corresponding diazomethane compound. Suitable oxidants include metal oxides, such as mercuric oxide, nickel peroxide, or hydrogen peroxide or chlorine (bleach). Typically, the oxidant is manganese oxide. More typically, this oxidation is conducted in the presence of a base, for instance a metal hydroxide and sodium sulphate. The metal hydroxide is typically an alkali metal hydroxide, for instance potassium hydroxide. A saturated solution

of the metal hydroxide is generally used. The solvent used for the metal hydroxide is suitably a polar protic solvent such as an alcohol, for instance ethanol. The solvent used for the solution of the hydrazone compound is suitably a polar aprotic solvent, for instance tetrahydrofuran (THF) or an ether.

In another broad aspect, disclosed herein is a ketone compound of formula (XXXI)



wherein:

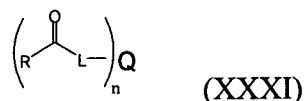
n is an integer equal to or greater than 2;

each L, which is the same or different, is a single bond or a linker group;

each R, which is the same or different, is a terminal group; and

Q is a polymer or a dendrimer.

In one embodiment of the ketone compound of formula (XXXI)



R, L, Q and n are as further defined hereinbefore.

The invention is further described in the following Examples:

EXAMPLES

All block co-polymers were obtained from Kraton.

Example 1: Diazo Modification of a hydrophilic polymer system

Route 1 – Synthesis of triazine linked tosyl hydrazone locust bean gum, with reference to Figure 2

Synthesis of 4-methyl-4'-nitrobenzophenone (1)

4-Nitrobenzoyl chloride (5.00 g, 26.0 mmol, 1 eq) was suspended in toluene (10 mL) and the cloudy yellow mixture was cooled to 0°C in an ice/water bath. Aluminium trichloride (4.50 g, 33.7 mmol, 1.25 eq) was added portionwise over a period of 20 min and the mixture was allowed to warm to room temperature. After stirring at room temperature for 2 hr HPLC indicated that the starting material had been consumed. The reaction was quenched by pouring onto an ice/1 M HCl solution where the product precipitated out as a yellow solid. The aqueous mixture was extracted with ethyl acetate (3×50 mL). The organic washings were dried over magnesium sulfate and concentrated under reduced pressure to give a yellow solid. The yellow solid was recrystallised from 2-propanol to give 4-methyl-4'-nitrobenzophenone (4.05 g, 62% yield) as a yellow crystalline solid.

Synthesis of 4-bromomethyl-4'-nitrobenzophenone (2)

4-Methyl-4'-nitrobenzophenone (46.80 g, 194.0 mmol, 1 eq) was dissolved in chloroform (400 mL) giving a pale yellow solution. *N*-Bromosuccinimide (69.10 g, 388.0 mmol, 2.0 eq) was then added portionwise over 5 min turning the solution cloudy. The mixture was heated to reflux and stirred for 7 hr and allowed to cool. The mixture was left to stand for 18 hr and then heated under reflux for a further 3 hr. After this time HPLC indicated that most of the starting material had been consumed and the 4-dibromomethyl-4'-nitrobenzophenone was forming as a side product. The reaction mixture was cooled, washed with saturated sodium thiosulfate solution (2×200 mL) and dried over magnesium sulfate. The solution was concentrated under reduced pressure to give a beige solid. The

solid was recrystallised from 30% petroleum ether/ethyl acetate to give 4-bromomethyl-4'-nitrobenzophenone (26.25 g, 42%)

Synthesis of 4-hydroxymethyl-4'-nitrobenzophenone (3)

4-bromomethyl-4'-nitrobenzophenone (3.20 g, 10.0 mmol, 1 eq) was dissolved in a 2:1 acetonitrile/water mixture (300 mL) and calcium carbonate (3.00 g, 30.0 mmol, 3 eq) was added. The turbid mixture was stirred under reflux for 60 hr. After this time the reaction mixture was allowed to cool and the solid calcium carbonate was filtered off. The solid was washed with ethyl acetate (10 mL) and the filtrate was concentrated under reduced pressure to give an off-white solid. The solid was dissolved in ethyl acetate and washed with concentrated hydrochloric acid. The organic solution was then neutralised with sodium bicarbonate, dried over magnesium sulfate and concentrated under reduced pressure to give 4-hydroxymethyl-4'-nitrobenzophenone (2.08 g, 81%) as a beige solid.

Synthesis of 4-di(ethyleneglycol)benzyl ether-4'-nitrobenzophenone (4)

4-Hydroxymethyl-4'-nitrobenzophenone (3.00 g, 11.7 mmol, 1 eq) was dissolved in THF (45 mL) and the yellow solution was cooled to 0°C in an ice/water bath. The sodium hydride (0.70 g, 17.5 mmol, 1.5 eq, 60% dispersion) was added portionwise over 10 min turning the solution a dark blue/black colour. The mixture was warmed to room temperature and stirred for 30 min. The mixture was cooled to 0°C and 2-(2-chloroethoxy) ethanol (1.48 mL, 14.0 mmol, 1.2 eq) was added dropwise over 5 min turning the solution a dark orange colour. The orange mixture was then allowed to warm to room temperature and stirred for a further 18 h. After this time the reaction was quenched with a small amount of water and the mixture was concentrated under reduced pressure to give an orange oil. The product was used in the next step without further purification due to the difficult work up involved with molecules such as this which exhibit surfactant properties.

Attachment of cyanuric chloride to 4-di(ethyleneglycol)benzyl ether-4'-nitrobenzophenone (5)

Cyanuric chloride (0.42 g, 2.3 mmol, 1.5 eq) and Hünig's base (0.63 mL, 2.3 mmol, 1.5 eq) were dissolved in tetrahydrofuran (20 mL) and the colourless solution was cooled to 0°C. A solution of 4-di(ethyleneglycol)benzyl ether-4'-nitrobenzophenone (0.50 g, 1.5 mmol, 1 eq) in tetrahydrofuran (5 mL) was added dropwise over 5 min to give an orange turbid mixture. The mixture was then allowed to warm to room temperature and stirred for 18 h. At this point HPLC showed that the starting material had been consumed and so the precipitate was filtered off. The filtrate was concentrated under reduced pressure to give an orange oil which was used in the next stage without further purification.

Coupling of triazine-linked 4-di(ethyleneglycol)benzyl ether-4'-nitrobenzophenone to Locust bean gum (6)

The triazine-linked 4-di(ethyleneglycol)benzyl ether-4'-nitrobenzophenone (0.74 g, 1.5 mmol, 500 eq) was dissolved in tetrahydrofuran (20 mL) and Hünig's base (0.32 mL, 1.8 mmol, 600 eq) was added to give an orange solution. Locust bean gum (1.00 g, 3 µmol, 1 eq) was added in one portion and the turbid mixture was heated to 50°C. The mixture was then stirred for 24 hr at which point HPLC indicated that there was no more starting material present in the reaction mixture. The reaction was cooled and filtered to yield an orange solid. The solid was washed with THF, dried and used in the next stage without further purification.

Formation of tosyl hydrazone from the Locust bean gum-triazine attached nitrobenzophenone (7)

The Locust bean gum-attached nitrobenzophenone (1.70 g, 1.5 mmol, 1 eq) was suspended in methanol (20 mL) and tosyl hydrazide (0.70 g, 3.8 mmol, 2.5 eq) was added portionwise over 2 min. The suspension was then heated to reflux for 24 hr and then allowed to cool to yield the product.

Route 2 – Synthesis of ether linked tosyl hydrazone locust bean gum, with reference to Figure 3

Attachment of Locust bean gum to 4-bromomethyl-4'-nitro-benzophenone (9)

Locust bean gum (1.00 g, 3 μ mol, 1 eq) was suspended in THF (20 mL) and the beige suspension was cooled to 0°C. Sodium hydride (0.05 g, 3.12 mmol, 106.0 eq, 60% dispersion) was added portionwise over 5 mins to give a brown suspension. The suspension was allowed to warm to room temperature and stirred for 10 mins. The suspension was then cooled again to 0°C and 4-bromomethyl-4'-nitro-benzophenone (1.00 g, 3.12 mmol, 105.8 eq) was added slowly over 30 mins. The mixture was then allowed to warm to room temperature and stirred for 18 hr. The reaction was quenched carefully with water (0.5 mL) and the dark brown solid was filtered from the mixture. The solid was washed with methanol and dried in air to give a fine brown solid (2 g). This compound was then used in the next step without further purification.

Formation of tosyl hydrazone from ether attached Locust bean gum benzophenone (10)

The benzophenone (2.00 g, 3.12 mmol, 1 eq) and tosyl hydrazide (1.45 g, 7.80 mmol, 2.5 eq) were mixed in methanol (15 mL) to give a beige suspension. The suspension was heated to reflux for 18 hr and then allowed to cool. The suspension was then filtered and used directly in the next step.

Example 2: Tosyl hydrazone modification of a polystyrene-containing block copolymer systems

Table 1 Overview of modified polymers and starting materials

Base Polymer	Soft "R" Block	% Styrene in polymer	% Modification (based on styrene portion)	Modified Code
D1102	Butadiene	28	7.5%	2a
D1184	Butadiene	31	7.5%	2b
D1153	Butadiene	29	7.5%	2c
D1111	Isoprene	22	7.5%	2d
G1652	Hydrogenated butadiene	30	7.5%	2e

Synthesis of tosyl hydrazone derivatives, with reference to Figure 4

General synthesis of benzophenone derivatives (1)

To a solution of the styrene block co-polymer in 1,2-dichloroethane was added 4-nitrobenzoyl chloride (1eq) and the mixture stirred until a solution was formed. Aluminium tri chloride (1.2eq) was added and the mixture stirred at RT for 18h. The mixture was diluted with water and the organic layer collected, washed with water and concentrated *in vacuo* to yield polymers (1a-e) as solids (Table 1).

General synthesis of 4-toulene sulfonyl hydrazone derivatives (2)

To a solution of the benzophenone derivative block co-polymer (1) in toluene was added 4-toulene sulfonyl hydrazide. The mixture was heated to 50°C for 18h then cooled, washed with 1M HCl_(aq) then concentrated *in vacuo* to yield polymers (2a-e) as solids. (Table 1)

Solvent stability of the polymers (2)

The solvent stability of the modified polymers was test by casting a film of the polymer from a 20% w/w solution in toluene:triethylamine (95:5) onto a PTFE block. The film was then dried in the air followed by heating to 150°C for 2h. The cured sheets where then supsened in a vial of organic solvent and shaken. The degree of stability was obsereved visually. (Table 3)

Table 2 Solvent stablity of modified polymers

Polymer	MEK Solublity	Toulene Solublity
D1102	Soluble	Soluble
2a	Insoluble	Insoluble

Adhesive strength via solution based application on FR4 epoxy resin

To a sample of FR4 epoxy resin (150x25x1.5mm) was applied the block co-polymer as a solution in toluene:triethylamine (95:5) (20 wt%) to give a coverage of 750mm². The layer

is rolled using a “k-bar” to achieve a 150 micron wet film thickness. A second sheet of FR4 epoxy resin is the applied to the adhesive and the sandwich is the clamped and heated to 150°C for 2 h before being allowed to cool for 24h. The adhesive strength is obtained using a T-Peel configuration. (Table 4)

Table 3 T-Peel adhesion of modified polymers on FR4 epoxy resin by solution application

Polymer	Mean Peel Strength (N/inch)
D1102	6.6
2a	13.8
D1184	14.2
2b	13.2
D1153	6.7
2c	12.7
G1652	4.1
2e	2.7

Adhesive strength via solution based application on FR4 epoxy resin

To a sample of FR4 epoxy resin (150x25x1.5mm) was applied the block co-polymer as a solution in toluene:triethylamine (95:5) (20 wt%) to give a coverage of 750mm². The layer is rolled using a “k-bar” to achieve a 150 micron wet film thickness. A second sheet of FR4 epoxy resin is the applied to the adhesive and the sandwich is the clamped and heated to 150°C for 16 h before being allowed to cool for 24h. The adhesive strength is obtained using a T-Peel configuration. (Table 5)

Table 4 T-Peel adhesion of modified polymers on FR4 epoxy resin by solution application

Polymer	Mean Peel Strength (N/inch)
D1102	6.6
2a	22.0

Adhesive strength via solution based application on GX13 epoxy resin

To a sample of GX13 epoxy resin (150x25x1.5mm) was applied the block co-polymer as a solution in toluene:triethylamine (95:5) (20 wt%) to give a coverage of 750mm². The layer is rolled using a “k-bar” to achieve a 150 micron wet film thickness. A second sheet of

GX13 epoxy resin is the applied to the adhesive and the sandwich is the clamped and heated to 150°C for 2 h before being allowed to cool for 24h. The adhesive strength is obtained using a T-Peel configuration. (Table 6)

Table 5 T-Peel adhesion of modified polymers on GX13 epoxy resin by solution application

Polymer	Mean Peel Strength (N/inch)
D1102	6.6
2a	17.8

Adhesive strength via film based application

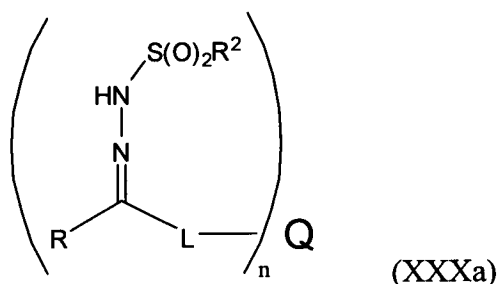
A film of the polymer was cast from a 20% w/w solution in toluene:triethylamine (95:5) onto a PTFE block and air dried. To a sample of FR4 epoxy resin (150x25x1.5mm) was applied the prviously dried film to give a coverage of 750mm². A second sheet of FR4 epoxy resin is the applied to the adhesive and the sandwich is the clamped and heated to 150°C for 2 h before being allowed to cool for 24h. The adhesive strength is obtained using a T-Peel configuration. (Table7)

Table 6 T-Peel adhesion of modified polymers as dry films on FR4 epoxy resin

Polymer	Mean Peel Strength (N/inch)
D1102	6.7
2a	20.9

CLAIMS

1. A functionalised compound which is a sulfonylhydrazone compound of formula (XXXa)

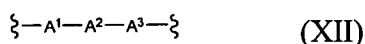


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} haloalkyl, C_{1-20} fluoroalkyl, C_{1-20} perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C_{1-10} alkylamino, di(C_{1-10})alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C_{1-10} alkoxy, aryloxy, haloalkyl, thiol, C_{1-10} alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C_{1-20} alkyl)silyl, aryldi(C_{1-20} alkyl)silyl, diaryl(C_{1-20} alkyl)silyl and triarylsilyl;

each L , which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R , wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-($O-C_{1-20}$ alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-($O-C_{1-20}$ alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''),

O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer.

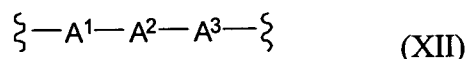
2. A functionalised compound according to claim 1 wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl, di(C₁₋₆ alkyl)amino, hydroxyl, nitro, cyano or methoxy.

3. A functionalised compound according to claim 1 or claim 2 wherein R² is C₁₋₆ alkyl, phenyl or naphthyl, which phenyl or naphthyl is unsubstituted or substituted with C₁₋₆ alkyl or di(C₁₋₆ alkyl)amino.

4. A functionalised compound according to any one of claims 1 to 3 wherein R² is *para*-tolyl.

5. A functionalised compound according to any one of the preceding claims wherein R is phenyl which is unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryl di(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl.

6. A functionalised compound according to any one of claims 1 to 5 wherein each L, which may be the same or different, is a group of formula (XII)



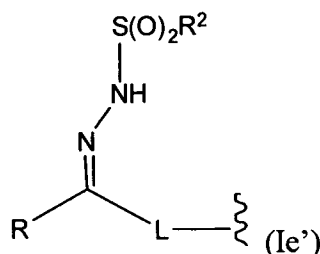
wherein:

A^1 is bonded to the carbon atom bonded to R, wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O) $_2$, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2-C_{1-20}$ alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2-C_{1-20}$ alkylene-O, $^*-$ arylene-O, $^*-$ heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O) $_2$, $^*-OC(O)$, $^*-N(R'')C(O)$, O, S, N(R''), $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2-C_{1-20}$ alkenylene and $^*-Z^2-C_{1-20}$ alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O) $_2$, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 .

7. A functionalised compound according to any one of claims 1 to 5 wherein each L is a single bond, such that each of the n carbene precursor groups of formula (Ie'),



wherein R and R² are as defined in any one of claims 1 to 4, is bonded directly to Q.

8. A functionalised compound according to any one of the preceding claims with the proviso that when L is a single bond, Q comprises at least n aryl or heteroaryl rings, wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring, thereby bonding the aryl or heteroaryl ring directly to the carbon atom which is bonded to R.

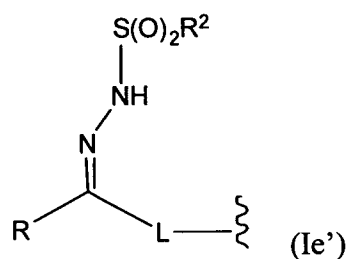
9. A functionalised compound according to any one of the preceding claims with the proviso that when L is a single bond, Q comprises at least n aryl rings, wherein each L which is single bond is attached directly to a said aryl ring, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

10. A functionalised compound according to any one of the preceding claims wherein L is a single bond and Q is a polymer which comprises at least n aryl rings, wherein each L which is single bond is attached directly to a said aryl ring, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

11. A functionalised compound according to any one of the preceding claims wherein Q comprises a polymer or dendrimer, wherein the polymer is a linear polymer, a branched polymer, a star polymer, a hyperbranched polymer, a homopolymer, a copolymer or a block copolymer.

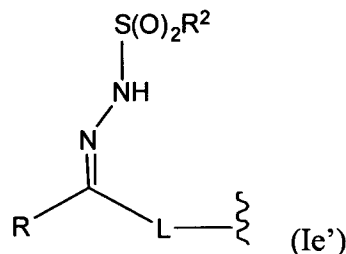
12. A functionalised compound according to claim 11 wherein the polymer comprises a polysaccharide, a protein, a polyester, a polyether, a polyacrylate, a polymethacrylate, polystyrene, a thermoplastic elastomer, polybutadiene, polyisoprene, SBS rubber, SIS rubber, a polycarbonate, polyetheretherketone (PEEK), a polyetherimides, a polyimide, a polysulfone, poly(vinyl chloride), a polysilanes, a polysiloxane, a polyurea, a polyurethane, polylactic acid, polyvinylidene chloride, a fluoro-polymer, a polyethylene imines, or a salt thereof.

13. A functionalised compound according to claim 11 wherein Q is a polymer or dendrimer bearing phenyl groups, and wherein each L is a single bond attached to a said phenyl group of Q.
14. A functionalised compound according to any one of the preceding claims wherein Q comprises polystyrene.
15. A functionalised compound according to any one of the preceding claims wherein Q is a polymer or dendrimer which is capable of forming phase domains.
16. A functionalised compound according to any one of the preceding claims wherein Q is a block copolymer or dendrimer, which block copolymer or dendrimer is capable of forming phase domains.
17. A functionalised compound according to any one of the preceding claims wherein Q is a block copolymer or dendrimer, which block copolymer or dendrimer comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, and wherein more than 50% of said n carbene precursor groups of formula (Ie'),



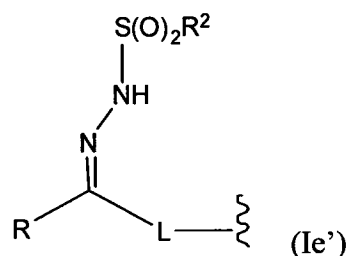
wherein R, R² and L are as defined in any one of the preceding claims, are bonded to said one or more thermoplastic polymer blocks A.

18. A functionalised compound according to claim 17 wherein at least 80% of said n carbene precursor groups of formula (Ie'),



wherein R, R² and L are as defined in any one of the preceding claims, are bonded to said one or more thermoplastic polymer blocks A.

19. A functionalised compound according to claim 17 or claim 18 wherein each of said n carbene precursor groups of formula (Ie'),



wherein R, R² and L are as defined in any one of the preceding claims, is bonded to said one or more thermoplastic polymer blocks A.

20. A functionalised compound according to any one of claims 17 to 19 wherein Q is a block copolymer having the structure A_z-(B-A)_y-B_x, wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20, provided that the sum of z, y and z is equal to or greater than 2.

21. A functionalised compound according to claim 20 wherein the block copolymer has the structure A-B-A, B-A-B, A-B, or (A-B)_m, wherein m is an integer from 1 to 20.

22. A functionalised compound according to any one of claims 17 to 19 wherein Q is a dendrimer or a radial block copolymer, which dendrimer or radial block copolymer is of the formula (Xa):



wherein:

q is an integer of from 3 to 100;

each P, which is the same or different, is a polymer arm having the structure

$A_z-(B-A)_y-B_x$, wherein each A is a linear or branched thermoplastic polymer block and each B is a linear or branched elastomeric polymer block, and wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20, provided that in each polymer P, the sum of z, y and z is equal to or greater than 1 and provided that, in at least one of said polymers P, the sum of z, y and z is equal to or greater than 2; and

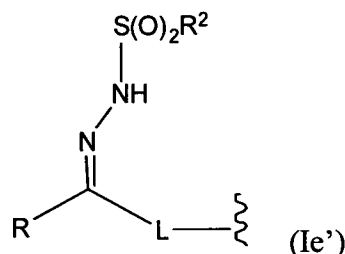
Core is a core moiety of the dendrimer or radial block copolymer of formula (Xa), to which each of the polymer arms P is attached.

23. A functionalised compound according to claim 22 wherein Core comprises an oligomer or polymer formed from a polyfunctional coupling monomer.
24. A functionalised compound according to claim 23 wherein the polyfunctional coupling monomer is an aryl ring substituted with from 2 to 4 unsubstituted or substituted C_{2-20} alkenyl groups.
25. A functionalised compound according to claim 23 or claim 24 wherein the polyfunctional coupling monomer is a divinyl substituted aryl ring, preferably *para*-divinyl benzene or *meta*-divinyl benzene.
26. A functionalised compound according to claim 22 wherein Core comprises a linear or branched thermoplastic polymer block, A^1 , and/or a linear or branched elastomeric polymer block, B^1 .
27. A functionalised compound according to claim 22 wherein Core comprises a polymer of formula $A^1_z-(B^1-A^1)_y-B^1_x$, wherein each A^1 is a linear or branched thermoplastic polymer block and each B^1 is a linear or branched elastomeric polymer block, and wherein x is 0 or 1, z is 0 or 1, and y is 0 or an integer from 1 to 20 provided that the sum of z, y and z is equal to or greater than 1.
28. A functionalised compound according to any one of claims 17 to 27 wherein each of said one or more thermoplastic polymer blocks A comprises aryl groups attached to a polymer backbone.

29. A functionalised compound according to claim 28 wherein each of the aryl groups is attached to said backbone by a single bond or via a C₁₋₄ alkyl linker group, or wherein each of the aryl groups is fused to a C₅₋₁₀ carbocyclic ring which forms part of said backbone.

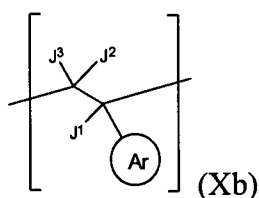
30. A functionalised compound according to claim 28 or claim 29 wherein the aryl groups are phenyl groups.

31. A functionalised compound according to any one of claims 28 to 30, wherein each of the carbene precursor groups of formula (Ie')



wherein R, R² and L are as defined in any one of the preceding claims, which is bonded to said one or more blocks A, is bonded to an aryl group of said one or more blocks A.

32. A functionalised compound according to any one of claims 17 to 31 wherein each of said one or more linear or branched thermoplastic polymer blocks, A, comprises monomer units of formula (Xb)



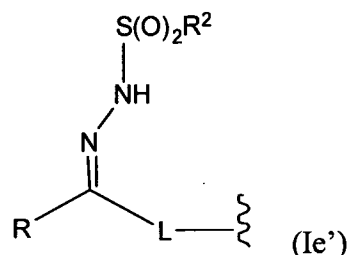
wherein

Ar is an unsubstituted or substituted aryl group; and

J¹, J² and J³, which are the same or different, are independently selected from H, unsubstituted or substituted C₁₋₁₀ alkyl, halo, unsubstituted or substituted C₁₋₁₀ alkoxy, amino, unsubstituted or substituted C₁₋₁₀ alkylamino, unsubstituted or substituted di(C₁₋₁₀)alkylamino, unsubstituted or substituted arylamino, unsubstituted or substituted diarylamino, unsubstituted or substituted arylalkylamino, unsubstituted or substituted C₂₋₁₀ alkenyl, unsubstituted or substituted aryl and unsubstituted or substituted heteroaryl,

wherein said unsubstituted or substituted C_{1-10} alkyl is optionally interrupted by $N(R'')$, O, S or arylene wherein R'' is H, C_{1-6} alkyl or aryl;

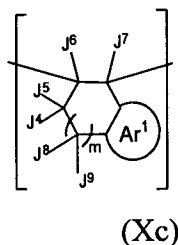
wherein each of the carbene precursor groups of formula (Ie')



wherein R, R^2 and L are as defined in any one of the preceding claims, which is bonded to said one or more blocks A, is bonded to a group Ar.

33. A functionalised compound according to claim 32 wherein Ar is a phenyl group and J^1 , J^2 and J^3 are each hydrogen.

34. A functionalised compound according to any one of claims 17 to 31 wherein each of said one or more linear or branched thermoplastic polymer blocks, A, comprises monomer units of formula (Xc)



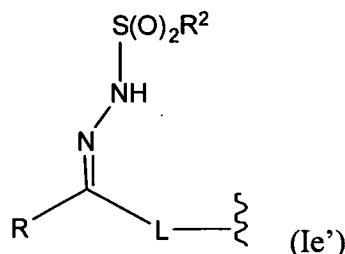
wherein

Ar^1 is an unsubstituted or substituted aryl group;

m is 0 or an integer from 1 to 6; and

J^4 , J^5 , J^6 , J^7 , J^8 and J^9 which are the same or different, are independently selected from H, unsubstituted or substituted C_{1-10} alkyl, halo, unsubstituted or substituted C_{1-10} alkoxy, amino, unsubstituted or substituted C_{1-10} alkylamino, unsubstituted or substituted di(C_{1-10})alkylamino, unsubstituted or substituted arylamino, unsubstituted or substituted diarylamino, unsubstituted or substituted arylalkylamino, unsubstituted or substituted C_{2-10} alkenyl, unsubstituted or substituted aryl and unsubstituted or substituted heteroaryl, wherein said unsubstituted or substituted C_{1-10} alkyl is optionally interrupted by $N(R'')$, O, S or arylene wherein R'' is H, C_{1-6} alkyl or aryl;

wherein each of the carbene precursor groups of formula (Ie')



wherein R, R² and L are as defined in any one of the preceding claims, which is bonded to said one or more blocks A, is bonded to a group Ar¹.

35. A functionalised compound according to claim 34 wherein Ar¹ is a phenyl ring, m is 0, and J⁴, J⁵, J⁶ and J⁷ are each hydrogen.

36. A functionalised compound according to any one of claims 32 to 35, wherein each of said one or more linear or branched thermoplastic polymer blocks, A, comprises at least 80 weight % of said monomer units of formula (Xb) or (Xc).

37. A functionalised compound according to any one of claims 32 to 35, wherein:
each of said one or more linear or branched thermoplastic polymer blocks, A, is a homopolymer block which comprises monomer units of formula (Xb) or monomer units of formula (Xc); or

wherein each of said one or more linear or branched thermoplastic polymer blocks, A, is a random copolymer block, which comprises co-monomer units of formula (Xb) or (Xc), and co-monomer units derived from an additional co-monomer.

38. A functionalised compound according to claim 37 wherein said additional co-monomer is a conjugated diene having from 4 to 24 carbon atoms.

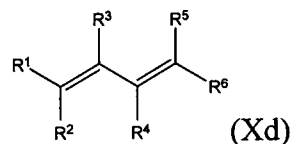
39. A functionalised compound according to any one of claims 17 to 37 wherein each of said one or more linear or branched thermoplastic polymer blocks, A, comprises poly(indene) or a poly(C₁₋₆ alkenyl-aryl), preferably wherein the poly(C₁₋₆ alkenyl-aryl) is poly(styrene).

40. A functionalised compound according to any one of claims 17 to 38 wherein each of said one or more linear or branched thermoplastic polymer blocks, A, comprises a

random copolymer of a C₁₋₆ alkenyl-aryl monomer and a conjugated diene monomer, which conjugated diene monomer has from 4 to 24 carbon atoms, and preferably wherein the C₁₋₆ alkenyl-aryl monomer is styrene.

41. A functionalised compound according to any one of claims 17 to 40 wherein each of said one or more linear or branched elastomeric polymer blocks, B, which are the same or different, comprises a polymer or copolymer of one or more conjugated diene monomers, or a hydrogenated polymer or copolymer of one or more conjugated diene monomers.

42. A functionalised compound according to claim 41, wherein the one or more conjugated diene monomers are selected from conjugated diene monomers of formula (Xd)



wherein R¹, R², R³, R⁴, R⁵ and R⁶, which are the same or different, are independently selected from H, unsubstituted or substituted C₁₋₂₀ alkyl and unsubstituted or substituted aryl.

43. A functionalised compound according to claim 41 or claim 42, wherein the one or more conjugated diene monomers are selected from conjugated diene monomers having from 4 to 24 carbon atoms.

44. A functionalised compound according to any one of claims 41 to 43, wherein the one or more conjugated diene monomers are selected from 1,3-butadiene, isoprene (2-methyl-1,3-butadiene), 2,3-dimethyl-1,3-butadiene, 2-ethyl-1,3-butadiene, 2-propyl-1,3-butadiene, 2-butyl-1,3-butadiene, 2-pentyl-1,3-butadiene (2-amyl-1,3-butadiene), 2-hexyl-1,3-butadiene, 2-heptyl-1,3-butadiene, 2-octyl-1,3-butadiene, 2-nonyl-1,3-butadiene, 2-decyl-1,3-butadiene, 2-dodecyl-1,3-butadiene, 2-tetradecyl-1,3-butadiene, 2-hexadecyl-1,3-butadiene, 2-isoamyl-1,3-butadiene and 2-phenyl-1,3-butadiene; and from: 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 1,3-octadiene, 6-methylene-2,7-octadiene, 1,3-nonyldiene, 1,3-decyldiene, and 1,3-dodecyldiene and the 2-methyl, 2,3-dimethyl, 2-ethyl, 2-propyl, 2-

butyl, 2-pentyl, 2-hexyl, 2-heptyl, 2-octyl, 2-nonyl, 2-decyl, 2-dodecyl, 2-tetradecyl, 2-hexadecyl, 2-isoamyl and 2-phenyl derivatives thereof.

45. A functionalised compound according to any one of claims 41 to 44, wherein the one or more conjugated diene monomers are 1,3-butadiene, isoprene, or a mixture thereof.

46. A functionalised compound according to any one of claims 41 to 45, wherein each of said one or more linear or branched elastomeric polymer blocks, B, which are the same or different, comprises a polymer block selected from poly(butadiene), poly(isoprene), poly(butadiene-co-isoprene), and hydrogenated derivatives thereof.

47. A functionalised compound according to claim 46 wherein the hydrogenated derivatives thereof are selected from poly(ethylene/butylene), poly(ethylene/propylene) and poly(ethylene/ethylene/propylene).

48. A functionalised compound according to any one of claims 17 to 47 wherein Q is selected from poly(styrene)-poly(butadiene)-poly(styrene) (SBS), poly(styrene)-poly(isoprene)-poly(styrene) (SIS), poly(styrene)-poly(butadiene/isoprene)-poly(styrene) (SIBS), poly(styrene)-poly(ethylene/butylene)-poly(styrene) (SEBS), poly(styrene)-poly(ethylene/propylene)-poly(styrene) (SEPS), and poly(styrene)-poly(ethylene/(ethylene/propylene))-poly(styrene) (SEEPS).

49. Use of a functionalised compound as defined in any one of the preceding claims as a cross linking agent.

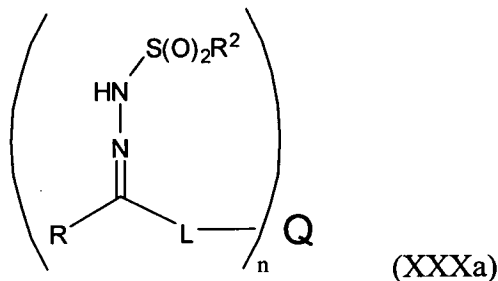
50. Use of a functionalised compound as defined in any one of the preceding claims as an agent for producing a chemically-bound three-dimensional network on or within a substrate.

51. Use of a functionalised compound as defined in any one of the preceding claims as an adhesive.

52. An adhesive composition comprising a functionalised compound as defined in any one of the preceding claims.

53. A process for cross linking or adhering a first substrate to a second substrate, which first and second substrates are the same or different, which process comprises

(a) contacting the first and second substrates with a functionalised cross linking compound which is a sulfonylhydrazone compound of formula (XXXa)

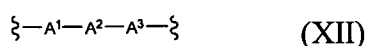


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O),

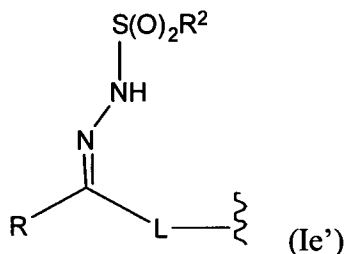
C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-Z²-arylene-O, *-Z²-heteroarylene-O, *-Z²-C₁₋₂₀ alkylene-O, *-arylene-O, *-heteroarylene-O, *-C₁₋₂₀ alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C₁₋₂₀ alkenylene, C₁₋₂₀ alkynylene, *-Z²-C₁₋₂₀ alkenylene and *-Z²-C₁₋₂₀ alkynylene, wherein Z² is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A³ to A²;

R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer; and

(b) generating carbene reactive intermediate groups from the n carbene precursor groups of formula (Ie')



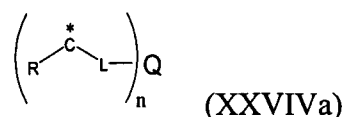
wherein R, R² and L are as defined above, so that at least one carbene reactive intermediate group reacts with the first substrate and at least one other carbene reactive intermediate group reacts with the second substrate, thereby cross linking or adhering the first and second substrates.

54. A process according to claim 53 wherein the functionalised cross linking compound is a functionalised compound as defined in any one of claims 2 to 48.

55. A cross-linked or adhered product comprising:

- (a) a first substrate;
- (b) a second substrate; and

(c) a cross linking moiety of formula (XXVIVa)



wherein

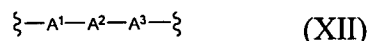
the first and second substrates are the same or different;

each * is a point of attachment of the cross linking moiety to the first substrate, the second substrate or to another moiety or molecule;

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-arylene, *-Z¹-heteroarylene and *-Z¹-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, wherein Z¹ is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A² to A¹, wherein each of said C₁₋₂₀ alkylene and C₁₋₂₀ perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl; and

A³ is a single bond or an unsubstituted or substituted group selected from *-Z²-arylene, *-Z²-heteroarylene, *-Z²-C₁₋₂₀ alkylene, arylene, heteroarylene, C₁₋₂₀ alkylene, *-

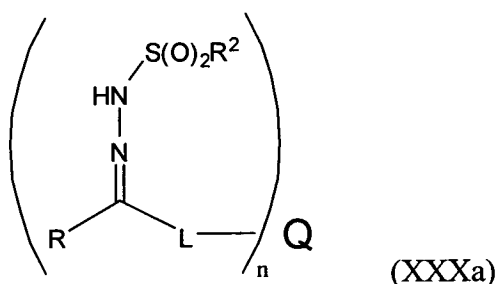
Z^2 -arylene-O, *- Z^2 -heteroarylene-O, *- Z^2 - C_{1-20} alkylene-O, *-arylene-O, *-heteroarylene-O, *- C_{1-20} alkylene-O, C(O), S(O)₂, *-OC(O), *-N(R'')C(O), O, S, N(R''), *-C(O)O, *-C(O)N(R''), *-S(O)₂O, C_{1-20} alkenylene, C_{1-20} alkynylene, *- Z^2 - C_{1-20} alkenylene and *- Z^2 - C_{1-20} alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ; and

Q is a polymer or a dendrimer.

56. A cross-linked or adhered product according to claim 55 wherein R is as defined in claim 5, L is as defined in any one of claims 6 to 10 and 13, and Q is as defined in any one of claims 7 to 48.

57. A process according to claim 53 or claim 54 or a cross-linked product according to claim 55 or claim 56 wherein the first substrate is a first polymer and the second substrate is a second polymer.

58. A process for producing a functionalised compound which is a sulfonylhydrazone compound of formula (XXXa)

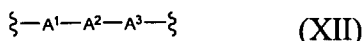


wherein:

n is an integer equal to or greater than 3;

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{1-20} haloalkyl, C_{1-20} fluoroalkyl, C_{1-20} perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C_{1-10} alkylamino, di(C_{1-10})alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C_{1-10} alkoxy, aryloxy, haloalkyl, thiol, C_{1-10} alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C_{1-20} alkyl)silyl, aryl di(C_{1-20} alkyl)silyl, diaryl(C_{1-20} alkyl)silyl and triarylsilyl;

each L, which may be the same or different, is a single bond or a group of formula (XII)



wherein:

A^1 is bonded to the carbon atom bonded to R, wherein A^1 is an unsubstituted or substituted group selected from arylene and heteroarylene;

A^2 is a single bond or an unsubstituted or substituted group selected from C_{1-20} alkylene, C_{1-20} perfluoroalkylene, arylene, heteroarylene, $^*-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, $^*-Z^1-C_{1-20}$ alkylene, $^*-Z^1-C_{1-20}$ perfluoroalkylene, $^*-Z^1$ -arylene, $^*-Z^1$ -heteroarylene and $^*-Z^1-C_{1-20}$ alkylene-(O- C_{1-20} alkylene-) $_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O) $_2$, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl; and

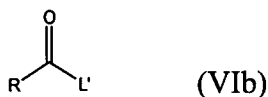
A^3 is a single bond or an unsubstituted or substituted group selected from $^*-Z^2$ -arylene, $^*-Z^2$ -heteroarylene, $^*-Z^2-C_{1-20}$ alkylene, arylene, heteroarylene, C_{1-20} alkylene, $^*-Z^2$ -arylene-O, $^*-Z^2$ -heteroarylene-O, $^*-Z^2-C_{1-20}$ alkylene-O, * -arylene-O, * -heteroarylene-O, $^*-C_{1-20}$ alkylene-O, C(O), S(O) $_2$, $^*-OC(O)$, $^*-N(R'')C(O)$, O, S, N(R''), $^*-C(O)O$, $^*-C(O)N(R'')$, $^*-S(O)_2O$, C_{1-20} alkenylene, C_{1-20} alkynylene, $^*-Z^2-C_{1-20}$ alkenylene and $^*-Z^2-C_{1-20}$ alkynylene, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O) $_2$, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C_{1-6} alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ;

R^2 is an unsubstituted or substituted C_{1-6} alkyl group or an unsubstituted or substituted aryl group; and

Q is a polymer or a dendrimer;

which process comprises:

(a) treating a first compound, Q', which is a polymer or a dendrimer and which bears at least n functional groups, with at least one second compound of formula (VIb)

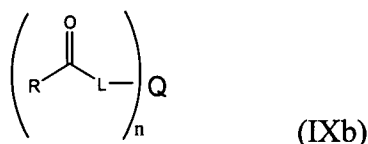


wherein:

L' is a leaving group or a reactive precursor to said group of formula (XII), wherein L' is reactable with a said functional group to couple the second compound to the first compound, and

R is selected from aryl and heteroaryl, which aryl and heteroaryl are unsubstituted or substituted by one, two, three, four or five groups, which groups are the same or different and are independently selected from C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ haloalkyl, C₁₋₂₀ fluoroalkyl, C₁₋₂₀ perfluoroalkyl, aryl, cyano, nitro, hydroxy, halo, carboxy, amino, C₁₋₁₀ alkylamino, di(C₁₋₁₀)alkylamino, arylamino, diarylamino, arylalkylamino, amido, acyl, acyloxy, acylamido, ester, C₁₋₁₀ alkoxy, aryloxy, haloalkyl, thiol, C₁₋₁₀ alkylthio, arylthio, sulfonic acid, sulfonyl, sulfonamide, tri(C₁₋₂₀ alkyl)silyl, aryldi(C₁₋₂₀ alkyl)silyl, diaryl(C₁₋₂₀ alkyl)silyl and triarylsilyl,

thereby producing a third compound of formula (IXb):

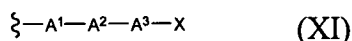


wherein Q, L, R and n are as defined above; and

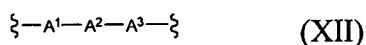
(b) treating the third compound with H₂N-N(H)S(O)₂R² in the presence of heat, wherein R² is an unsubstituted or substituted C₁₋₆ alkyl group or an unsubstituted or substituted aryl group, thereby producing said hydrazone compound of formula (XXXa).

59. A process according to claim 58 wherein R² is as defined in any one of claims 2 to 4.

60. A process according to claim 58 or claim 59 wherein L' is a group of formula (XI)



and L is a group of formula (XII)



wherein:

A¹ is bonded to the carbon atom bonded to R, wherein A¹ is an unsubstituted or substituted group selected from arylene and heteroarylene;

A² is a single bond or an unsubstituted or substituted group selected from C₁₋₂₀ alkylene, C₁₋₂₀ perfluoroalkylene, arylene, heteroarylene, *-C₁₋₂₀ alkylene-(O-C₁₋₂₀ alkylene-)_m wherein m is 1 to 20, *-Z¹-C₁₋₂₀ alkylene, *-Z¹-C₁₋₂₀ perfluoroalkylene, *-Z¹-

arylene, $^{*}\text{-Z}^1\text{-heteroarylene}$ and $^{*}\text{-Z}^1\text{-C}_{1-20}\text{ alkylene-(O-C}_{1-20}\text{ alkylene-)}_m$ wherein m is 1 to 20, wherein Z^1 is selected from O, S, C(O), S(O), S(O)₂, N(R''), C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein * is the point of attachment of A^2 to A^1 , wherein each of said C_{1-20} alkylene and C_{1-20} perfluoroalkylene groups is optionally interrupted by N(R''), O, S or arylene, and wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl;

A^3 is a single bond or an unsubstituted or substituted group selected from $^{*}\text{-Z}^2\text{-arylene}$, $^{*}\text{-Z}^2\text{-heteroarylene}$, $^{*}\text{-Z}^2\text{-C}_{1-20}\text{ alkylene}$, arylene, heteroarylene, $\text{C}_{1-20}\text{ alkylene}$, C(O), S(O)₂, $^{*}\text{-OC(O)}$, $^{*}\text{-N(R'')C(O)}$, O, S, N(R''), $^{*}\text{-C(O)O}$, $^{*}\text{-C(O)N(R'')}$, $^{*}\text{-S(O)}_2\text{O}$, $\text{C}_{1-20}\text{ alkenylene}$, $\text{C}_{1-20}\text{ alkynylene}$, $^{*}\text{-Z}^2\text{-C}_{1-20}\text{ alkenylene}$ and $^{*}\text{-Z}^2\text{-C}_{1-20}\text{ alkynylene}$, wherein Z^2 is selected from O, S, N(R''), C(O), S(O), S(O)₂, C(O)O, OC(O), C(O)N(R'') and N(R'')C(O), wherein each R'' is independently selected from H, C₁₋₆ alkyl and aryl, and wherein * is the point of attachment of A^3 to A^2 ;

and, in the group of formula (XI):

X is H, a halo group or a leaving group,

provided that when A^3 is a single bond, $^{*}\text{-Z}^2\text{-arylene}$, $^{*}\text{-Z}^2\text{-heteroarylene}$, $^{*}\text{-Z}^2\text{-C}_{1-20}\text{ alkylene}$, arylene, heteroarylene, $\text{C}_{1-20}\text{ alkylene}$ or S(O)₂, X is other than H and provided that when A^3 is O, S, N(R''), -C(O)O-^{*} , -C(O)N(R'')-^{*} or $\text{-S(O)}_2\text{O-}^{*}$, X is other than a halo group.

61. A process according to claim 60 wherein Q and Q' comprise a polymer or dendrimer, wherein the polymer is a linear polymer, a branched polymer, a star polymer, a hyperbranched polymer, a homopolymer, a copolymer or a block copolymer.

62. A process according to any one of claims 58 to 61 wherein Q' is a polymer or a dendrimer which bears n functional groups which are n aryl or heteroaryl groups, and wherein Q is a polymer or dendrimer comprising n linker groups which are arylene or heteroarylene groups, wherein each of said arylene or heteroarylene groups is attached to L.

63. A process according to any one of claims 58 to 62 wherein Q and Q' comprise a block copolymer or dendrimer, which block copolymer or dendrimer comprises one or more linear or branched thermoplastic polymer blocks, A, and one or more linear or branched elastomeric polymer blocks, B, wherein more than 50% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

64. A process according to claim 63 wherein at least 80% of said n functional groups of Q' are bonded to said one or more thermoplastic polymer blocks A.

65. A process according to claim 63 or claim 64 wherein each of said n functional groups of Q' is bonded to said one or more thermoplastic polymer blocks A.

66. A process according to any one of claims 63 to 65 wherein said n functional groups of Q' are aryl groups, preferably phenyl groups.

67. A process according to claim 66 wherein each L is a single bond and L' is a leaving group.

68. A process according to claim 67 wherein said leaving group, L', is a halo group, preferably a chloro group.

69. A process according to claim 68 wherein the functionalised compound is as defined in claim 60 or claim 61 and wherein the reaction between Q' and the compound of formula (VIb) in step (a) is a Friedel-Crafts Acylation.

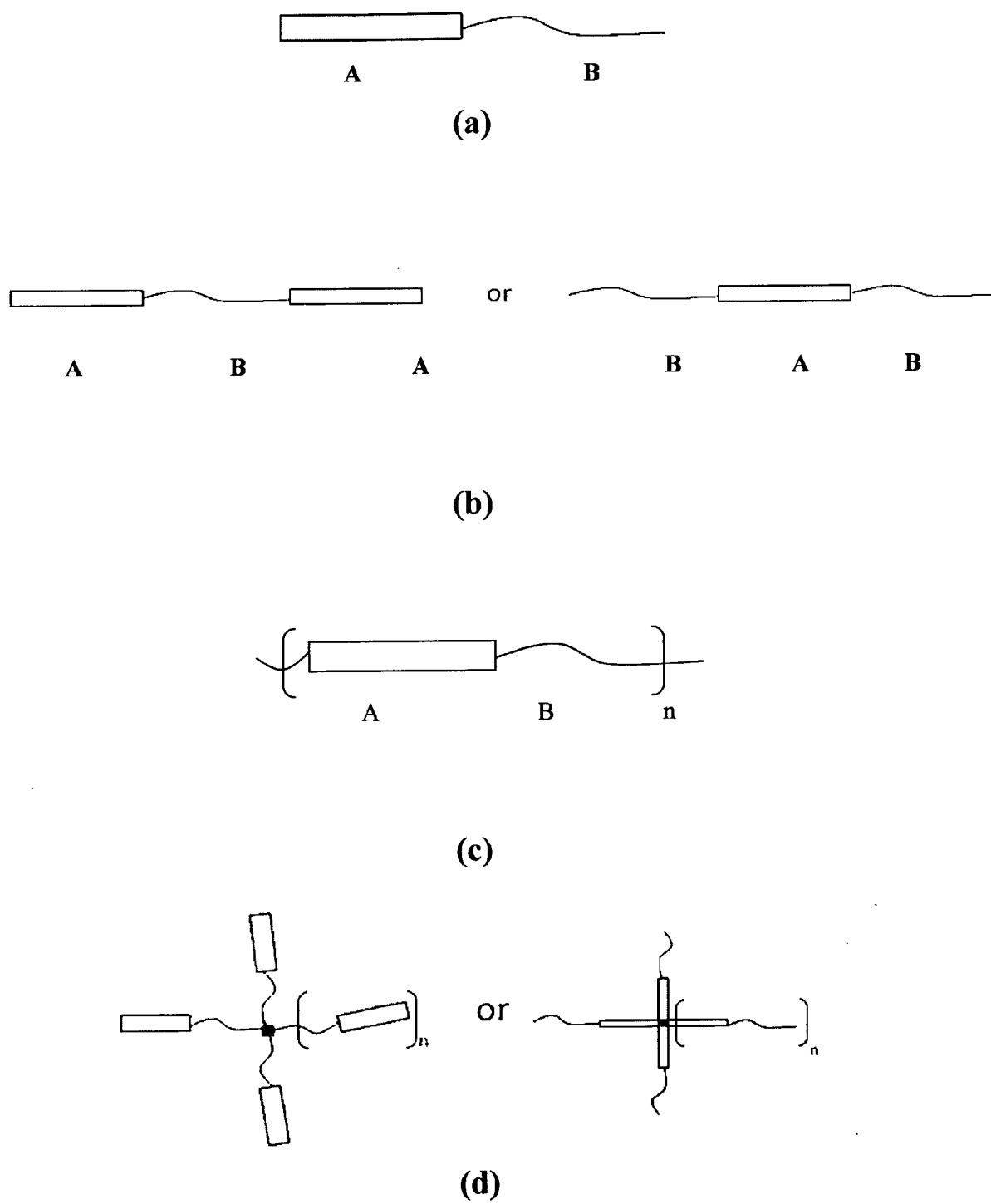
70. A process according to any one of claims 63 to 68 wherein Q and Q' comprise a block copolymer or dendrimer as further defined in any one of claims 16 to 48.

71. A process according to any one of claims 58 to 70 with the proviso that when L is a single bond and L' is a leaving group, said n functional groups of Q' are n aryl or heteroaryl rings, wherein Q comprises said n aryl or heteroaryl rings and wherein each L which is single bond is attached directly to a said aryl or heteroaryl ring of Q, thereby bonding the aryl or heteroaryl ring directly to the carbon atom which is bonded to R.

72. A process according to any one of claims 58 to 71 with the proviso that when L is a single bond and L' is a leaving group, Q' is a polymer and said n functional groups of Q' are n aryl rings, wherein Q is a polymer which comprises said n aryl rings and wherein each L

which is single bond is attached directly to a said aryl ring of Q, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

73. A process according to any one of claims 58 to 72, wherein L is a single bond, L' is a leaving group, Q' is a polymer and said n functional groups of Q' are n aryl rings, and Q is a polymer which comprises said n aryl rings, wherein each L which is single bond is attached directly to a said aryl ring of Q, thereby bonding the aryl ring directly to the carbon atom which is bonded to R.

**Fig. 1**

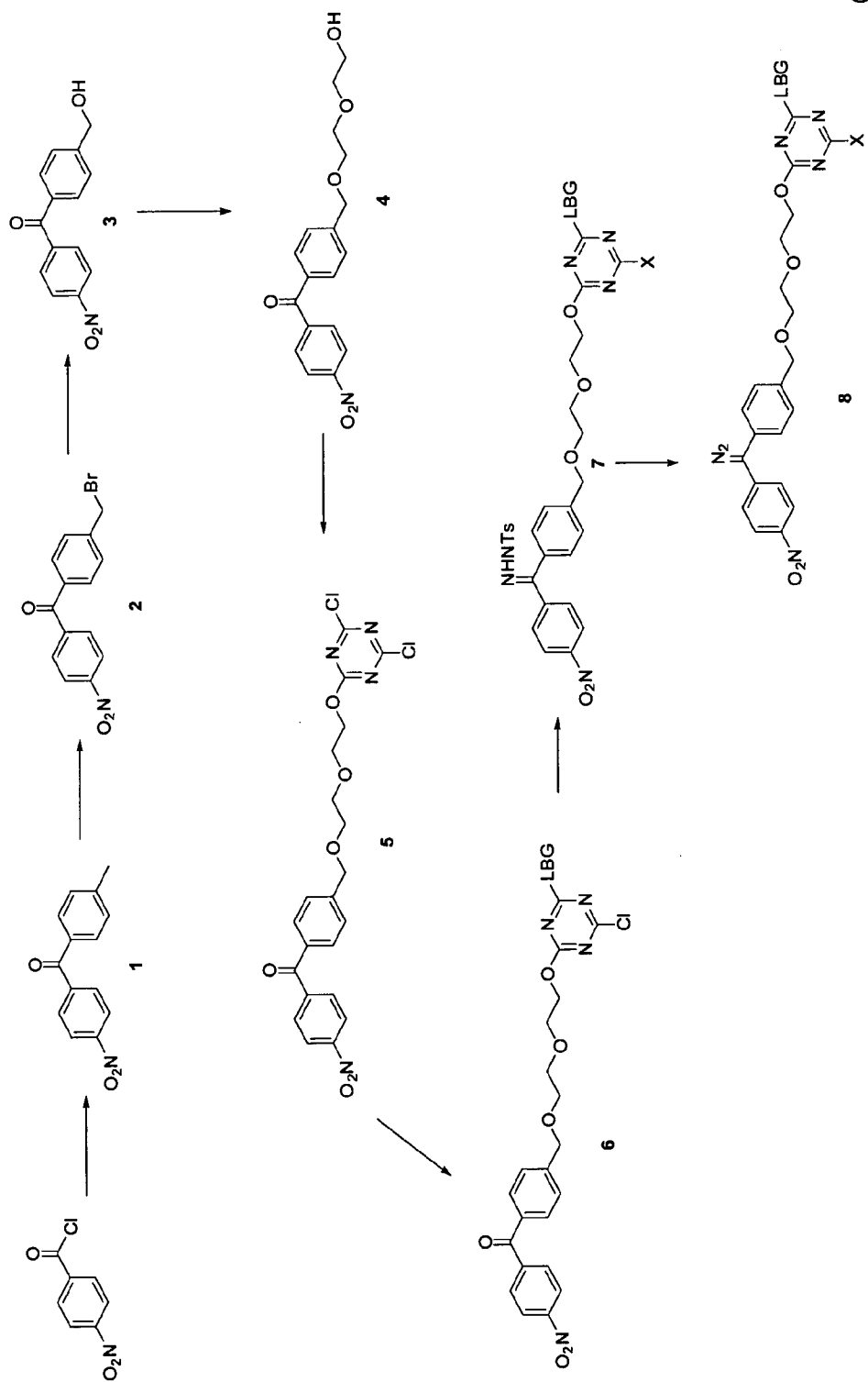


Fig. 2

(8 generated *in situ*)

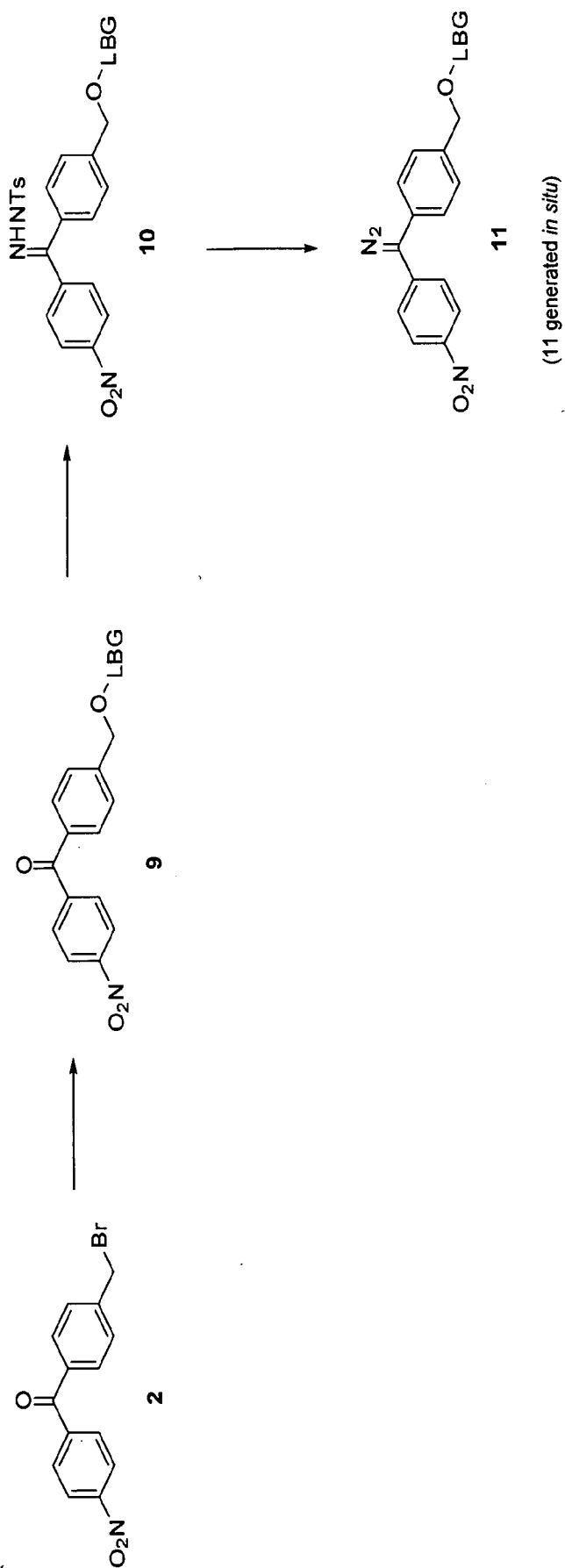


Fig. 3

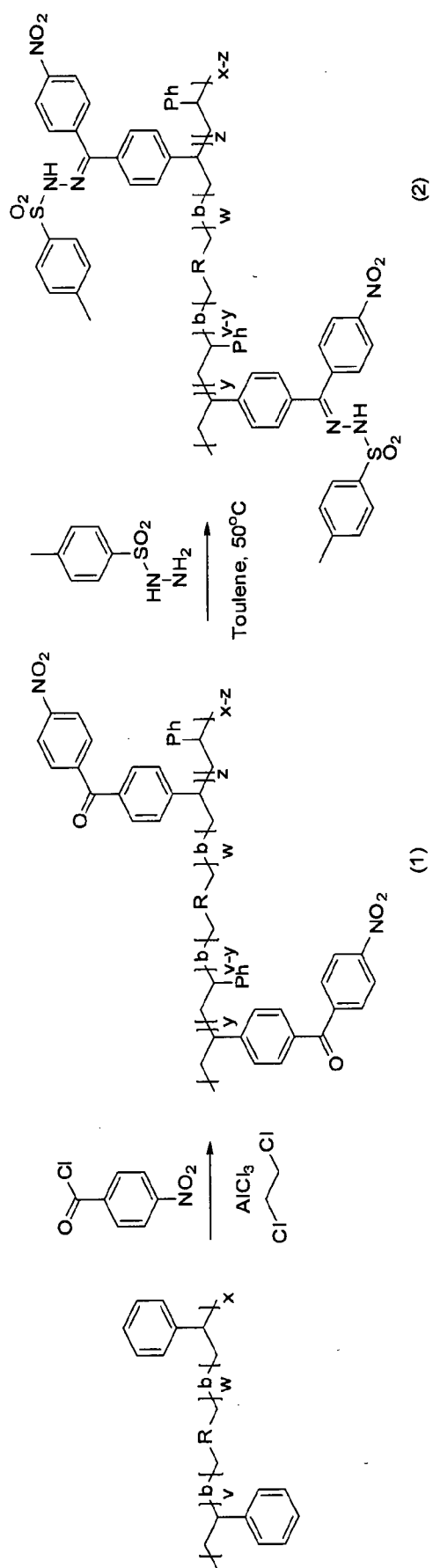


Fig. 4